Technology Development for Iron and Cobalt Fischer-Tropsch Catalysts

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Burtron H. Davis

Enrique Iglesia (UC/B Subcontract)

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University of Kentucky Research Foundation

201 Kinkead Hall

Lexington, KY 40506

University of California-Berkeley (Subcontract)

Laboratory for the Science and Application of Catalysis

Department of Chemical Engineering

University of California at Berkeley

Berkeley, CA 94720

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Abstract

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Two metals have the properties to be considered as the base for catalysts for Fischer-Tropsch synthesis: iron and cobalt. During the past 75 years there have been many reports on catalysts based on these two metals. However, most of these studies have been conducted so that it is difficult to make valid comparisons among the many studies. The studies for this contract have been conducted under conditions that permit catalyst properties to be directly compared under similar process conditions. Furthermore, the process variables have been varied over a range of conditions. The results permit comparisons of the activity and selectivity properties with catalyst composition to be made for a common process condition and this adds much reliability to the correlations that are developed. Furthermore, iron and cobalt catalysts have been compared under similar process conditions and the similarities and differences from these two catalysts have been defined. In brief, the data provide a data base that will be useful for potential process developers to make a valid selection of catalyst type and composition that will fit their specific conditions. To date, potential process developers have utilized the data base to select a catalyst composition and then to contract specific studies that fall outside the current contract to develop the optimum conditions for the company's process.

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A detailed study of the structure evolution, site characteristics, effect of promoters and activity and selectivity behavior of Fe-based Fischer-Tropsch Synthesis (FTS) catalysts have been carried out in this project, using a variety of tools such as *in situ* X-ray absorption spectroscopy, measurement of product evolution using mass spectrometry, high-pressure fixed-bed reactor studies as well as temperature programmed techniques. Iron carbide (Fe_xC) surface layers provide the active sites for the FTS reaction. Zn functions as a structural promoter by

preventing the collapse of the Fe oxide matrix during high temperature pretreatment. K promotes CO chemisorption, increases reduction/carburization of Fe oxides, increases product molecular weight, olefin content and minimizes secondary hydrogenation and isomerization reactions. Cu and Ru promote the reduction rates of Fe oxide by providing H₂ dissociation sites, and also enhance the carburization process. These faster reduction and carburization rates result in smaller Fe_xC crystallites that lead to a greater active site density. A similar effect was also achieved via synthesis of high surface area Fe-Zn precursors by employing a solvent (isopropanol) with a lower surface tension than water to wash the precipitates. A Fe-Zn-Cu₈-K₄ catalyst thus prepared compares well with a typical Co/SiO₂ catalyst in terms of hydrocarbon productivities.

In this project, attempts were also made to study the enhancement of FTS rates, product molecular weight and olefin content caused by water during FTS reactions on Co-based catalysts. Reactions with CO-H₂ and CO-D₂ mixtures showed that the kinetic isotope effect was unchanged with changes in water partial pressure in the reactor, which indicates that water does not participate in the kinetically relevant steps in FTS. In addition, the total CO-binding site density monitored using *in situ* IR spectroscopy was unchanged during H₂O addition, which indicated that the rate enhancement did not reflect a change in the site density. Similarly, transient experiments performed by switching from synthesis gas to H₂, showed that the total carbon determined from the CH₄ evolution transient did not change significantly with added H₂O, which showed that either the total carbon measured thus was a combination of active and inactive carbon during FTS or that the total amount of active carbon did not change sufficiently to account for the observed increase in FTS rates with water addition.

Table of Contents

	<u>Page</u>
Disclaimer	1
Abstract	2
Table of Contents	4
Executive Summary	7
Task 1. Iron Catalyst Preparation	14
A. Fischer-Tropsch Synthesis: Activity and Selectivity for Group I Alkali Promoted Iron-Based Catalysts	14
B. Fischer-Tropsch Synthesis: Group II Alkali Metal Promoted Catalysts	44
C. Effect of Structural Promoters on Iron Catalysts	69
D. Fischer-Tropsch Synthesis: Influence of Process Parameters on Activity and Selectivity of a Potassium Promoted Iron Catalyst	86
Task 2. Catalyst Testing	109
A. Deuterium Isotope Effects with a Precipitated Iron Catalyst in Slurry Phase Fischer-Tropsch Synthesis	109
B. Fischer-Tropsch Synthesis with Precipitated Iron Catalysts Using Hydrogen Rich Syngas	119
C. Impact of Potassium on the Activation Energy of Precipitated FTS Catalysts	134
D. Fischer-Tropsch Synthesis: Influence of Startup Media on Activity and Selectivity Over Magnesium Iron Promoted Catalysts	147
E. Two Alpha Fischer-Tropsch Product Distribution. A Role for Vapor Liquid Equilibrium?	165
F. Fischer-Tropsch Synthesis: Induction and Steady-State Activity of High-Alpha Potassium Promoted Iron Catalysts	190
G. Study of Deactivation of Iron Based Fischer-tropsch Synthesis Catalysts ..	218
H. Deactivation and Regeneration of Alkali Metal Promoted Iron Fischer-Tropsch Synthesis Catalysts	233
I. Overview of Reactors for Liquid Phase Fischer-Tropsch Synthesis	248
J. Slurry Bubble Activities	371

Task 3. Catalyst Characterization	384
A. Impact of Copper on an Alkali Promoted Iron Fischer-Tropsch Catalyst ...	384
B. Mössbauer Spectroscopy of Iron-Based Fischer-Tropsch Catalysts: Impact of Activation Procedure	408
C. Mössbauer Study of Precipitated Unpromoted and Potassium Promoted Iron Fischer-Tropsch Synthesis Catalyst	429
D. Characterization of Iron Phase Change During Fischer-Tropsch Synthesis Reaction	438
E. Characterization of promoted Cobalt FTS Catalysts	444
F. Fischer Tropsch Synthesis: Support, Loading, and Promoter Effects on the Reducibility of Cobalt Catalysts	478
G. Characterization of Pt-Re Promoted Co/Al ₂ O ₃ Catalysts	522
H. EXAFS Characterization of Used 0.2% Re - 15% Co/Al ₂ O ₃ Catalysts	533
Task 4. Wax/Catalyst Separation	550
A. A Summary of the CAER Experience with Catalyst/Wax Filtration	550
B. Filtration with High Alpha Unsupported Fe Catalysts	574
C. Initial Filtering Studies with Pall Corporation Filters	579
D. Hi-alpha Catalyst and Special Filter	598
Task 5. Oxygenates	614
Task 6. Literature Review of Prior Fischer-Tropsch Synthesis with Co Catalysts	615
Task 7. Co Catalyst Preparation	1390
A. Fischer-Tropsch Synthesis. Effect of CO Pretreatment on a Ruthenium Promoted Co/TiO ₂	1390
B. Preparation of Promoted Cobalt Fischer-Tropsch Synthesis Catalysts	1401
C. Fischer-Tropsch Synthesis: Effect of Small Amounts of Boron, Ruthenium and Rhenium on Co/TiO ₂ Catalysts	1404
Task 8. Co Catalyst Testing for Activity and Kinetic Rate Correlations	1426
A. Comparison of Fischer-tropsch Synthesis in Conventional Fixed Bed, CSTR and Supercritical Reactors on Unpromoted Cobalt Catalyst	1426
B. CO and CO ₂ Hydrogenation Over Co/SiO ₂ Catalyst	1437
C. CO and CO ₂ Hydrogenation over Co-Pt/Al ₂ O ₃ Catalyst	1446

D.	The CSTR studies of Co(10)/B(x)/TiO ₂ Fischer-Tropsch Catalysts	1454
E.	Study of Supercritical Phase Fischer-Tropsch Synthesis	1461
Task 9.	Co Catalyst Life Testing	1474
A.	Deactivation Study of Co-Re-Al ₂ O ₃ Catalysts	1474
B.	Effect of Water on the Fischer-Tropsch Catalytic Properties of Ruthenium Promoted Co/TiO ₂ Catalyst	1484
C.	Deactivation Rates for Co Catalysts	1494
D.	Fischer-Tropsch Synthesis: Deactivation of Noble Metal Promoted Co/Al ₂ O ₃ Catalysts	1511
E.	Cobalt Catalyst Life Testing and Deactivation	1539
F.	Fischer-Tropsch Synthesis: Effect of Water on the Catalytic Properties of a Co/SiO ₂ Catalyst	1549
Task 10.	Co Catalyst Mechanism Study	1573
A.	The Formation of Branched Hydrocarbons in the Fe and Co Catalyzed FT Reactions	1573
B.	D ₂ O Tracer Studies in Co Catalyzed Fischer-Tropsch Reaction	1612
C.	Fischer-Tropsch Synthesis: Supercritical Conversion Using a Co/Al ₂ O ₃ Catalyst in a Fixed Bed Reactor	1626
D.	Assessment of Internal Diffusion Limitation on Fischer-Tropsch Product Distribution	1657
E.	Product Distribution of Fischer-Tropsch Synthesis	1685
Task 11.	University of California, Berkeley (Subcontract)	1708
Task 12.	Reporting and Management	1834

Executive Summary

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Iron Catalysts

Two metals have the properties to be considered as the base for catalysts for Fischer-Tropsch synthesis: iron and cobalt. During the past 75 years there have been many reports on catalysts based on these two metals. However, most of these studies have been conducted so that it is difficult to make valid comparisons among the many studies. The studies for this contract have been conducted under conditions that permit catalyst properties to be directly compared under similar process conditions. Furthermore, the process variables have been varied over a range of conditions. The results permit comparisons of the activity and selectivity properties with catalyst composition to be made for a common process condition and this adds much reliability to the correlations that are developed. Furthermore, iron and cobalt catalysts have been compared under similar process conditions and the similarities and differences from these two catalysts have been defined. In brief, the data provide a data base that will be useful for potential process developers to make a valid selection of catalyst type and composition that will fit their specific conditions. To date, potential process developers have utilized the data base to select a catalyst composition and then to contract specific studies that fall outside the current contract to develop the optimum conditions for the company's process.

The impact of the range of alkali promoters (Groups I and II) have been evaluated for the first time under a common set of conditions. The objectives was to define whether potassium, the commonly used promoter, was the most active (it is) and whether the relative fraction of carbon monoxide that is converted to the desired product (hydrocarbons) rather than water (or carbon dioxide) could be controlled by selection of the promoter. While modest improvements

in selectivity could be induced by variation of the alkali promoter, the ultimate improvement does not appear encouraging.

The simplest approach to commercial operation is to maintain a constant catalyst bed activity by catalyst addition and withdrawal. A variety of catalyst activation schemes are available. The work has defined chemical changes that take with the catalyst during activation and related the catalyst composition to catalytic activity. For a range of catalysts, it has been shown that activation with carbon monoxide is superior to activation in hydrogen or synthesis gas. The data should cause developers to consider carbon monoxide for catalyst activation even though this may require a separate scheme to produce a pure carbon monoxide stream. However, the data provide the developer with another and more reasonable option: activate with synthesis gas at atmospheric pressure. This latter option provides an approach to obtain the same high catalyst activity with a readily available gas stream.

The studies have defined catalyst changes that occur during the initial 150-300 hours of catalyst use. During this period both activity and selectivity changes. Fortunately, the activity increases to a maximum and then declines by 10-20% to attain a steady-state activity. The catalyst changes that lead to this rapid activity decline to steady state have not been identified. The selectivity changes vary: methane selectivity declines and this is desirable, water-gas-shift activity to produce carbon dioxide increases significantly and this is not desirable. The lower the operating temperature the more significant these slow catalyst changes occur. Additional studies are needed to provide a better understanding to provide control measures.

Iron catalyst deactivation occurs through two pathways: one of these is considered to be physical and occurs through attrition of the initial catalyst form to produce much smaller particles that plug the filter and the other is by chemical changes of the catalyst. The work has conclusively shown that deactivation through chemical changes is not a significant problem and

that deactivation rates of less than 1% CO conversion/week is easily attainable for an iron catalyst that has the correct composition and is operated under the appropriate reaction conditions. On the other hand, physical changes due to attrition remains an unsolved problem. Even with a support, the fine iron particles are formed and these plug filters. The results indicate that the preferred approach is to develop a filter that will operate with the fine particles. To this end, a filter provided by the Pall Corp. shows promise and has been utilized in laboratory reactors for 1500 hours without indication of being plugged with fine catalyst particles. A cross-flow filtering technique has been developed during studies using the CAER 2-inch bubble column reactor and a patent has been applied for this technique.

In summary, the studies have provided a basis for preparing a catalyst that will produce a desired product slate ranging from low molecular weight to a product that contains 50+% wax product boiling above diesel range products.

Studies with the cobalt catalyst has been directed toward developing understanding of the impact of process variables on activity and selectivity as well as identifying changes that take place in the catalyst during use.

It has been demonstrated that the addition of a Group VIII noble metal promoter has beneficial effects on the initial activity of the catalyst but that the promoted catalyst may deactivate more rapidly. Catalyst characterization studies, primarily using X-ray absorption spectroscopy equipment at Brookhaven National Laboratory, have shown that a significant fraction of the deactivation is due to metallic cobalt oxidation during the synthesis.

Cobalt Catalysts

A comparison of the use of a common cobalt-alumina catalyst in conventional fixed bed reactor, continuous stirred tank reactor (slurry reactor) and supercritical fixed bed reactor has been made. It has been shown that supercritical pressure conditions are beneficial only at high

density conditions; that is, only when there is a high partial pressure of a component is present in concentrations that approach the critical pressure. For Fischer-Tropsch synthesis, this means that a component that is a liquid at room temperature is required and that it is likely that the separation and recycle of the components will make the utility of supercritical synthesis of questionable benefit for commercial operations. Briefly, the gain in catalyst stability will not off-set the added cost of separations and recycle. More importantly, there were only minor, if any, differences in product selectivity among the products from the various operating reactors.

Cobalt catalysts, lacking water-gas-shift activity, must operate in the presence of high partial pressure of water. In spite of this, kinetic expressions to date have not included water. Studies at various partial pressure of water while other variables were held constant have been conducted. These studies show that the impact of water on the catalytic activity is dependent upon the support and may even vary with the properties of a particular support. Thus, for some silica supports the conversion increases with increasing water partial pressure whereas with other silica supports the conversion may decrease. This study has provided the most extensive definition of the impact of water with the range of cobalt catalysts and under comparable reaction conditions. Kinetic expressions have been developed that include water partial pressure. More importantly, catalyst characterization studies as the material is used to effect Fischer-Tropsch synthesis have defined chemical changes that occur for the cobalt catalyst.

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A detailed study of the structure evolution, site characteristics, effect of promoters and activity and selectivity behavior of Fe-based Fischer-Tropsch Synthesis (FTS) catalysts have been carried out in this project, using a variety of tools such as *in situ* X-ray absorption spectroscopy, measurement of product evolution using mass spectrometry, high-pressure fixed-bed reactor studies as well as temperature programmed techniques. Our simultaneous isothermal

switch transients and X-ray absorption spectroscopic studies have shown that Fe oxides reduce and subsequently carburize to form a mixture of Fe carbide phases (Fe_xC) and these carbides especially the near-surface layers provide the active sites for the FTS reaction.

Zn when present as a promoter maintains the structural integrity of Fe oxide matrix and prevents its collapse during high temperature pretreatment, hence increase in Zn loading results in higher surface areas. However, this also results in the formation of a less reducible, less active ZnFe_2O_4 phase, which results in optimum Zn/Fe ratios (~ 0.1) being responsible for the highest FTS rates. K promotes CO chemisorption and decreases hydrogen chemisorption, and increases carburization rates of Fe oxides. This results in higher FTS rates, higher product molecular weight, minimization of secondary hydrogenation and isomerization reactions, and increased olefin content. Cu and Ru reduce at lower temperatures, and hence by providing H_2 dissociation sites promote the reduction and carburization rates of Fe oxides. These faster reduction and carburization rates result in shorter diffusion distances and hence lead to the formation of smaller Fe_xC crystallites that in turn lead to a greater active site density for FTS.

Replacement of Cu by Ru on Fe-Zn-K resulted in almost a two-fold increase in FTS rates and the unchanged product selectivities on unpromoted and Ru and Cu-promoted Fe-Zn-K indicates that when K is present, Ru and Cu do not function as chemical promoters for FTS reactions. A novel CO chemisorption technique was developed to determine the density of CO-binding sites on each of these catalysts and our results showed that Ru and Cu increase the total density of CO-binding sites, which increases the catalyst activity.

An alternate way to enhance FTS rates was followed via the synthesis of high surface area Fe-Zn oxide precursors, by employing isopropanol, a solvent that has a significantly lower surface tension than water for washing the precipitates. The lower surface tension minimizes the reduction in surface area caused by the pore-mouth pinching process during high temperature

treatment. A Fe-Zn-Cu₈-K₄ catalyst thus prepared, showed nearly two-fold increase in FTS rates with unchanged product selectivities when compared to its low surface area counterpart. Furthermore, we have also successfully tested this high surface area sample at conditions typically employed for Co-FTS catalysts and rare for Fe catalysts (473 K and 2 MPa) and our results show that this catalyst compares well with a typical Co/SiO₂ catalyst in terms of hydrocarbon productivities. Hence Fe catalysts when prepared in a highly dispersed form can provide selective and active alternative to Co catalysts.

In this project, studies were also conducted with FTS reactions on Co/SiO₂ to investigate the mechanism and the effect of water on the reaction in detail. Water enhances FTS rates, decreases CH₄ and increases C₅₊ selectivities, and also increased olefin content. Reactions with CO-H₂ and CO-D₂ mixtures showed an inverse kinetic isotope effect and this was a combination of kinetic and equilibrium effects. The kinetic isotope effect was unchanged with changes in water partial pressure in the reactor, which effectively ruled out the participation of water in the kinetically relevant steps in the reaction mechanism.

In addition, we also investigated the possibility of water promoting the active site density and hence providing a rate enhancement. In one set of experiments, the total number of CO-binding sites was monitored using *in situ* IR spectroscopy under FTS conditions. This study showed that the large enhancements in FTS rates with water concentrations did not reflect a corresponding change in the density of CO-binding sites.

In a parallel study, we performed switch transient experiments, in which FTS reaction was carried out on a Co/TiO₂ catalyst at steady state and the flow was switched to H₂. The resulting CH₄ transient evolution, which gave information on the total active carbon hydrogenated during this switch, was monitored with and without the addition of water. These studies showed that the total carbon determined thus did not change significantly with added

H₂O, which showed that either the total carbon measured thus was a combination of active and inactive carbon during FTS or that the total amount of active carbon did not change significantly to account for the large increase in FTS rates under the same conditions.

Task 1. Iron Catalyst Preparation

The objective of this task is to produce robust intermediate- and high- α catalysts.

A. Fischer-Tropsch Synthesis: Activity and Selectivity for Group I Alkali Promoted Iron-Based Catalysts

Abstract

The impact of the Group I alkali metals upon the activity of iron catalysts has been obtained at medium pressure synthesis conditions and at the same conversion levels. The relative impact of the alkali metal depends upon the conversion level with potassium being the promoter that impacts the highest activity at all conversion levels. At low conversions, Li is nearly as effective as potassium in improving the catalytic activity but is the poorest promoter at high conversion levels. In fact, three alkalis (Li, Cs and Rb) should be viewed as inhibitors since they decrease the catalytic activity for CO conversion below that of the unpromoted iron catalyst. The differences in the impact of the various Group I alkali metals at lower ($< \sim 40\%$) conversions are slight but become much greater at higher CO conversion levels. The major differences of the alkali metals at higher conversion levels is due to the impact of the promoter upon the water-gas-shift reaction. At higher conversion levels, with a syngas of $H_2/CO = 0.7$, the water-gas-shift reaction becomes rate controlling because hydrogen production becomes the rate limiting factor in the Fischer-Tropsch synthesis. The basicity of the promoter appears to be the determining factor for the rate of catalyst deactivation and on the secondary hydrogenation of ethene.

Keywords: promoter, alkali; Fischer-Tropsch synthesis, iron catalyst; Group I metal; potassium, lithium, cesium, rubidium

Introduction

The Fischer-Tropsch synthesis (FTS) offers the possibility of converting a mixture of hydrogen and carbon monoxide (synthesis gas or “syngas”) into clean hydrocarbons, free from sulfur. This syngas is usually produced from natural gas or coal, and exhibits a lower H_2/CO ratio for coal gasification. As carbon number of the hydrocarbon produced can range from 1 to over 100, this process can be used to produce high-value transportation fuels, such as gasoline (C_5 - C_{11}) and diesel fuels (C_{12} - C_{18}). Several metals, such as nickel, cobalt, ruthenium and iron, have been shown to be active for this reaction (1), which can be represented as:

where n is the average H/C ratio, usually between 2.1 and 2.5

However, only iron- and cobalt-based catalysts appear to be economically feasible at an industrial scale. Because catalysts may also be active for the water-gas shift (WGS) reaction

a syngas presenting a low H_2/CO ratio, as that produced by coal gasification in advanced gasifiers, can be directly used for FTS. Further, this reaction consumes the water product, which may act as a poison for FTS catalysts, as the following expression for the Fischer-Tropsch rate shows (2):

$$-r_{CO+H_2} = \frac{kP_{H_2}}{1 + b(P_{H_2O}/P_{H_2}P_{CO})} \quad (3)$$

Typical iron-based catalysts contain varying amounts of structural additives, such as silica or alumina, and chemical promoters, such as potassium and copper, known to, for example, increase the overall FTS activity or to facilitate the reduction of iron oxide to metallic iron during hydrogen activations (3). Many studies have been made on potassium-promoted

catalysts, which have been shown to either decrease or increase the FTS activity (1) of an iron catalyst. However, few reports of the effect of the other alkalis are available (4). One report shows that their effectiveness decreases in the order Rb, K, Na, Li (1). While much work has been conducted, there are few studies that provide data that allow a direct comparison of the effectiveness of the various Group I alkali metals. One example of a direct comparison utilized atmospheric pressure reaction conditions and an iron catalyst base that was prepared by the ignition of the nitrate salt. The conversion with these catalysts, presumably having low activity, was not stable with time (Figure 1) (4,5) and showed that K and Rb were the superior alkali promoters. Dry (6) reported for precipitated iron catalysts that the stronger bases of Group I elements are key promoters and that the relative activities of catalysts containing equal atomic amounts of Group I metals were: K, 100; Na and Rb $\approx$ 90; Li, $\sim$ 40. Dry indicated that Rb was out of line, probably due to its high wax selectivity. Dry and Oosthuizen (7) utilized fused iron catalysts in which the alkali was present during the fusion step or was added by impregnation after the fusion step. For the reduced catalyst, the basicity, determined from CO₂ adsorption, increased in the order Ba, Li, Ca, Na and K. The amount of methane decreased as the surface basicity increased. The activity data were obtained at atmospheric pressure at 290°C with a gas having a H₂/CO ratio of 3.2. Pilot plant data were obtained at 250 psig (1.72 MPa) and 593 K, in a fluidized bed reactor, and these supported the trend observed at one atmosphere pressure.

Röper (8) provides a ranking of the efficiency of alkali promoters as: Rb $\succ$ K $\succ$ Na $\succ$ Li. However, this ranking was based at least in part on the results described above.

In spite of the recognized importance of the alkali promoter, data to document their relative influence are not abundant. Furthermore, the data that are available have been obtained under conditions that may not be applicable for slurry phase operations. The purpose of this study is to compare the effects of iron-based catalysts, promoted with different alkalis (Li, Na, K,

Rb and Cs) on FTS. The catalysts have been used in a slurry reactor and data were obtained over a wide range of syngas space-velocities. Further, activities and selectivities, as well as hydrocarbon production rates and compositions, have been obtained at similar carbon monoxide conversions.

Experimental

Catalysts

A precipitated iron-silica catalyst with atomic ratio 100Fe/4.6Si was prepared by continuous coprecipitation in a stirred tank reactor, using a process which has been described previously (9). The alkali (Li, Na, K, Rb and Cs) was then added by incipient wetness impregnation with an aqueous alkali carbonate to obtain an alkali:iron atomic ratio of 1.44:100. Copper, a known promoter, was not added in order to avoid complications from its presence. The catalyst, promoted or unpromoted, undergoes complex physical and chemical changes during activation and use (10). The physical changes for unpromoted and potassium promoted iron show that the surface area of the catalyst increases slowly with use, presumably due to the slow deposition of high surface area carbon (10). The pore size distribution changes to eliminate the microporosity during the activation step and during use the average pore size of the mesoporosity increases slowly (10).

Reaction System and Product Analysis

A 1-liter continuous stirred tank reactor (CSTR) was used. Analysis of all products were made using a variety of chromatographs. More details of the reaction system and the product analysis have been reported previously (11).

The catalyst (5 g) was mixed in the reactor with 310 g of melted octacosane, previously treated to remove a bromide impurity, that was used as the start-up solvent. The stirring speed was set at 750 rpm before the reactor pressure was increased to 175 psig (1.308 MPa) with

carbon monoxide at a flow rate of 25 NL/hr. The reactor temperature was then increased to 543 K at a heating rate of 2 K/min. The catalyst was pretreated at 543 K for a total of 22 hours.

After this period, the reactor was fed with syngas at a constant H_2/CO ratio of 0.67 by introducing and increasing the H_2 flow during a 2 hr period. The pressure, temperature and stirring speed were maintained at 175 psig (1.308 MPA), 543 K and 750 rpm, respectively. After the catalyst reached steady state, as evidenced by a constant syngas conversion, the feed gas space velocity was varied between 5 and 65 NL/hr/g(Fe) and maintained at each flow rate for 24 hours. The catalyst activity was measured periodically at preset “standard” conditions (a space velocity of 10 N/hr/g(Fe)) to determine whether the catalyst had deactivated. Conversion versus reaction time was plotted for the “standard” conditions and this relationship was used to correct each measured activity to that of the fresh catalyst. The conversions of carbon monoxide, the exit flow rate being known, was measured. FTS products were collected in three traps maintained at 473, 373 and 273 K (11), and then weighed and analyzed.

Results

Carbon Monoxide Conversion

The conversion values are corrected, according to the linear deactivation rate obtained from the values of conversions at different times-on-stream, by returning to the standard flow rate of 10NL/hr/g(Fe) at intervals during the run (Figure 2). The lowest deactivation rate is obtained by the lithium promoted catalyst, with a rate of 0.48% CO conversion/week. The deactivation rates of sodium, potassium, rubidium and cesium catalysts are 0.84, 1.23, 1.80 and 2.75% CO conversion/day, respectively. We can thus conclude that the more basic the alkali, the higher the deactivation rate.

The experimental CO conversion data cover a wide range of values, from about 15 to over 90%. Conversions are dependent on space-time and alkali. The potassium promoted

catalyst shows the highest conversions, especially at higher space-times. The activity rankings are obtained at 20 through 60% CO conversion levels by comparing the relative flow rates needed to obtain this conversion level. At the higher flow rates, the catalyst promoted with lithium exhibits the same conversion as the catalyst that contains potassium, but above a space-time of about 0.1 hr g(Fe)/NL the Li-promoted catalyst exhibits the lowest conversions. At 20% CO conversion level, the unpromoted catalyst yielded the same activity as K, Na and Li promoted catalysts; however, for this conversion level the Cs and Rb promoted catalyst is only about half as active as the K-promoted catalyst. At the 40% conversion level, the ranking changes somewhat. The K- and Na-promoted catalysts have about the same activity, but the unpromoted catalyst now has only about 0.68 of the activity of the K-promoted catalyst. At this CO conversion level, Li, Rb and Cs promoted catalysts exhibit only about half the activity of the K-promoted catalyst (Table 1). At the 60% CO conversion level, the Na-promoted and the unpromoted catalyst has only about 0.64 of the activity of the K-promoted catalyst. The Rb-promoted catalyst shows only about 0.33 the activity of the K-promoted catalyst and the Cs- and Li-promoted catalyst have only 0.28 the activity of the K-promoted catalyst.

Product Partial Pressures

Since a CSTR was used, the partial pressures are the same throughout the reactor. A first appreciation of the WGS reaction activity can be made from plots of water (Figure 3) and carbon dioxide (Figure 4) partial pressures in the reactor. For all catalysts, the water partial pressure shows a rapid increase at low space times, then reaches a maximum before declining. This result is consistent with previous studies made with potassium promoted iron catalysts (12). The catalyst promoted with lithium shows the highest water partial pressure at all space-times. The initial increase, at CO conversions close to that of potassium, indicates that this catalyst is less active for the WGS reaction than the other alkali metal promoted catalyst. This can also be

verified by considering the carbon dioxide partial pressure, which is much higher for the catalyst promoted with potassium.

Rates of FTS and WGS Reaction

As mentioned earlier, carbon monoxide can be converted either into hydrocarbon products and water, or into carbon dioxide and hydrogen. It is thus interesting to compare the rates of these two reactions and they can be calculated:

$$r_{WGS} = r_{CO_2} \quad (4)$$

and

$$r_{FTS} = r_{CO} - r_{CO_2} \quad (5)$$

As the WGS reaction needs the water produced by the FTS, an inequality:

$$r_{WGS} \leq r_{FTS} \quad (6)$$

is always observed. All FTS rates exhibit dependence on space-time and decrease with increasing space-time (Figure 5). Further, all WGS-reaction rates show a maximum at about the same space-time (Figure 6), and this occurs at about the same time as when the water partial pressure attains its maximum value.

The K-promoted catalyst exhibits the highest WGS rates over the total flow range utilized. The Na promoted catalyst is almost as active as the K-promoted catalyst. Surprisingly, the unpromoted iron catalyst has a higher rate than three of the alkali promoted catalysts, and since it does not appear that the maximum rate was attained at even the highest flow used, the iron catalytic activity may be as high as any of the alkali promoted catalysts. At the intermediate flow rates, the Li-promoted catalyst is more active than the Cs- and Rb-promoted catalysts but these three promoted catalysts approach a similar rate at about space velocity of about 0.1.

Carbon Utilization

A perceived disadvantage of using iron-based catalysts is that a large proportion of the carbon monoxide that is converted into carbon dioxide rather than the desired hydrocarbons. This is a perceived disadvantage since the rejection of carbon dioxide results in a lower conversion of hydrogen. The extent of the WGS reaction needs to be defined. One measure is the WGS-reaction quotient, which can be expressed as:

$$RQ_{WGS} = \frac{P_{CO_2} P_{H_2}}{P_{CO} P_{H_2O}} \quad (7)$$

However, at lower conversion levels RQ_{WGS} may be dominated by the large partial pressures of the unconverted hydrogen and carbon monoxide. It is illustrative to consider the extent of the WGS-reaction by calculating the fraction of carbon monoxide converted to hydrocarbons:

$$\text{Fraction of CO producing hydrocarbon} = \frac{r_{FTS}}{r_{CO}} \quad (8)$$

As the rate of the FTS is always at least as large as the WGS reaction rate, the fraction is always greater than 0.5. It is immediately evident that the fractions of CO converted to hydrocarbons, and therefore the ratio of the relative rates for FTS and WGS, drop dramatically with space-time (Figure 7). The catalyst promoted with potassium shows the lowest fraction of carbon monoxide transformed into hydrocarbon products at almost all space-times. However, the fractions for all catalysts approach a constant value at the high space-times. Even so, at high space-times, the Cs-promoted catalyst make slightly more efficient utilization of the carbon monoxide to produce hydrocarbon products.

Hydrocarbon Product Selectivity

FTS produces many hydrocarbons and it is impossible to produce only a desired product, such as gasoline (C_5 - C_{11}) or diesel fuels (C_{12} - C_{18}). Figure 8 shows the hydrocarbon product distributions over different alkali metal promoted iron catalysts at a space velocity of 10 NL/hr/g-Fe. Alkalinity did not affect the C_1 production while it yielded a 5-7% difference in other fractions. The unpromoted catalyst produced the highest C_2 - C_4 and the lowest gasoline (C_5 - C_{11}) and diesel (C_{12} - C_{18}) fractions. Among the Group I alkalis, Na yielded the highest C_2 - C_4 and gasoline fractions and the lowest diesel and C_{19+} fractions. Potassium, however, produced the lowest C_2 - C_4 and gasoline, but the highest C_{19+} fractions. Similar results were obtained from Li, Cs and Rb-promoted catalysts.

Another important selectivity is the fraction of the hydrocarbons that are represented by light hydrocarbon gases, especially methane. As shown in Figure 9, the fraction of methane produced does not increase rapidly over the CO conversion range of 20 to 90%. Except for the Li-promoted and the unpromoted iron catalysts, the fraction of methane in the hydrocarbon products does not depend upon the alkali promoter.

The fraction of alkenes can depend upon the amount of promoter and the data in Figure 10 clearly show that the fraction of ethene depends strongly upon the promoter. For the unpromoted catalyst, only about 20% of the C_2 hydrocarbons is represented by ethene. The Li- and Na-promoted catalysts produce about 50% of the unsaturated C_2 product, ethene. Cs-, Rb- and K-promoted catalysts have the highest olefin selectivity, producing about 80% of the unsaturated product, ethene. The fraction of alkene decreases as the CO conversion increases.

Discussion

The results obtained during this study for the promoted catalysts are directly comparable since the conversions were: (a) obtained under the same reaction conditions, (b) a common precipitated iron base catalyst was used and (c) the catalysts had the same atomic alkali content.

The relative catalytic activities for the alkali promoted catalysts are dependent upon the conversion levels as shown in Table 1. Thus, at low conversion levels, Li is about as effective as K but at intermediate and high conversion levels it is the least effective promoter. The WGS reaction is slower than the FT reaction so that it appears that the relative rates of the FT and WGS reactions is responsible for the difference in total CO conversion.

While the total conversion is an important consideration, in at least some instances the relative rates of FTS and WGS are more important; that is, selectivity is more important than productivity. The data in Figure 6 show that, at lower conversion levels, FTS is relatively rapid compared to WGS so that a higher fraction of CO is converted to hydrocarbons. The advantage of the more rapid FTS rate cannot be maintained throughout the CO conversion since the decreasing H_2/CO ratio causes the rate determining step to change from FTS to the WGS reaction. Thus, above about 50% CO conversion, the rate of FTS depends upon the production of hydrogen by the WGS reaction. It has been observed that the rate of FTS is not inhibited by the addition of water with the syngas feed, at least up to a ratio of $H_2O/CO = 0.3$; the only impact of the added water is to increase the rate of the WGS reaction (15). Thus, it does not appear that water partial pressure has a significant impact upon the FTS kinetics due to its impact by competitive adsorption, at least at the lower CO conversion levels.

The ranking of the effectiveness of the alkali metal promoters cannot be due only to their basicity unless the alkalis undergo changes in basicity in a way that depends upon CO conversion. While the amount of water that is present in the reactor may impact the basicity, it

does not appear that the differences in water partial pressure is large enough to make this a reasonable explanation. It appears more likely that the kinetic impact of water is responsible for the changes in the effectiveness of the promoters and its dependence on the CO conversion level. There appears to be two ways in which water may impact the relative effectiveness of the alkali promoters. First, at the lower conversion levels, water can impact the rate because of the competition of its adsorption with that of the CO and/or H₂ reactants and the nature of the alkali promoter may impact this factor differently. At the higher CO conversion levels, the depletion of hydrogen because of the slowness of the WGS reaction may become the more important factor. Thus, the least effective WGS catalyst will cause hydrogen depletion at a lower CO conversion level and force the FTS rate to be limited by the rate of the WGS reaction. As indicated above, the presence of added water did not impact the FTS rate at lower CO conversion levels to a measurable extent with the K-promoted catalyst and it is concluded that the impact of water does not impact the kinetics with the iron catalyst under low temperature conditions.

Basicity is a frequently used term in the literature and, together with acidity, forms the basis for much of catalysis. These terms are fundamental but the so-called acid-base “theories” are in reality merely definitions of what an acid or base is. Furthermore, apart from aqueous solutions and the well-established pH scale, the definitions are not quantitative. Nevertheless, it is convenient to use the terminology to describe catalysis. One area where this has been done is to describe promotion of iron catalysts (7).

The Lux-Flood definition describes acid-base chemistry in terms of the oxide ion. A base is an oxide donor and an acid is an oxide acceptor. This acidity scale may be based on the difference in the acidity parameters, ($a_B - a_A$), of a metal oxide and a nonmetal oxide being the square root of the enthalpy of reaction of the acid and base (16). On this basis, with water

chosen to calibrate the scale at a value of 0.0, cesium oxide is the most basic oxide. The Group I oxides of interest have the following acidity (opposite to basicity) parameters: Cs_2O , -15.2; Rb_2O , -15.0; K_2O , -14.6; Na_2O , -12.5; and Li_2O , -9.2.

A complicating factor is the leveling effect. All acids and bases stronger than the characteristic cation and anion of the solvent will be “leveled” to the latter. Thus, in water solvent an acid will not be stronger than H_3O^+ and a base cannot be stronger than OH^- . In the Lux-Flood system, a base cannot be stronger than O^{2-} .

For Group I cations with a noble-gas configuration, in an aqueous solution, hydrolysis of the metal ion is greatest for Li. K^+ , Rb^+ and Cs^+ are not measurably hydrolyzed in aqueous solution (17). Thus, based on an aqueous solution, the larger Group I metal cations are not basic. Considering the aqueous bases, the interaction between the metal ion and the hydroxide ion is essentially electrostatic so that pK_b varies in a linear fashion with q^2/r , where q is the charge on the ion and r is the ionic radius and pK_b refers to the loss of the hydroxide group. On this basis, LiOH ($\text{pK}_b = 0.18$) has the lowest basicity of the alkali metals. NaOH ($\text{pK}_b = -0.8$) is a stronger base than LiOH . The other hydroxides, KOH , RbOH , and CsOH , are even stronger bases with pK_b approaching the limiting value of -1.7 for these three hydroxides.

In light of the above, it does not seem reasonable to assign a particular value to the basicity of the Group I metal promoters. Thus, in the following the basicity of the Group I promoters will be compared on a linear scale based on their position in the Periodic Table. When this is done, the catalyst deactivation rate is shown to increase in going down the row position in the Periodic Table (Figure 2). The catalytic activity appears to initially increase in going down the Periodic Table, attain a maximum at K and then decline in going further down the Periodic Table (Figures 11 and 12) at a low space velocity of 10 NL/hr/g-Fe. The nearly constant FT rate for all of the promoters is primarily due to the differences in the WGS activity

with Na and K exhibiting a much higher rate than the other promoted catalysts (Figure 13). The selectivity for ethylene, based on ethene and ethane, exhibits the same trend as for CO conversion; thus, the most basic Group I metal oxides exhibit the highest ethylene selectivity (Figure 14). Olefin ratio of C_4 remained stable over different alkali promoted catalyst. Thus, the alkali promoted catalyst that exhibits the highest hydrogenation activity for CO exhibits the lowest hydrogenation activity for ethene. This implies that it is the relative adsorptivity of CO and ethene that determines the hydrogenation activity; based upon this assertion, ethene competes with CO adsorption best with the unpromoted iron catalyst and becomes less competitive as the promoter is located lower in the Periodic Table.

In summary, the relative effectiveness of the Group I alkali metal promoters is not easily defined. In general, potassium promotion provides the superior catalyst from the activity viewpoint for both FTS and WGS reactions. The relative effectiveness of the alkali metal promoters depends upon the level of CO conversion. Furthermore, an iron catalyst that does not contain alkali is more active than catalysts that contain Li, Cs or Rb. Thus, three of the five alkali metals may be viewed, at least at lower levels of CO conversion, as catalyst poisons. Alkali metals show the greatest impact on the selectivity by impacting the fraction of alkene in the C_2 hydrocarbon fraction.

Apart from WGS activity, the basicity of the promoter defines the relative catalytic activity. However, because of the uncertainty of the chemical compound that represents the alkali promoter in the working catalyst and the variety of definitions of basicity, the comparison based on the position in the Periodic Table appears to be as, and perhaps more, reasonable than any of the current basicity scales.

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Table 1					
Ranking of Alkali Promoters at Various CO conversion Levels					
CO conversion, %	Activity Ranking				
20	Li = K = 1Na = Un*			Rb = Cs = 0.56	
40	K = Na = 1	Un = 0.68	Li = 0.59	Rb = 0.49	Cs = 0.48
60	K = 1	Un = 0.68	Na = 0.64	Rb = 0.34	Cs = Li = 0.28
* = unpromoted catalyst.					

Figure 1. Effect of adding 0.5% alkali on activity of 5 g of Fe-Cu (4:1) catalyst. Reproduced from ref. (5).

Figure 2. Deactivation curves for Group I alkali metal promoted catalysts established at standard conditions.

Figure 3. Water partial pressure as a function of space time for iron and promoted iron catalysts.

Figure 4. Carbon dioxide partial pressures as a function of space time for iron and promoted iron catalysts.

Figure 5. Fischer-Tropsch rate vs. space time.

Figure 6. WGS rates as a function of space time for iron and promoted iron catalysts.

Figure 7. FT to CO rate ratio vs. space time.

Figure 8. Distributions of hydrocarbon fractions produced using Group I alkali metal promoted catalysts.

Figure 9. Methane selectivity as a function of carbon monoxide conversion for iron and promoted iron catalysts.

Figure 10. Alkene selectivity of C₂ hydrocarbons as a function of carbon monoxide conversion for iron and promoted iron catalysts.

Figure 11. CO conversion vs. alkalinity.

Figure 12. Fischer-Tropsch rate vs. alkalinity.

Figure 13. Water-gas shift rate vs. alkalinity.

Figure 14. Olefin ratios (C_2 and C_4) vs. alkalinity.

B. Fischer-Tropsch Synthesis: Group II Alkali Metal Promoted Catalysts

Abstract

The effects of four Group II alkali-earth metal (barium, beryllium, calcium and magnesium) and potassium promoters on iron Fischer-Tropsch Synthesis (FTS) catalysts product selectivity, syngas conversion and productivity are compared. Iron FTS catalysts promoted with Group II alkali metals have lower overall FTS activity and lower alpha values than a potassium promoted iron catalyst. All Group II metal promoters yielded higher carbon utilization than a potassium promoted catalyst regardless of the space time. Carbon dioxide selectivity and water-gas shift (WGS) quotient indicate that a potassium promoted iron catalyst possesses better WGS activity than any Group II metal promoted catalyst at high CO conversion. At a low CO conversion, however, K, Ba and Be promoted catalysts produce a similar WGS activity. Among the Group II metals a barium promoted catalyst has the highest WGS activity while a magnesium promoted catalyst showed the lowest WGS activity.

A potassium promoted catalyst generated the highest yield of CO₂ and hydrocarbon but the lowest methane rate. All five catalysts yielded a similar C₃ and C₄ olefin ratio, but a K promoted catalyst produced a notably higher C₂ olefin fraction than Group II metal promoted catalysts. FTS product distributions indicate that a potassium promoted catalyst generated a higher C₁₉₊ fraction than the other Group II metal promoted catalysts. At a low space time, the potassium promoted catalyst had a lower methane selectivity than Group II metal promoted catalysts but at high space times, all except Ba promoted catalysts had a similar methane selectivity.

Keywords: Fischer-Tropsch synthesis; iron catalyst; promoter, alkali earth metals; barium, potassium, beryllium, magnesium, calcium

Introduction

Fischer-Tropsch synthesis converts a mixture of CO and H₂ that can be produced from coal or natural gas to liquid fuels. One of the advantages of FTS is that the process can be designed to produce gasoline, diesel and/or chemicals. There are two types of operating modes, the low temperature, which is for production of wax, and the high temperature FTS, which is designed for production of gasoline and alkenes.

In FTS process, the hydrocarbon is produced from CO and H₂, which can be expressed as

where n is defined as $n = 1/(1-\alpha)$ or it can be rearranged as $\alpha = 1 - (1/n)$.

When an iron catalyst is used for the FTS reaction, the water gas shift (WGS) reaction can also occur. This side reaction consumes CO and water produced in the FTS process to produce additional hydrogen:

Potassium has long been used as a promoter for iron catalysts to increase the alkene yield and to decrease the CH₄ selectivity [1]. It is also believed that potassium can also increase FTS and water-gas shift catalytic activity [2]. In spite of the widespread use of potassium as a promoter, little work has been reported to allow a direct comparison of promoters at medium or high pressure FTS conditions. We have recently compared potassium to other Group I alkali metal promoters under medium pressure conditions appropriate for slurry reactor operations [3]. The present work extends the work with Group I to include promoters in Group II of the Periodic Table.

Promoted iron FTS catalysts with Fe:alkali-earth metal = 100:1.44 atomic ratio of Group II elements (beryllium, magnesium, calcium and barium) were used in this study. The influence

of alkali-earth on product selectivity, productivity, water gas shift and FTS activity are compared with results obtained from FTS reactions over potassium promoted iron catalyst.

Experimental

Preparation of alkali metal promoted catalysts

Four iron catalysts promoted with Be, Ba, Ca and Mg and one with potassium were prepared and tested in this study. An atomic ratio of 1.44:100 of promoter to iron was used. Precipitated iron catalysts were prepared with tetraethyl orthosilicate, iron nitrate, potassium carbonate and copper nitrate. Ferric nitrate solution was first prepared by dissolving $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in distilled and demonize water, and the amount of tetraethyl orthosilicate needed to make Si:Fe of 4.6:100 atomic ratio was added. The mixture was stirred vigorously until the tetraethyl orthosilicate hydrolyzed. The tetraethyl orthosilicate and iron nitrate mixture was then added to a continuous stirred tank reactor (CSTR) precipitation vessel together with a stream of ammonium hydroxide. By maintaining the slurry pH at 9 and an average residence time of 6 minutes, a base catalyst material with an iron to silicon atomic ratio of 100:4.6 was obtained. The slurry was collected using a vacuum drum filter and washed twice with demonize water. The final filter cake was dried in an oven with flowing air at 110°C for 24 hours. The catalyst was crushed to approximately $60\ \mu\text{m}$ and calcined for 4 hours in a 350°C oven under an air flow.

In this study, the iron catalyst was impregnated with an aqueous nitrate solution of barium, beryllium, calcium or magnesium for alkali-earth metal promoted catalysts, and K_2CO_3 solution for potassium promoted catalyst. Alkali-earth metal or potassium solution was added to obtain a promoter to iron atomic ratio of 1.44:100. Following the impregnation, the catalyst was dried at 110°C overnight with good mixing. Thus, catalysts promoted with four Group II alkali-earth metals and one with potassium were prepared for FTS studies.

In-situ catalysts activation

The iron catalyst needs to be activated with either H₂, CO or synthesis gas. Activation procedures can have a significant effect on the selectivity and activity of iron catalyst [4]. It was reported that catalysts activated with CO yielded more long-chain hydrocarbons than syngas and H₂ activated catalysts. In addition, activation conditions may also influence the performance of the iron catalyst. In this study, the potassium promoted iron catalyst was pretreated with CO at 270°C and 1.2 MPa for 24 hours. The reduction of Fe₂O₃ with CO occurs in two steps:

In addition, CO₂ may be formed by the Boudouard reaction:

Previous work in our lab showed that, following a 24-hour activation, approximately 50 % to 100% more carbon was present in the catalyst mass than was needed to form Fe₅C₂ [4]. Gradual oxidation of unpromoted Fe₅C₂ to Fe₃O₄ was observed when iron catalyst was used in FTS [4]. The results showed that at the end of the run an unpromoted iron catalysts had been completely oxidized to Fe₃O₄.

Reactor system

A one-liter CSTR was used in this study (Figure 1). A sintered metal filter was installed to remove the wax samples from the catalyst slurry in the reactor. The wax sample was extracted through the internal filter and collected in a hot trap (200°C). The components in the vapor space of the reactor continuously passed to a warm trap (100°C) and cold trap (0°C) that were used to collect samples of oil, light wax and water. Tail gas from the cold trap was analyzed with an HP quick GC.

After the catalyst was activated with CO, syngas was introduced at a rate of 10 NL/hr/gram-catalyst. CO and H₂ were introduced to a gas mixing vessel using mass controllers to provide a simulated synthesis gas. This flow rate was maintained until the activity became constant and was used as the standard reaction condition. Then the gas space velocity was varied in the range of 3 to 60 NL/hr/g-Fe to collect kinetic data. Other reaction conditions were maintained at 270°C, 1.2 MPa and a stirrer speed of 750 rpm.

Product sampling and analysis

Gas, water, oil, light and heavy reactor wax samples were collected daily and analyzed. Table 1 gives the summary of the instruments for gas and liquid product analysis. A heavy wax sample was taken from the 200°C hot trap connected to the filter. Vapor phase above the slurry phase passed to the warm (100°C) and the cold (0°C) traps outside the reactor. The light wax and water mixture was collected from the warm trap and an oil plus water sample from the cold trap. Tail gas from the cold trap was analyzed with an online HP Quad Series Micro GC and molar compositions of C₁-C₇ olefins and paraffins were obtained. Hydrogen and carbon monoxide conversions and CO₂ produced were calculated based on the gas product online GC analysis results and the gas flow measured at the reactor outlet. Hydrogen, carbon monoxide and syngas conversion were obtained using the following formula:

$$\text{Conversion} = \frac{(N_{\text{in}} - N_{\text{out}})}{N_{\text{in}}} \times 100\%$$

The oil and light wax samples were mixed before being analyzed with an HP 5790A GC. The heavy wax was analyzed with an HP5890 Series II Plus GC while the water sample was analyzed with an HP5890 GC.

Results and Discussion

Effect on Fischer-Tropsch synthesis activity

For a synthesis gas of $H_2:CO = 0.7:1$, Figure 2 shows the results of CO conversion over the catalysts promoted with Group II alkali-earth metals (Ba, Be, Ca and Mg) and potassium. The potassium promoted catalyst yielded the highest overall CO conversion of 70% at the base reaction conditions. The calcium promoted FTS catalyst yielded the lowest initial conversion of 47% while all other Group II alkali-earth metal promoted catalysts produced CO conversions of 50-56% range.

Deactivation rate (%/day) for these five catalysts was obtained from the CO conversion results of over 500 hours of FTS reaction. As described in the experimental section, FTS base reaction conditions were established and then the space velocity was changed from 3 to 50 NL/h/g-iron before the reaction conditions were switched back to the original standard one. Overall deactivation rate was calculated based on the total reaction time; therefore, the overall deactivation rate may be higher than during a run without reaction condition changes. As indicated in Figure 3, beryllium and barium yielded a low deactivation rate of 0.07 and 0.15% per day, respectively, while potassium and calcium were 0.88 and 0.91, respectively. Magnesium promoted catalysts yielded the highest deactivation rate (2.24%/day) among all five catalysts tested. For potassium, this is a faster deactivation rate when the same catalyst is used at one flow rate (3.1 NL/hr gcat) and a high (90%) initial CO conversion. Presumably altering the reaction conditions causes a higher deactivation rate.

Figure 4 shows the results of CO conversions at various space velocities (NL/g-Fe/h) (space time = $h \cdot g\text{-Fe}/NL$) following establishment of stable activity at the base condition. At low space time, all Group II alkali-earth metal promoted catalysts produced a CO conversion similar to the potassium promoted catalyst. At an intermediate range of space time, however, the

catalysts showed different CO conversions. Potassium yielded the highest overall CO conversion at both a high and a medium space time. At a high space time, magnesium yielded a similar conversion to potassium. Both beryllium and barium showed nearly the same CO conversion in the full range of the space time of 3 to 50 h•g-Fe/NL. Calcium produced the lowest CO conversion at a space time above 0.1 h•g-Fe/NL, and showed the lowest activity at a high space time.

Effect on Fischer-Tropsch synthesis selectivity

Figures 5 and 6 show the rates of hydrocarbon, methane, CO₂ and water formation for FTS reactions catalyzed with Group II alkali-earth metal and potassium promoted catalysts under the reaction conditions (270°C, 175sig and H₂:CO of 0.67:1) at the same low CO conversion (20%). All Group II alkali-earth metal promoted catalysts produced a higher hydrocarbon rate than the potassium promoted catalyst at this CO conversion. A 3.2 to 3.7 g/h/g-iron hydrocarbon rate was obtained for Group II alkali-earth metal promoted catalysts while the potassium promoted catalyst generated a lower hydrocarbon rate of 2.75 g/h/g-iron. Figure 6 shows that the rate for methane production for the potassium promoted catalyst was lower than all Group II alkali-earth metal promoted catalysts. While the potassium promoted catalyst produced a similar CO₂ rate to that of Be and Ba, it yielded a lower water production rate than other Group II alkali-earth metal promoted catalysts. This result shows that the potassium promoted catalyst generated a higher WGS activity than Group II alkali-earth metal promoted catalysts. The data in Figure 6 also show that calcium and magnesium promoted catalysts produced lower CO₂ rates than other alkali-earth metal promoted catalysts.

Olefin ratio was calculated from the following equation:

$$\text{Olefin ratio} = \frac{\text{Olefin}}{(\text{Olefin} + \text{Paraffin})}$$

Figure 7 shows the olefin ratio from FTS over potassium and Group II alkali-earth metal promoted iron catalysts compared at the same 20% CO conversion. The data show that all Group II alkali-earth metal and potassium promoted catalysts yielded similar C_3 and C_4 olefin ratios that fall in the 0.85-0.90 range. Ethene fraction, however, shows a significant difference between potassium and Group II alkali-earth metal promoted catalysts. An ethene fraction of 0.76 was obtained for the C_2 fraction for the potassium promoted catalyst while an ethene fraction of 0.30-0.35 was obtained for the Group II alkali-earth metal promoted catalysts.

The distribution of hydrocarbon fractions (Figure 8) show that potassium produced more C_{19+} than the Group II alkali-earth metal promoted catalysts. The potassium promoted catalyst produced a similar amount of C_{12} - C_{18} fraction as the Be and Ca promoted catalysts but a smaller gasoline fraction (C_5 - C_{11}) than the Group II alkali-earth metal promoted catalysts. Among the Group II alkali-earth metal promoters, Ca produced the largest gasoline fraction (44.9%) and the smallest gas (C_1 - C_4) and C_{19+} fraction while the Ba promoted catalyst generated the highest C_{19+} and C_1 - C_4 fractions.

Figure 9 shows the CO_2 selectivity obtained from FTS reactions catalyzed by Group II alkali-earth metal promoted catalysts. In this study, space time varied in the range of 0.02 to 0.33 hr-g(Fe)/l, i.e., space velocities in the range of 3 to 50 NL/h/g(Fe). The potassium promoted catalyst produced more CO_2 than any alkali-earth metal promoted catalyst in the whole range of space time although the CO_2 selectivity trends converge at a space time of about 0.1. Magnesium and calcium promoted catalysts produced a lower CO_2 yield than beryllium and barium promoted catalysts. At a low space velocity, the barium promoted catalyst generated the most CO_2 while all the other Group II alkali-earth metal promoted catalysts produced a similar CO_2 selectivity (40-42%). Therefore, calcium and magnesium promoted catalysts gave better carbon utilization than beryllium and barium promoted catalysts. The potassium promoted

catalysts produced a lower carbon utilization than any of the Group II alkali-earth metal promoted catalysts. Higher CO₂ production from the potassium promoted catalyst suggests that it had a better WGS activity.

As another measure of carbon utilization, methane selectivity is shown in Figure 10. Although the potassium promoted catalyst produced the most CO₂, it generated the least methane at high space velocity among the five catalysts tested in this study. Except at a low space velocity, all Group II alkali-earth metal promoted catalysts generated similar amounts of methane.

Over the range of CO conversion (space time range), the potassium promoted catalyst provided a lower water partial pressure than the other promoted catalysts (Figure 11). Even so, all of the promoted catalyst produced the maximum water partial pressure at about the same space time (0.05; 40-50% CO conversion).

The carbon usage ratio (fraction of CO converted to hydrocarbons) was lower for the potassium promoted catalyst than for the Group II alkali-earth promoted catalysts. The utilization ratio for the four alkali-earth promoted catalysts are similar (Figure 12).

The alpha values obtained for the promoted catalyst are summarized in Figure 13. The potassium promoted catalyst had the largest alpha value, 0.80. There was a gradual decline in alpha for the alkali-earth promoted catalysts as the promoter was located lower in the Periodic Table, attaining 0.75 as the lowest value.

Conclusion

Iron FTS catalysts promoted with Group II alkali-earth metals produced lower overall FTS activity and lower alpha values than a potassium promoted iron catalyst. The lowest alpha values were obtained from Ba and Ca promoted catalysts. Among the Group II alkali-earth metals, Mg and Ba promoters caused slightly higher FTS activity than Be and Ca promoted

catalysts. The catalytic activity of the potassium promoted catalyst declined more rapidly when the conditions were changed than when operating at the same temperature, pressure and 3.1 NL/hr gFe (90% CO conversion initially). Ba and Be promoted catalysts showed better stability than the potassium and calcium promoted catalysts which were more stable than the magnesium promoted catalyst. All Group II alkali-earth metal promoted catalysts yielded a higher carbon utilization than the potassium promoted catalyst regardless of the space time.

Carbon dioxide production shows that the potassium promoted catalyst possesses better WGS activity than any Group II alkali-earth promoted catalyst, even at a high CO conversion. At a low CO conversion, however, K, Ba and Be promoted catalysts had similar WGS activity. Barium promotion generated the highest WGS activity while magnesium promotion showed the lowest WGS activity among the Group II alkali-earth metals. The higher WGS activity for the potassium promoted catalyst led to a lower carbon utilization rate than for the Group II alkali-earth promoted catalysts.

Although the C₃ and C₄ olefin/paraffin ratio did not vary with promoter, a notably higher C₂ olefin/paraffin ratio was obtained for the potassium promoted catalyst than for the Group II alkali-earth promoted catalysts. The yield of various hydrocarbon product fractions varied only slightly among the promoted iron catalysts.

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Table 1		
Analyzers for FTS Products		
Analyzer	Sample	GC Detector
HP Quad Series Micro GC	Gas	TCD
HP 5890A Series II	Water	TCD
Agilent 6890	Oil + Light Wax	FID
HP 5890 Series II Plus	Heavy Wax	FID

Figure 1. CSTR Fischer-Tropsch system reactor system.

**Figure 2. Effect of promoter on iron FTS catalyst activity
(270°C, 1.2 Mpa and 10 sl/h/g-iron)**

Figure 3. Deactivation Rate of potassium and alkali earth promoted catalysts (270°C, 1.3MPa, 10NL/h/g-iron)

Figure 4. Effect of alkali promoter on CO conversion
(270°C, 1.2 MPa)

Figure 5. Hydrocarbon rate at 20% CO conversion

Figure 6. Production of CO₂ H₂O and CH₄ at 20% CO conversion

Figure 7. Effect of alkali promoters on olefin ratios at 20% CO conversion

Figure 8. Effect of promoters on hydrocarbon distribution at 20% CO conversion

Figure 9. Influence of alkali nature on CO₂ selectivity (◇, K; □, Be; Δ, Mg; x, Ca; ○, Ba).

Figure 10. Alkali nature on methane selectivity (◆, K; ■, Be; ▲, Mg; x, Ca; ", Ba).

Figure 11. Effect of the promoter on the water partial pressure (◆, K; ■, Be; ▲, Mg; x, Ca; ○, Ba).

Figure 12. Effect of promoter on the carbon utilization (CO to hydrocarbon/CO converted)
 (♦, K; ■, Be; ▲, Mg; x, Ca; ○, Ba).

Figure 13. Effect of promoter on alpha values

C. Effect of Structural Promoters on Iron Catalysts

Synthesis of the Catalysts

The Fe-Al samples were prepared by co-precipitation of iron and aluminum from nitrate solutions at constant pH of 8.5. Iron nitrate (1.3M) and aluminum nitrate (1.43M) solutions were mixed to yield a given Al/Fe ratio. Ammonium hydroxide (30% NH_3) was used as the precipitant. About 100 cm^3 deionized water was placed in a large beaker and heated to 85°C using a magnetic stirrer/hotplate. The pH was adjusted to 8.5 by addition of an appropriate quantity of NH_4OH . The temperature was held at 85 °C throughout the precipitation procedure. The solution of Fe^{3+} and Al^{3+} ions was added slowly to the beaker with continuous stirring. Simultaneously, the NH_4OH was added at a rate such that the pH was maintained at a constant value of 8.5. The resulting precipitate was filtered using vacuum filtration and washed with deionized water until the pH of the filtrate was measured to be in the range 7.0 to 7.5. The precipitate was subsequently dried in an oven overnight at 110°C followed by calcination in static air at 400°C for 10 hours. Samples were prepared that contained from 0% to ~25% Al. The samples were analyzed for iron content following calcination using ICP. The iron content by weight in the unpromoted samples was found to contain 70% Fe (average of 3 analyses) which agrees very well with the theoretical value of 69.994% in Fe_2O_3 , confirming that the sample was hematite. XRD analysis also provided further proof that the samples contained hematite. Table 1 lists the compositions of the promoted iron catalysts.

The Fe-Si samples were already available in the lab. They were prepared by hydrolyzing an appropriate quantity of tetraorthosilicate (TEOS) in the acidic $\text{Fe}(\text{NO}_3)_3$ solution followed by precipitation using NH_4OH . They had silicon contents of up to ~8% Si, had been calcined at 400°C and were used without any further treatment. Their compositions are summarized in Table 2.

XRD analysis of the samples showed that as the degree of loading of the promoter increased the samples became more amorphous. The samples were then treated in an oven at 600°C for 24 hours to improve crystallinity.

BET Surface Area Measurements

Nitrogen sorption isotherms were measured using a Micromeritics TriStar 3000 instrument. Prior to analysis each sample was outgassed at 160°C for at least 12 hours to a pressure less than 100 mTorr. The results of the analyses for the samples calcined at 400°C and 600°C are presented in Tables 3 and 4. It can readily be seen that as the quantity of the promoter is increased the surface area also increases. Also, as the temperature of the calcination is increased the surface area decreases. Representative plots illustrating the trend in change of surface area with increasing atomic percent of structural promoter for both the Al and Si additions are shown in Figures 1 and 2, respectively.

XRD Analysis

The samples containing varying atom percentages of the structural promoters Al or Si were prepared in order to investigate whether they are capable of entering into solid solution with the hematite and hence be well dispersed throughout the oxide mass. Whether or not these promoters had entered into solid solution was determined from their effect on the lattice parameters of the magnetite. Powder X-Ray Diffraction was used to determine the unit cell dimensions of the hematite. Hematite has a hexagonal structure and thus two cell dimensions, a_0 and c_0 , had to be determined. X-Ray Diffractograms were obtained for all samples. Figures 3 and 4 show the diffractograms obtained for the Al and Si promoted iron oxide samples calcined at 400°C. It can be seen that the Al promoted samples are not very crystalline at loadings greater than about 7 atom%. In contrast, the Si promoted samples are quite amorphous to X-Rays,

crystallinity only evident for the very small atomic fractions. It appears that the Si retards the crystallization of the Fe_2O_3 to a much greater degree than the presence of the Al. In order to make accurate lattice parameter determinations a greater degree of crystallinity is required so all the samples were heated in an oven to 600°C for 24 hours and the resulting diffractograms are shown in Figures 5 and 6. In all cases Fe_2O_3 was identified as the only species present. At the higher levels of Al addition, 17.9% and 24.22%, there is evidence of another species present but this has yet to be identified. The ten most intense peaks of the diffractograms were each analyzed individually using the fitting program WINFIT to determine accurate peak locations in terms of 2θ . These 2θ values together with their corresponding Miller indices were input to the program UnitCell to calculate the lattice parameters for the hexagonal Fe_2O_3 . It was found that as the quantity of the promoter increased there was a shift in all 2θ to higher values indicating that the promoter had entered the hematite lattice and was influencing its dimensions. These shifts in the lattice dimensions are shown as a function of the promoter concentration in Figures 7 to 10. The shift to higher 2θ values resulted in a decrease in both a_0 and c_0 lattice parameters. This is to be expected as the ionic radii of both Al^{3+} and Si^{4+} , $0.5\text{\AA}$ and $0.41\text{\AA}$, respectively, are both less than that of Fe^{3+} ($0.64\text{\AA}$), and would lead to a contraction of the unit cell. The shifts in the lattice dimensions are taken as evidence that the cations have entered into the hematite lattice.

Table 1		
Al Content of the Samples		
Sample	Al/Fe	Atom % Al
8A	---	0
10A	0.0118	1.17
3A	0.02	1.96
4A	0.044	4.21
5A	0.0706	6.6
6A	0.1335	11.77
7A	0.218	17.9
9A	0.3197	24.22

Table 2		
Si Content of the Samples		
Sample	Si/Fe	Atom % Si
FeSiO	---	0
FeSi ₂	0.02	1.96
FeSi ₄	0.044	4.21
FeSi ₈	0.08	7.41

Table 3			
Results of BET Analysis of Samples Treated at 400°C			
Sample	BET S.A. m ² /g	Pore Volume cm ³ /g	Average Pore Radius nm
8A	33.44	0.19	11.4
10A	133.5	0.24	3.6
3A	46.19	0.2	8.5
4A	19.05	0.13	13.6
5A	99.6	0.25	4.9
6A	176.6	0.25	2.8
7A	232.6	0.24	2.1
9A	215.3	0.22	2.1
FeSiO	23.7	0.18	12.0
FeSi ₂	78.9	0.2	5.1
FeSi ₄	163.2	0.24	2.9
FeSi ₈	193.5	0.24	2.5

Table 4			
Results of BET Analysis of Samples Treated at 600°C			
Sample	BET S.A. m ₂ /g	Pore Volume cm ³ /g	Average Pore Radius nm
8B	9.95	0.11	22.6
10B	11.6	0.12	20.9
3B	15.2	0.14	18.5
4B	14.9	0.11	14.4
5B	25.4	0.2	15.9
6B	36.4	0.22	11.9
7B	44.0	0.18	8.3
9B	52.9	0.18	6.6
FeSiOB	4.3	0.03	13.5
FeSi ₂ B	36.8	0.19	10.4
FeSi ₄ B	64.3	0.2	6.2
FeSi ₈ B	98.3	0.21	4.2

Figure 1. Variation of BET surface area with increasing atomic percent of Al. All samples were calcined at 600°C.

Figure 2. Variation of BET surface area with increasing atomic percent of Si. All samples were calcined at 600°C.

Figure 3. X-ray diffractograms of Al promoted hematite samples calcined at 400°C.

Figure 4. X-ray diffractograms of Si promoted hematite samples calcined at 400°C.

Figure 5. X-ray diffractograms of Al promoted hematite samples calcined at 600°C.

Figure 6. X-ray diffractograms of Si promoted hematite samples calcined at 600°C.

Figure 7. Variation of unit cell parameter a_0 with concentration of Al promoter.

Figure 8. Variation of unit cell parameter c_0 with concentration of Al promoter.

Figure 9. Variation of unit cell parameter a_0 with concentration of Si promoter.

Figure 10. Variation of unit cell parameter c_0 with concentration of Si promoter.

D. Fischer-Tropsch Synthesis: Influence of Process Parameters on Activity and Selectivity of a Potassium Promoted Iron Catalyst

Abstract

Process parameters can play an important role in a chemical process. Study of the effect of reaction temperature, pressure and other parameters is necessary for process development, design and optimization. Factorial design is an effective approach for chemical process parametric studies. By experimental design, the number of trials was minimized. Although two-level factorial design failed to detect the nonlinearity of the process between the high- and low-level of factors concerned, it is still more effective to conduct several two-level experiments than to perform a series of three- to four-level experiments. Two-level factorial design can reveal both the single factor effect and the cross interactions between these factors. Results from this study show that temperature has the most important influence on CO and H₂ conversions, CO₂ and CH₄ selectivity and hydrocarbon production for this rate. Pressure and space velocity played a less significant role. Cross interactions between the factors are sometime not negligible, such as the interaction between temperature and other two factors (pressure and space velocity). Little difference in CO conversion was observed for FTS with 1.44 and 5.00 K:Fe catalysts at low temperature (230°C). The two catalysts yielded similar CO₂ and CH₄ selectivity at a high temperature. Hydrocarbon rate was higher for K5.00 than the K1.44 catalyst.

Introduction

The Fischer-Tropsch synthesis (FTS) process, which converts carbon monoxide and hydrogen to hydrocarbons and oxygenates, makes coal or natural gas a promising alternative to petroleum. The mechanism and kinetics of the FTS process have been investigated (Dry, 1996; van der Laan and Beenackers, 1999; Raje and Davis, 1997; Adesina, 1996; Dry, 1981;

Zimmerman and Bukur, 1990; Ribeiro, et al., 1997; Hindermann, et al., 1993). The process can be simplified as the following two reactions:

Average molecular weight of the hydrocarbon products depends on reactions conditions and catalyst. When an iron catalyst is utilized in the FTS, a significant amount of carbon is consumed in the water gas shift (WGS) reaction, as shown by the second reaction. The complexity of the FTS process is the major obstacle in understanding the mechanism and defining the kinetics. A variety of proposals for the FTS mechanism are based on the surface species and various elementary reaction steps. Different kinetic equations were expressed in power-law based on the empirical data and the mechanism proposals from the literature (van der Laan and Beenackers, 1999).

Process parameters, i.e, reaction temperature, pressure and space velocity, have a significant influence on FTS kinetics, catalyst activity and selectivity. Due to the complexity of the FTS process, development of the FTS technology leads to the complications in the theoretical interpretation of the research data. A well designed experiment using statistic principles could sharply lower the cost of the experimental investigation. A common method to conduct the experiment is to change one factor at a time. Although it remains a conservative research approach, it is neither sufficient nor possible to detect the interactions between the factors involved. In this study, we investigate the effect of these process parameters, i.e., reaction temperature, pressure and space velocity, on carbon monoxide and hydrogen conversion, carbon dioxide and methane selectivity, and hydrocarbon rate. Experiments were conducted using a 3-factor, 2-level factorial design approach. The influence of each factor on

conversion and selectivity, and interactions between temperature, pressure and space velocity are discussed based on the experimental results.

Experimental

Preparation of Unpretreated Catalyst

Two iron catalysts promoted with potassium were prepared and tested in this study. Table 1 gives the compositions of the catalysts used in this study. The ratios shown in Table 1 are all atomic ratios relative to iron. Precipitated iron catalysts were prepared with tetraethyl orthosilicate, iron nitrate, potassium carbonate and copper nitrate.

Copper is widely used as a promoter for iron FTS catalyst. It was believed that copper can facilitate the activation process. Copper can also minimize the sintering of iron catalysts by lowering the reduction temperature (Dry, 1981). In this study, the 100Fe/4.6Si catalyst base powder was impregnated with the proper amount of aqueous $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ solution to give an atomic composition of 100Fe/4.6Si/2.0Cu. The amount of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ added will depend on the iron content of the base catalyst. In addition to copper, potassium is also an important promoter for an iron catalyst to improve the FTS activity and selectivity. Details of catalyst preparation was given elsewhere (Luo and Davis, 2001).

In-situ Activation of Unpretreated Catalysts

The iron catalyst needs to be activated with H_2 , CO or synthesis gas. Activation procedures can have a significant effect on the selectivity and activity of iron catalyst (Zimmerman and Bukur, 1990; Ribeiro, et al., 1997). It was reported that catalysts activated with CO yielded higher long-chain hydrocarbons than syngas and H_2 activated catalysts. In addition, activation conditions may also influence the activity and selectivity of the iron catalyst.

In this study, the potassium promoted iron catalysts were pretreated with CO at 270°C, 1.2 MPa for 24 hours. The reduction of Fe₂O₃ with CO occurs in two steps:

In addition, CO₂ and C may be formed by the Boudouard reaction:

Our previous work showed that approximately 50 % to 75% more carbon was present in the catalyst mass than was needed to form Fe₅C₂ (O'Brien, et al., 1996). Gradual oxidation of Fe₅C₂ to Fe₃O₄ was observed when iron catalyst was used in FTS and a catalyst with long-term stability consists of a mixture of Fe₃O₄ and iron carbides.

Reactor System

A one-liter continuous stirred tank reactor (CSTR) was used in this study. A sintered-metal filter was installed to remove the wax samples from the catalyst slurry. The wax sample was extracted through the internal filter and collected in the hot trap (200°C). A warm trap (100°C) and cold trap (0°C) were used to collect oil, light wax and water samples. Tail gas from the cold trap was analyzed with an HP quick GC.

A gas mixer fed with a CO and an H₂ stream fitted with mass controllers was used to provide a simulated synthesis gas with an H₂:CO ratio of 0.7. After the catalyst was activated with CO, syngas was introduced at a rate of 10 l-hr⁻¹g⁻¹ (based on iron). Reaction conditions were 230°C, 1.2MPa and a stirrer speed of 750 rpm.

Product Sampling and Analysis

Daily gas, water, oil, light and heavy wax samples were collected and analyzed. Table 2 gives the summary of the instruments for gas and liquid product analysis. A heavy wax sample was taken from the 200°C hot trap connected to the filter. Vapor phase above the slurry phase

passed to the warm (100°C) and the cold (0°C) traps outside the reactor. The light wax and water mixture was collected from the warm trap and an oil plus water sample from the cold trap. Tail gas from the cold trap was analyzed with an online HP Quad Series Micro GC. Molar compositions of C₁-C₇ olefins and paraffins were thus obtained. Hydrogen and carbon monoxide conversions were calculated based on the gas product GC analysis results and the gas flow measured at reactor outlet. Carbon monoxide conversion, CO₂ and CH₄ selectivity, and hydrocarbon rate were obtained using the following formulas:

$$CO \text{ Conversion} = \frac{N_{CO-in} - N_{CO-out}}{N_{CO-in}} \bullet 100\%$$

$$CH_4 \text{ Selectivity} = \frac{N_{CH_4-out}}{(N_{CO-in} - N_{CO-out} - N_{CO_2-out})} \bullet 100\%$$

$$CO_2 \text{ Selectivity} = \frac{N_{CO_2-out}}{(N_{CO-in} - N_{CO-out})} \bullet 100\%$$

$$Hydrocarbon \text{ Rate} = 14.3 \bullet \left(\frac{N_{CO-in} f}{M_{Iron}} - \frac{N_{CO_2-out}}{M_{Iron}} \right)$$

where N is the molar flow rate in moles/hour, f is the fractional conversion of CO, and M is the weight of active metal (Fe) in grams.

The oil and light wax samples were mixed before analysis with an HP 5790A GC. The heavy wax was analyzed with an HP5890 Series II Plus GC while the water sample was analyzed with an HP5890 GC.

Results and Discussions

Experiment Design

The purpose of factorial experimental design is to limit the number of experiments required to investigate the influence of the factors involved in a process. By proper design of the experiment, it is also possible to study the interaction between the factors concerned. In this study, FTS reaction temperature, pressure and space velocity were studied as the factors that affect the results of conversion and selectivity. A higher temperature may yielded a higher CO conversion, but it may also result in a higher undesired CO₂ and CH₄ selectivity. Studying the effect of each of these factors can lead to a better understanding of the process and establishment of a mathematical model that can be used in process design.

A process can be described by a mathematical expression as a function of factors $x_1, x_2, x_3, \dots$, i.e.

$$Y = f(x_1, x_2, x_3, \dots)$$

This can be expressed with an approximate equation as follows:

$$Y = B_o + \sum_j B_j Z_j + \sum_{i < j} B_{ij} Z_i Z_j + \sum_j B_{jj} Z_j^2 + \dots$$

Two-level factorial experimental design can provide the maximum information from a minimum number of research trials (Anderson, 1974). It is believed that two-level factorial design is the most effective, although three- or four-level design can detect the nonlinearity in functional relationships between the factors and the response variable. However, two-level experiments require much fewer trials than a three- or four-level design so that it is more cost effective to conduct several two-level experiments than the latter.

An eight-run experiment was designed based on the three factor and two-level factorial design, as shown in table 3. It is important that the actual experiment was conducted in a

random order instead of the order listed in the table to ensure the integrity of the experiment. Based on literature and our own experience, a typical FTS conditions of 250°C, 2MPa and 7.5L h⁻¹g was chosen as the middle point of the experimental variables. The low (-1) and high (+1) level pairs for temperature, pressure and space velocity were 230/270°C, 1.2/2.9 MPa and 5.0/10.0 SL h⁻¹gFe⁻¹, respectively. Figures 1 through 5 give the response of CO and H₂ conversion, hydrocarbon rate and CO₂ and CH₄ selectivity for the reaction catalyzed with a potassium (g•h⁻¹gFe⁻¹) promoted iron catalysts.

The effect of a single factor is defined as the “main effect” and that between any two factors named as “interaction.” While the main effect depicts the influence of a single factor, interaction effects describe the effect of one factor on the behavior of the other. Main effect is calculated by the following equation:

$$E_T = \text{average response at low level of factor T} - \text{average response at high level of factor T}$$

$$= \frac{(Y_{T_2P_1S_1} + Y_{T_2P_1S_2} + Y_{T_2P_2S_1} + Y_{T_2P_2S_2})}{4} - \frac{(Y_{T_1P_1S_1} + Y_{T_1P_1S_2} + Y_{T_1P_2S_1} + Y_{T_1P_2S_2})}{4}$$

where Y is the response such as CO conversion, CO₂ selectivity or hydrocarbon rate; T, P and S are three factors defined in this study, i.e., temperature, pressure and space velocity, respectively. A positive effect indicates the response variable changes in the same direction as the factor changes while a negative effect behaves the opposite.

Interaction effect between two factors is calculated in the same way:

$$I_{TP} = \text{Effect of P at level 2 of Factor T} - \text{Effect of P at level 1 of Factor T}$$

$$= \frac{(Y_{T_2P_2} - Y_{T_2P_1}) - (Y_{T_1P_2} - Y_{T_1P_1})}{2}$$

In case of a 3-factor experiment, interaction can also be calculated by substituting the four terms in the above equation as:

$$\begin{aligned} Y_{T_2P_2} &= \frac{1}{2} \bullet (Y_{T_2P_1S_1} + Y_{T_2P_1S_2}) \\ Y_{T_2P_1} &= \frac{1}{2} \bullet (Y_{T_2P_1S_1} + Y_{T_2P_1S_2}) \\ Y_{T_1P_2} &= \frac{1}{2} \bullet (Y_{T_1P_2S_1} + Y_{T_1P_2S_2}) \\ Y_{T_1P_1} &= \frac{1}{2} \bullet (Y_{T_2P_1S_1} + Y_{T_2P_1S_2}) \end{aligned}$$

Carbon Monoxide and Hydrocarbon Conversion

Based on the above concepts, a factorial design and response scheme for each series of FTS reactions was designed as shown in Table 4. An eight-run experiment was carried out for each catalyst at two temperature, pressure and space velocity levels. The middle level of the variables was based of the literature and our previous work. Table 5 shows the results of two series of experiments using two potassium promoted iron catalysts. It is shown in Table 5 and Figure 1 that reaction temperature produced the largest effect on CO conversion when K1.44 (Fe:K = 100:1.44) catalyst was used. When temperature (Factor T) changed from 230 to 270°C, average CO conversion increased by 26.8%. A much smaller effect of 6.64% was caused by pressure. Space velocity (Factor S) generated a negative effect on CO conversion because conversion decreased as the space velocity increased. Interactions between pressure and space velocity and the three-factor interaction are considered to be insignificant (<1%). Because of the normal experimental error, we neglect the two interaction effect (PS and TPS). The interaction between temperature and space velocity, and that between temperature and pressure were 5 and 8%, respectively. Reaction over K5.00 (Fe:K = 100:5) catalyst produced results (Table 5 and Figure 1) that are similar to the K1.44 catalyst. Temperature effect was as high as 31.08% and space velocity 20.70% while the effect of pressure and interactions of PS and TPS showed insignificant values (1-3%). Interaction between temperature and pressure was -8.78% and

between temperature and space velocity was -14.0% when K5.00 catalyst was used in FTS reaction.

Hydrogen conversion showed a behavior similar to CO conversion for FTS reaction over both potassium promoted iron catalysts. For both catalysts, temperature yielded an effect (25.0 and 26.9%) greater than that of space velocity (12.6 and 22.4%) on H₂ conversions. Pressure effect showed an even smaller effect on potassium promoted catalysts. All interaction effects were below 6%, which were much less important than a single main effect.

Figures 1 and 2 also show that the highest CO and H₂ conversions over potassium catalysts were obtained at high level of temperature and low level of space velocity. Pressure did not show an important role in CO and H₂ conversions as shown in Table 5 and Figures 1 and 2. Little change in CO conversion was observed between K1.44 and K5.00 catalyzed FTS reactions at low temperature (230°C).

Methane Selectivity

Methane selectivity for potassium promoted catalysts was appreciably affected by temperature only. Neither pressure nor space velocity played an important role in methane selectivity. All interaction effects except that between temperature and pressure were insignificant. Average CH₄ selectivity at the low temperature level (230°C) was 0.54 and 1.94% at 270°C. A pressure increase from 1.2 to 2.9 MPa raised the CH₄ selectivity from 0.98 to 1.5% while an increase in space velocity showed little change in CH₄ selectivity. Interaction of temperature and pressure showed a value of -0.56% and the results in Table 5 revealed a negligible level of interactions between other factors. The FTS reaction over K5.00 catalyst showed similar results and showed a slightly lower effect of temperature and interaction between temperature and pressure. When temperature level changed from 230 to 270°C, CH₄ selectivity increased from 0.96 to 1.85%, which is the largest main effect among all three factors. Similar

to K1.44 catalyst, K5.0 catalyst also revealed an interaction effect between temperature and pressure of 0.29%, which is the only appreciable value among all interactions. At a high temperature (270°C), both K1.44 and K5.00 catalysts yielded similar methane selectivity as indicated in Figure 3.

Carbon Dioxide Selectivity

For both catalysts, temperature had a more important effect on CO₂ selectivity than pressure and space velocity. All interaction effects with the K1.44 catalyst were not appreciable while FTS over K5.00 catalyst showed a moderate interaction of 4.62 and -3.17% between TP and PS, respectively. As shown in Table 5, a temperature change from 230 to 270°C over K1.44 catalyst resulted in an average CO₂ selectivity increase by 19.3%. When the K5.0 catalyst was utilized, a temperature increase resulted in a CO₂ increase by 16.2%. Pressure effect over potassium promoted catalysts, however, showed a much less important effect than that of temperature. Carbon dioxide selectivity decreased by 1.59% over K1.44 catalyst and by 7.18% over K5.00 catalyst when pressure changed from 1.2 to 2.9 MPa. Similarly, CO₂ selectivity decreased by 5.48% over K1.44 catalyst and by 5.74% over K5.00 catalyst were found when the space velocity increase from 5.0 to 10.0 SLh⁻¹gFe⁻¹.

Hydrocarbon Rate

Similar to all other effects, temperature had the most important influence on hydrocarbon rate. As shown in Table 5, a temperature change from 230 to 270°C resulted in an increase in hydrocarbon rate by 0.41 g/h/g-Fe over K1.44 catalyst and by 0.34 g/h/g-Fe over K 5.00 catalyst. Pressure and space velocity, however, affected the hydrocarbon rate to a much less extent, ranging from 0.04 to 0.14 g/h/g-Fe when potassium promoted catalysts were utilized. It is also found from Table 5 that the effect of pressure was greater than that of space velocity when K1.44 catalyst was used while the opposite result was observed when the K 5.00 catalyst was used. All

interaction effects were insignificant when K1.44 potassium promoted catalysts were used. When K5.00 catalyst was used, interactions between TS and TPS were -0.20 and -0.12, respectively. The other two interactions (TS and PS) were only 0.06 and -0.07.

Figure 5 shows that overall hydrocarbon rate over K5.00 catalyst is significantly higher than over K1.44 catalyst. As shown in Figure 5, a hydrocarbon rate of $0.68 \text{ gh}^{-1}\text{gFe}^{-1}$ was obtained when K.500 catalyst was used while the K1.44 catalyst yielded only $0.17 \text{ gh}^{-1}\text{gFe}^{-1}$ hydrocarbon under the same condition. When K5.00 catalyst was used, hydrocarbon yields at the first six data points were two to three times higher than that when K1.44 catalyst was used.

Conclusions

Factorial design is an effective approach for studying process parameters. By designing the experiment, the number of trials was minimized and the cost and time were significantly saved. Although two-level factorial design failed to detect the nonlinearity of the process between the high and low level of factors concerned, it is still the more effective way to conduct several two-level experiments than to perform a series of experiment of three- or four-level. In addition, two-level factorial design reveals the interactions between factors.

Acknowledgment

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Nomenclature

Y	Response
E	Main effect of a factor
I	Interaction between factors
N	Molar flow (mol/hr)
f	Fractional conversion (%)

Subscript

T	Reaction temperature
P	Reaction pressure
S	Space velocity
T1	Temperature at low level
T2	Temperature at high level
P1	Pressure at low level
P2	Pressure at high level
S1	Space velocity at lower level
S2	Space velocity at high level

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Table 1					
Alkali Promoted Catalysts used in this Study ^a					
Catalyst ID	Fe	Si	Cu	K	Catalyst Loading (g) ^b
K 1.44	100	4.6	2.0	1.44	9.59
K 5.00	100	4.6	2.0	5.00	32.20
a. Atomic ratio. b. Grams catalyst in 300g start-up oil.					

Table 2		
Analyzers for FTS Products		
Analyzer	Sample	GC Detector
HP Quad Series Micro GC	Gas	TCD
HP 5890 GC Series II	Water	TCD
HP 5790A GC	Oil + Light Wax	FID
HP 5890 Series II Plus	Heavy Wax	FID

Table 3			
Three-Factor and Two-Level Factorial Experiment Plan			
Run ID	Temperature (°C)	Pressure ^a (MPa)	Space Velocity (SL h ⁻¹ g-Fe ⁻¹)
A	230	1.2	5
B	230	1.2	10
C	230	2.9	5
D	230	2.9	10
E	270	1.2	5
F	270	1.2	10
G	270	2.9	5
H	270	2.9	10
a. Gauge pressure.			

Table 4								
Experiment Design and Response Scheme for CO Conversion Study with K1.44 Catalyst								
Standard Run Order	Actual Run Order	Response (CO Conversion)	Temperature		Pressure ^a		Space Velocity	
			Factor T		Factor P		Factor S	
			Level	(°C)	Level	(MPa)	Level	(SL h ⁻¹ gFe ⁻¹)
A	3	21.6	-1	230	-1	1.2	-1	5
B	8	15.9	-1	230	-1	1.2	+1	10
C	1	22.1	-1	230	+1	2.9	-1	5
D	6	17.3	-1	230	+1	2.9	+1	10
E	5	49.4	+1	270	-1	1.2	-1	5
F	7	30.3	+1	270	-1	1.2	+1	10
G	4	63.2	+1	270	+1	2.9	-1	5
H	2	21.1	+1	270	+1	2.9	+1	10
a. Gauge pressure.								

Table 5									
Summary of Effect Analysis from Three-Factor Two-Level Experiment Design									
Response Variable	Catalyst ID	Average Response	Factor T (°C)	Factor P (MPa)	Factor S (Sl h ⁻¹ gFe ⁻¹)	Interaction TP	Interaction TS	Interaction PS	Interaction TPS
CO Conversion (%)	K1.44	32.6	26.8	6.64	-13.0	5.69	-7.67	-0.51	-1.00
	K5.00	34.5	31.1	-2.38	-20.7	-8.78	-14.0	1.61	-3.07
H ₂ Conversion (%)	K1.44	30.1	26.9	10.7	-12.6	4.83	-5.66	-1.83	1.22
	K5.00	34.8	25.0	1.48	-22.4	-4.26	-6.15	-2.05	1.70
CH ₄ Selectivity (%)	K1.44	1.24	1.39	0.52	0.01	-0.56	0.05	-0.08	-0.03
	K5.00	1.40	0.89	0.07	-0.04	0.29	-0.02	-0.11	0.01
CO ₂ Selectivity (%)	K1.44	28.9	19.3	-1.59	-5.48	0.60	-0.53	-0.18	-1.26
	K5.00	35.2	16.2	-7.18	-5.74	4.62	0.44	-3.17	0.43
Hydrocarbon Rate (g h ⁻¹ gFe ⁻¹)	K1.44	0.34	0.41	0.14	0.06	0.08	0.04	0.03	0.04
	K5.00	0.55	0.34	0.04	0.11	-0.20	-0.07	0.06	-0.12

Figure 1. CO Conversion

1: 230°C, 2.9MPa, 5 SL h⁻¹gFe⁻¹; 2: 230°C, 2.9MPa, 10 SL h⁻¹gFe⁻¹;
 3: 230°C, 1.2MPa, 5 SL h⁻¹gFe⁻¹; 4: 230°C, 1.2MPa, 10 SL h⁻¹gFe⁻¹;
 5: 270°C, 2.9MPa, 5 SL h⁻¹gFe⁻¹; 6: 270°C, 2.9MPa, 10 SL h⁻¹gFe⁻¹;
 7: 270°C, 1.2MPa, 5 SL h⁻¹gFe⁻¹; 8: 270°C, 1.2MPa, 10 SL h⁻¹gFe⁻¹

Figure 2. H₂ Conversion

1: 230°C, 2.9MPa, 5 SL h⁻¹gFe⁻¹; 2: 230°C, 2.9MPa, 10 SL h⁻¹gFe⁻¹;
 3: 230°C, 1.2MPa, 5 SL h⁻¹gFe⁻¹; 4: 230°C, 1.2MPa, 10 SL h⁻¹gFe⁻¹;
 5: 270°C, 2.9MPa, 5 SL h⁻¹gFe⁻¹; 6: 270°C, 2.9MPa, 10 SL h⁻¹gFe⁻¹;
 7: 270°C, 1.2MPa, 5 SL h⁻¹gFe⁻¹; 8: 270°C, 1.2MPa, 10 SL h⁻¹gFe⁻¹

Figure 3. Methane selectivity

1: 230°C, 2.9MPa, 5 SL h⁻¹gFe⁻¹; 2: 230°C, 2.9MPa, 10 SL h⁻¹gFe⁻¹;
 3: 230°C, 1.2MPa, 5 SL h⁻¹gFe⁻¹; 4: 230°C, 1.2MPa, 10 SL h⁻¹gFe⁻¹;
 5: 270°C, 2.9MPa, 5 SL h⁻¹gFe⁻¹; 6: 270°C, 2.9MPa, 10 SL h⁻¹gFe⁻¹;
 7: 270°C, 1.2MPa, 5 SL h⁻¹gFe⁻¹; 8: 270°C, 1.2MPa, 10 SL h⁻¹gFe⁻¹

Figure 4. CO₂ Selectivity

1: 230°C, 2.9MPa, 5 SL h⁻¹gFe⁻¹; 2: 230°C, 2.9MPa, 10 SL h⁻¹gFe⁻¹;
 3: 230°C, 1.2MPa, 5 SL h⁻¹gFe⁻¹; 4: 230°C, 1.2MPa, 10 SL h⁻¹gFe⁻¹;
 5: 270°C, 2.9MPa, 5 SL h⁻¹gFe⁻¹; 6: 270°C, 2.9MPa, 10 SL h⁻¹gFe⁻¹;
 7: 270°C, 1.2MPa, 5 SL h⁻¹gFe⁻¹; 8: 270°C, 1.2MPa, 10 SL h⁻¹gFe⁻¹

Figure 5. Hydrocarbon rate

1: 230°C, 2.9MPa, 5 SL h⁻¹gFe⁻¹; 2: 230°C, 2.9MPa, 10 SL h⁻¹gFe⁻¹;
 3: 230°C, 1.2MPa, 5 SL h⁻¹gFe⁻¹; 4: 230°C, 1.2MPa, 10 SL h⁻¹gFe⁻¹;
 5: 270°C, 2.9MPa, 5 SL h⁻¹gFe⁻¹; 6: 270°C, 2.9MPa, 10 SL h⁻¹gFe⁻¹;
 7: 270°C, 1.2MPa, 5 SL h⁻¹gFe⁻¹; 8: 270°C, 1.2MPa, 10 SL h⁻¹gFe⁻¹

Task 2. Catalyst Testing

The objective of this task is to obtain catalyst performance on the catalysts prepared in Task 1.

A. Deuterium Isotope Effects with a Precipitated Iron Catalyst in Slurry Phase

Fischer-Tropsch Synthesis

The impact of deuterium on the Fischer-Tropsch (FT) synthesis was studied with a precipitated iron catalyst in the slurry phase. As indicated in the summary, the data will provide design data for slurry reactors and separators. Deuterium has been used by several research groups to better understand the mechanism of CO hydrogenation. Inverse ($k_H/k_D < 1$), normal ($k_H/k_D > 1$) and no isotope effect ($k_H/k_D = 1$) have been reported (1). The conflicting results are thought to arise because rate of reaction is a combination of kinetic and equilibrium factors (2).

Experimental

Precipitated iron catalyst (100Fe/4.6Si/1.44K, atomic basis) (5g) was added to 310 g of Polywax 3000 (Petrolite, average M.W.=3000) which had been melted at 130°C in a one liter CSTR. The catalyst was activated with CO as follows. The reactor stirrer was set at 750 rpm, CO flow was started at 25 slph, the pressure was increased to 175 psig and the temperature was increased to 270°C at 2°C/min. These conditions were maintained for 24 hours and then the CO flow was lowered to 9.55 slph and D₂ flow was started at 6.52 slph. Fischer-Tropsch conditions were: whsv=5.0 sl h⁻¹ g-Fe⁻¹, D₂/CO=0.67, 270°C and 175 psig. Periodically D₂ was stopped and H₂ was used. The time on stream for each gas is shown in Table 1.

H₂ or D₂ and CO flow rates were controlled by two mass flow controllers (Brooks Instruments) with the resulting synthesis gas composition regulated by adjusting the flow rate of the appropriate gas. The synthesis gas, after passing through a 2 L mixing vessel, was delivered to the catalyst slurry through a dip tube that extended to below the impeller blade. The reactor

effluent exited the reactor and passed sequentially through two traps maintained at 60°C and 0°C. Accumulated reactor wax was removed daily through a tube fitted with a porous metal filter (0.5 µm) and collected in a 200°C trap. Uncondensed effluent was fed to a multichannel on-line refinery gas analyzer (Hewlett Packard Quad Series Micro GC) for determination of CO, H₂, D₂, CO₂, CH₄ and C₂ - C₈ alkanes and alkenes.

After 130 hours of FTS with D₂, 25 ml of a solution of 5.0 g of 1-heptene (C₇H₁₄, Aldrich) and 5.0 g of 1-octene (C₈H₁₆, Aldrich) in decalin (Aldrich) were pumped into the reactor over a two hour period with a LDC/Milton Roy pump. Liquid samples were collected four hours and 24 hours after pumping the alkene mixture. Liquid samples will be analyzed by GC-MS to determine the relative rates of alkene isomerization and hydrogenation.

Results and Discussion

Through the first 137 hours of FTS with D₂, there was an induction period in which the syngas conversion gradually increased to 86% (Figure 1). During this time, 90.8 g of deuterated liquid hydrocarbon products were collected. The use of Polywax 3000 polyethylene, low vapor pressure under reaction conditions, as a slurry medium prevented the condensed liquid products from being contaminated with hydrogen containing compounds from the initial slurry medium. During slurry phase FTS, a significant amount of product is held-up in the reactor which can influence the product distribution. Samples collected after D₂ was stopped will be analyzed by GC-MS to determine the reactor hold-up time of alkanes and alkenes as a function of carbon number.

Syngas conversion was stable after about 137 hours on stream and at this time D₂ was stopped and H₂ was started. There was a rapid decrease in syngas conversion from 86% to 78% during the first 24 hours after H₂ was started and during the next 200 hours (TOS=330 h), the syngas conversion gradually decreased to 74% (Figure 1). After this time, H₂ was stopped and

D₂ was restarted. Switching back to D₂ caused the syngas conversion to increase to 83% within 24 hours of the change. Conversion remained constant for 48 hours and then H₂ was restarted. Once again the syngas conversion rapidly decreased after D₂ was stopped and H₂ was started.

The FT rate responded similarly as the syngas conversion (Figure 2); however, the water-gas shift (WGS) rates increased only slightly after changes from D₂ to H₂ were made (Figure 3).

The FT and WGS rates are defined as follows:

$$r_{FT} = r_{CO} - r_{CO_2} \quad (1)$$

$$r_{WGS} = r_{CO_2} \quad (2)$$

where r_{CO} is the rate of CO conversion and r_{CO_2} is the rate of CO₂ formation. When the switch from H₂ to D₂ was made after 330 hours on stream, the FT rate increased from 0.054 to 0.064 mol h⁻¹ g-Fe⁻¹ and the WGS rate increased from approximately 0.044 to 0.047 mol h⁻¹ g-Fe⁻¹. There was significant variance in the WGS shift data (Figure 3); however, it is clear that the WGS rate decreased after the initial switch from D₂ to H₂ was made and increased when the switch from H₂ to D₂ was made. The isotope effect (k_H/k_D) observed for the FT rate was 0.85 and approximately 0.93 for the WGS rate.

There was also an isotope effect observed for CH₄ selectivity and alkene selectivity. CH₄ selectivity is defined as follows:

$$CH_4sel = \frac{r_{CH_4}}{r_{FT}} \times 100 \quad (3)$$

where r_{CH_4} is the rate of CH₄ production. Figure 4 shows that the methane selectivity increased steadily from approximately 5% to 20% throughout the run. A decrease in the CH₄ selectivity

from 9.0% to 7.4% was observed when H₂ was switched to D₂ after 330 hours on stream. This is a relative decrease of 18%. When D₂ was switched back to H₂ the CH₄ selectivity increased to 9.7%. Similar trends were observed for C₂, C₃ and C₄ alkene selectivity (Figure 5) which is defined as the molar ratio, alkene/(alkene+alkane). Initially the alkene selectivity decreased as the syngas conversion increased during the first 137 hours on stream. After the conversion stabilized, the C₂, C₃ and C₄ alkene selectivity were 0.11, 0.69, and 0.74, respectively. Switching from H₂ to D₂ caused the C₂, C₃ and C₄ alkene selectivity to increase to 0.19, 0.73, and 0.77, respectively. This corresponds to relative increases of 73%, 6% and 4% for the C₂, C₃ and C₄ alkene selectivity, respectively.

The isotope effect with deuterium is probably the combination of equilibrium and kinetic effects (2-4). The proposed steps for the hydrogenation of carbon monoxide are:

It has been proposed that the rate determining step of the FT synthesis is the hydrogenation of one of the surface carbon species shown in equation six, where k₁, k₂ or k₃ are rate constants (2).

Equations 4 and 5 are assumed to be at equilibrium. The rate of product formation is:

$$R(P) = k_x \theta_C \theta_H^x \quad (7)$$

where x is the number of H in the CH_x species formed during the rate determining step. Under typical FT conditions, it is assumed that $\theta_C \approx 1$ and θ_H is determined by the equilibrium constant (K_H) for dissociative chemisorption of H_2 and the competition for vacant sites by CO and H_2 .

The surface coverage of H is given by:

$$\theta_H = K_H^{1/2} P_{H_2}^{1/2} (1 + b P_{CO})^{-1/2} \quad (8)$$

and the rate of product formation is equal to:

$$R(P) = k_1 K_H^{1/2} P_{H_2}^{1/2} (1 + b P_{CO})^{-1/2} \quad (9)$$

where x and θ_C from equation 7 are both equal to 1(2). It is generally accepted that $k_{1,H} > k_{1,D}$ and $K_D > K_H$. Switching from D_2 to H_2 would effect both k_1 and $K_{H(D)}$ in opposite directions so whether there is an inverse, normal or no isotope effect would depend on the magnitude of change in k_1 and $K_{H(D)}$.

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Table 1	
Time on Stream for D ₂ and H ₂	
Time on stream (h)	Gas
0 - 137	D ₂
138 - 330	H ₂
331 - 384	D ₂
385 - 859	H ₂

Figure 1. Syngas conversion as a function of time on stream.

Figure 2. Effect of deuterium on FT rate.

Figure 3. Effect of deuterium on C₂, C₃ and C₄ alkene selectivity.

Figure 4. Effect of deuterium on CH₄ selectivity.

B. Fischer-Tropsch Synthesis with Precipitated Iron Catalysts Using Hydrogen Rich Syngas

Introduction

The two most common sources of syngas proposed for Fischer-Tropsch synthesis are coal and natural gas. The FTS reaction requires a H_2/CO ratio greater than 2:1.

Advanced coal gasifiers produce syngas that is deficient in hydrogen with respect to the FTS stoichiometry (1). Iron based FTS catalysts are capable of utilizing hydrogen lean syngas because they are also active for the water-gas shift reaction. Unconverted CO can react with H_2O generated by the FTS to produce additional H_2 .

The overall effect is a decrease in catalyst efficiency because a significant amount of CO is converted to CO_2 ; however, the need for an external water-gas shift step is eliminated.

Cobalt catalysts have much lower water-gas shift activity than iron catalysts and are generally not suitable for FTS with coal derived syngas without an external water-gas shift step. Syngas derived from natural gas is more hydrogen rich than coal derived syngas and as a consequence is better suited for cobalt catalysts. Using iron based catalysts for the conversion of syngas derived from natural gas is more complicated because the water-gas shift is not needed to the same extent as with coal derived syngas and will result in lower catalyst efficiency. We have shown that when using hydrogen lean syngas, typical of that derived from coal, it is possible to decrease the water-gas shift rate relative to the FTS rate by operating at low to moderate conversion (30% to 50%) (2,3). At low conversion, the FTS rate is higher than the water-gas shift rate; as the conversion is increased, the water-gas shift rate approaches the rate of the FTS (Figure 1). For syngas with $H_2/CO=0.67$, the H_2/CO usage ratio is equal to the H_2/CO ratio of

the syngas at conversions between 40 and 70% (H_2 conversion = CO conversion, Figure 1) depending on the type and amount of promoters present. By running a low conversion with H_2/CO usage ratio equal to the H_2/CO ratio of the syngas it is possible to operate with recycle or with multiple reactors in series without having to adjust the syngas composition (4). Using recycle or multiple reactors allows for higher productivity and more efficient use of CO. In the present study we have conducted FTS on precipitated iron catalysts with syngas typical of that obtained from natural gas. The amount of potassium promoter and the reaction conditions (pressure, temperature, gHSV and H_2/CO ratio) were changed to optimize the catalyst efficiency.

Experimental

Catalysts were prepared by continuous precipitation from aqueous $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (1.17 M) and concentrated NH_4OH (15.6M) in a continuous stirred tank reactor at pH 9.5. Hydrolyzed tetraethyl orthosilicate was added to the iron(III) nitrate solution to give an atomic ratio of 100Fe/4.6Si. The catalyst slurry was filtered continuously with one or more six inch rotary drum vacuum filters. The resulting catalyst cake was washed and filtered twice with a volume of distilled deionized water equal to the volume of the previous filtrate. A 5 kg catalyst batch was precipitated in this manner, oven dried in flowing air at 110°C and crushed to -325 mesh. The catalyst was calcined in air at 350°C for 4 hours. The 100Fe/4.6Si precursor was impregnated with aqueous $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and dried at 110°C to give an atomic composition of 100Fe/4.6Si/2.0Cu. The catalyst was then impregnated with aqueous KNO_3 to give atomic compositions of 100Fe/4.6Si/2.0Cu/1.44K, 100Fe/4.6Si/2.0Cu/3.0K and 100Fe/4.6Si/2.0Cu/5.0K.

All FTS runs were conducted in a one liter autoclave operated as a continuous stirred tank reactor (CSTR). 5 g of each catalyst were suspended in 310 g of Ethylflo 164 hydrocarbon

oil (Ethyl Corporation) which is a 1-decene trimer. H_2 and CO flow rates were controlled by two mass flow controllers (Brooks Instruments) with the resulting synthesis gas composition regulated by adjusting the flow rate of the appropriate gas. The synthesis gas, after passing through a 2 L mixing vessel, was delivered to the catalyst slurry through a dip tube that extended to below the impeller blade. The reactor effluent exited the reactor and passed sequentially through two traps maintained at 60°C and 0°C . Accumulated reactor wax was removed daily through a tube fitted with a porous metal filter ($0.5\ \mu\text{m}$). Uncondensed effluent was directed to an on-line Hewlett Packard 4 channel Quad Series Micro GC for determination of CO , H_2 , CO_2 , CH_4 and C_2 - C_8 alkanes and alkenes. Liquid samples were analyzed with a Hewlett-Packard 5890 GC equipped with a 60 m DB-5 capillary column.

All catalysts were activated with CO. CO flow (25 slph) was started at ambient temperature and 1.3 MPa and the temperature was increased to 270°C at 2°C min^{-1} . After reaching the activation temperature, the conditions were maintained for 24 h. Initial FTS conditions were 270°C , 1.3 MPa, $H_2/CO=1.7$ and $ghsv=40\ \text{sl h}^{-1}\ \text{g-Fe}^{-1}$. Temperature, pressure, $ghsv$ and H_2/CO feed ratio were changed periodically as outlined in Table 1.

Results

Condition 1, 270°C , 1.3 MPa, $H_2/CO=1.7$, $ghsv=40\ \text{sl h}^{-1}\ \text{g-Fe}^{-1}$.

Syngas conversion data for the three runs are shown in Figure 2. Under the initial conditions, the syngas conversion ranged between 41 and 46% for the three catalysts which is indistinguishable within the expected experimental error. Hydrocarbon rates (Figure 3) were between 3.4 and $3.8\ \text{g h}^{-1}\ \text{g-Fe}^{-1}$. Methane selectivity (Figure 4) decreased with increasing potassium loading from 11 to 7 to 5% (carbon converted to hydrocarbon) for the 1.44K, 3.0K

and 5.0K loadings, respectively. The H_2/CO usage ratio increased with decreasing potassium loading; however, all were much lower than the H_2/CO feed ratio of 1.7 (Figure 5).

Condition 2, 270°C, 1.3 MPa, $H_2/CO=1.7$, $ghsv=65\text{ sl h}^{-1}\text{ g-Fe}^{-1}$.

In order to suppress the water-gas shift rate relative to the FTS rate and subsequently increase the H_2/CO usage ratio, the $ghsv$ was increased from 40 to 65 $\text{sl h}^{-1}\text{ g-Fe}^{-1}$ for each catalyst. Increasing the $ghsv$ caused the syngas conversion to decrease to 33%, 34% and 26% and the methane selectivity to decrease to 10%, 5.3% and 4.0% for the 1.44K, 3.0K and 5.0K catalysts, respectively. In addition, hydrocarbon rate increased for all catalysts. The ratio of water gas shift rate (rate of CO_2 production) to FT rate (rate of CO converted less CO_2) decreased (Figure 6); however, the H_2/CO usage did not increase significantly for any of the catalysts.

Condition 3, 250°C, 1.3 MPa, $H_2/CO=1.7$, $ghsv=22\text{ sl h}^{-1}\text{ g-Fe}^{-1}$.

The temperature was lowered to 250°C and the $ghsv$ was simultaneously lowered to 22 $\text{sl h}^{-1}\text{ g-Fe}^{-1}$ to maintain reasonable conversion. The syngas conversion increased slightly for each catalyst to 35%-39%. The ratio of water-gas shift rate to FT rate decreased (Figure 6) and the H_2/CO usage ratio increased for all catalysts (Figure 5). Hydrocarbon production rate decreased substantially from 4.6, 4.6 and 4.0 $\text{g h}^{-1}\text{ g-Fe}^{-1}$ to 1.75, 1.75 and 1.62 $\text{g h}^{-1}\text{ g-Fe}^{-1}$ for the 1.44K, 3.0K and 5.0K catalysts, respectively. Methane selectivity also decreased for each catalyst.

Condition 4, 250°C, 2.5 MPa, $H_2/CO=1.7$, $ghsv=22\text{ sl h}^{-1}\text{ g-Fe}^{-1}$.

The pressure was increased to 2.5 MPa and all other conditions were maintained. Syngas conversion (50 to 53%) and hydrocarbon productivity (2.26, 2.41 and 2.48 $\text{g h}^{-1}\text{ g-Fe}^{-1}$ for 1.44K, 3.0K and 5.0K, respectively) increased for each catalyst. Methane selectivity decreased for the 1.44K and 3.0K catalysts but increased for the 5.0K catalyst (Figure 4). The H_2/CO usage ratio

increased for all three catalysts; however, they remained well below the H_2/CO feed ratio of 1.7 (1.19, 1.44K; 0.99, 3.0K; 0.89, 5.0K).

Condition 5, 230°C, 2.5 MPa, $H_2/CO=1.7$, $ghsv=22\text{ sl h}^{-1}\text{ g-Fe}^{-1}$.

Temperature was decreased to 230°C and all other reaction conditions were held constant. Syngas conversion and hydrocarbon production rate decreased for each catalyst; however, the largest drop was for the 5.0K catalyst (Figures 2-3). Methane selectivity decreased from 8.0% to 4.1% for the 1.44K catalyst, from 4.0% to 2.2% for the 3.0K catalyst and from 4.6% to 2.3% for the 5.0K catalyst. The relative water-gas shift rate decreased substantially for each catalyst and correspondingly the H_2/CO usage ratio increased to 1.46 (1.44K), 1.24 (3.0K) and 1.12 (5.0K).

Condition 6, 230°C, 3.2 MPa, $H_2/CO=1.7$, $ghsv=22\text{ sl h}^{-1}\text{ g-Fe}^{-1}$.

Increasing the pressure from 2.5 MPa to 3.2 MPa caused the syngas conversion and hydrocarbon production rate to decrease. Methane selectivity was not effected significantly for any K loading as was the case for the H_2/CO usage ratio.

Condition 7, 230°C, 3.2 MPa, $H_2/CO=1.4$, $ghsv=22\text{ sl h}^{-1}\text{ g-Fe}^{-1}$.

The H_2/CO feed ratio was decreased to 1.4. There was no appreciable effect on the syngas conversion or the hydrocarbon production rate. The H_2/CO usage ratio closely approached the feed ratio for the 1.44K catalyst (1.33); however, it was lower for the 3.0K (1.17) and 5.0K (1.09) catalysts. Methane selectivity decreased for each catalyst (Figure 4).

Condition 8, 230°C, 3.2 MPa, $H_2/CO=2.0$, $ghsv=22\text{ sl h}^{-1}\text{ g-Fe}^{-1}$.

Increasing the H_2/CO feed ratio to 2.0 had no effect on the syngas conversion or the hydrocarbon production rate as compared to the same conditions with H_2/CO feed ratio of 1.7. Methane selectivity increased with the increase in H_2/CO feed ratio. The H_2/CO usage ratio increased for each catalyst but was lower than the feed ratio (Figure 5).

Discussion

There was little difference in the FT activity of the 1.44K and 3.0K catalysts; however, the 5.0K catalyst had slightly lower syngas conversion and hydrocarbon production rate under most of the conditions studied. Increasing potassium decreased methane selectivity (Figure 4), increased the water-gas shift reaction rate relative to the FT rate (Figure 6) and decreased the H_2/CO usage ratio (Figure 5).

In an effort to make the H_2/CO usage ratio equivalent to the H_2/CO ratio of the syngas, reaction pressure, temperature and ghsv were varied. Increasing the ghsv (Condition 2) decreased the syngas conversion and increased the hydrocarbon production rate. The decrease in conversion caused the methane selectivity and relative water-gas shift reaction to decrease. Increasing the ghsv had little impact on the H_2/CO usage ratio. Increasing the reaction pressure (Conditions 4 and 6) had mixed results for the FT activity and product. When the pressure was increased from 1.3 MPa to 2.5 MPa at 250°C (Condition 4) the syngas conversion and hydrocarbon productivity rate increased sharply for each catalyst. Despite the increase in conversion, methane selectivity decreased, the water-gas shift rate relative to the FT rate decreased and the H_2/CO usage ratio increased slightly. In contrast, increasing the pressure from 2.5 MPa to 3.2 MPa at 230°C had very little effect on FT activity or selectivity. It is not clear from the current data if there is an optimum pressure or if pressure changes have a different effect at 250°C and 230°C. Reaction temperature also has a large impact on FT activity and selectivity. When the temperature was reduced from 250°C to 230°C (Condition 5) the syngas conversion and hydrocarbon production rate decreased as expected. There was a large decrease in methane selectivity and a substantial increase in H_2/CO usage ratio for all three catalysts.

The impact of changing the H_2/CO ratio of the syngas was also studied. Decreasing the H_2/CO syngas ratio from 1.7 to 1.4 (Condition 7) had no impact on the syngas conversion or the

hydrocarbon production rate; however, methane selectivity decreased appreciably for each catalyst. The 1.44K catalyst had a H_2/CO usage ratio of 1.33 while it was somewhat lower for the 3.0K (1.17) and 5.0K (1.09) catalysts. When the H_2/CO syngas ratio was increased to 2.0 (Condition 8) there was no significant change in FT activity and the methane selectivity increased. The H_2/CO usage ratio for each catalyst was below the H_2/CO syngas ratio: 1.54 for the 1.44K catalyst, 1.32 for the 3.0K catalyst and 1.20 for the 5.0K catalyst. Only the 1.44K catalyst operating at 230°C, 3.2 MPa, $H_2/CO=1.4$ and $ghsv=22 \text{ sl h}^{-1} \text{ g-Fe}^{-1}$ had a H_2/CO usage ratio comparable to the H_2/CO syngas ratio.

Conclusions

Potassium had little impact on FT activity but did effect selectivity and in particular the water-gas shift reaction. Potassium increased the water-gas shift rate relative to the FT rate and as a consequence decreased the H_2/CO usage ratio. Pressure and temperature can have significant effects on the activity and selectivity of iron based FT catalysts using syngas similar to that obtained from natural gas. By simultaneously decreasing temperature and increasing pressure it was possible to increase the H_2/CO usage ratio while also maintaining reasonable FT activity. Only the catalyst with atomic composition 100Fe/4.6Si/2.0Cu/1.44K was able to maintain a H_2/CO usage ratio similar to the H_2/CO syngas ratios. In general, the water-gas shift activity of the 100Fe/4.6Si/2.0Cu/3.0K and 100Fe/4.6Si/2.0Cu/5.0K catalysts was too high.

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Table 1					
FTS Conditions					
Condition	Time (h)	Temperature (°C)	Pressure (MPa)	ghsv (sl h ⁻¹ g-Fe ⁻¹)	H ₂ /CO
1	0-24	270	1.3	40	1.7
2	24-48	270	1.3	65	1.7
3	48-120	250	1.3	22	1.7
4	120-144	250	2.5	22	1.7
5	144-168	230	2.5	22	1.7
6	168-286	230	3.2	22	1.7
7	286-310	230	3.2	22	1.4
8	310-332	230	3.2	22	2.0

Figure 1. CO and H₂ conversion as a function of reciprocal space velocity for a 100Fe/4.6Si/2.2K catalyst. (F), CO conversion and (G), H₂ conversion.

Figure 2. Syngas conversion as a function of time on stream for (F), 100Fe/4.6Si/2.0Cu/1.44K, (G), 100Fe/4.6Si/2.0Cu/3.0K and (Δ), 100Fe/4.6Si/2.0Cu/5.0K catalysts. Conditions are identified on time line above graph (as defined in Table 1).

Figure 7. Hydrocarbon production rate as a function of time on stream for (F), 100Fe/4.6Si/2.0Cu/1.44K, (G), 100Fe/4.6Si/2.0Cu/3.0K and (Δ), 100Fe/4.6Si/2.0Cu/5.0K catalysts. Conditions are identified on time line above graph.

Figure 8. Methane selectivity as a function of time on stream for (F), 100Fe/4.6Si/2.0Cu/1.44K, (G), 100Fe/4.6Si/2.0Cu/3.0K and (Δ), 100Fe/4.6Si/2.0Cu/5.0K catalysts. Conditions are identified on time line above graph.

Figure 9. H_2/CO usage ratio as a function of time on stream for (F), $100Fe/4.6Si/2.0Cu/1.44K$, (G), $100Fe/4.6Si/2.0Cu/3.0K$ and (Δ), $100Fe/4.6Si/2.0Cu/5.0K$ catalysts. Conditions are identified on time line above graph.

Figure 10. Ratio of water-gas shift rate to Fischer-Tropsch rate as a function of time on stream for (F), 100Fe/4.6Si/2.0Cu/1.44K, (G), 100Fe/4.6Si/2.0Cu/3.0K and (Δ), 100Fe/4.6Si/2.0Cu/5.0K catalysts. Conditions are identified on time line above graph.

C. Impact of Potassium on the Activation Energy of Precipitated FTS Catalysts

Several kinetic models have been proposed for iron based Fischer-Tropsch catalysts.

Anderson (1) proposed a rate expression in which water inhibits the FT rate:

$$-R_{\text{CO}+\text{H}_2} = \frac{kP_{\text{H}_2}P_{\text{CO}}}{P_{\text{CO}} + bP_{\text{H}_2\text{O}}} \quad (1)$$

Anderson noted that at syngas conversion below 60%, the FT rate was first order with respect to hydrogen and zero order with respect to carbon monoxide (equation 2).

$$-R_{\text{CO}+\text{H}_2} = kP_{\text{H}_2} \quad (2)$$

Huff and Satterfield proposed a rate expression based on the carbide mechanism in which the rate limiting step was the hydrogenation of a surface carbide species (2). This model also accounted for inhibition by water (equation 3).

$$-R_{\text{CO}+\text{H}_2} = \frac{kP_{\text{CO}}P_{\text{H}_2}^2}{P_{\text{CO}}P_{\text{H}_2} + bP_{\text{H}_2\text{O}}} \quad (3)$$

Ledakowicz has proposed two rate expressions (3) in which the FT rate is inhibited by CO_2 adsorption (equation 4).

$$-R_{\text{CO}+\text{H}_2} = \frac{kP_{\text{CO}}P_{\text{H}_2}}{P_{\text{CO}} + cP_{\text{CO}_2}} \quad (4)$$

and a general rate expression which accounts for both H_2O and CO_2 inhibition (equation 5).

$$-R_{\text{CO}+\text{H}_2} = \frac{kP_{\text{CO}}P_{\text{H}_2}}{P_{\text{CO}} + aP_{\text{H}_2\text{O}} + cP_{\text{CO}_2}}$$

Using these and other rate equations, the activation energy of the FT reaction with iron catalysts has been determined to fall within a broad range of 71 to 103 kJ mol⁻¹. The impact of promoters on the activation energy has not been reported. Satterfield has reported an activation energy of 83 kJ mol⁻¹ for a fused iron catalyst promoted with K, Ca, Si, and Al (2). Bukur has reported activation energies of for precipitated iron catalysts promoted with K, Cu and SiO₂ (4). A systematic study of the effect of potassium on the FT activation energy has not been reported. Potassium can either increase or decrease the activity of iron-based catalysts depending on the H₂/CO ratio of the syngas and the range of syngas conversion studied. Furthermore, the CO conversion increases, attains a maximum, and then decreases as the amount of potassium in the catalyst is increased. As a consequence it is possible that potassium will impact the activation energy of the FT reaction.

Experimental

Five catalysts with atomic composition 100Fe/4.6Si, 100Fe/4.6Si/0.36K, 100Fe/4.6Si/0.71K, 100Fe/4.6Si/1.4K and 100Fe/4.6Si/2.2K were studied. 15.0 g of catalyst and 290 g of C₃₀ oil were loaded into 1000 ml autoclaves. The catalysts were activated with CO at 270°C and 175 psig for 24 h. Initial FTS conditions were 270°C, 175 psig, H₂/CO=0.67 and gHSV=5.0 sl h⁻¹ g-Fe⁻¹. After the syngas conversion stabilized, the temperature was lowered to 250°C for 24 hours and then to 230°C for 24 hours. The temperature was then increased to 270°C to determine whether catalyst deactivation had occurred.

Results

Syngas conversion profiles for each potassium loading are shown in Figures 1-5. Syngas conversion stabilized after about 120 hours on steam for each catalyst. After decreasing the temperature to 250°C and then 230°C, the temperature was increased to 270°C. In each case the conversion was higher than before the temperature reductions. This occurred even after most of

the catalysts appeared to be deactivating slightly before the initial temperature reductions. In order to insure consistency, kinetic data were obtained from the initial temperature reductions. Syngas conversion as a function of potassium loading at each temperature is shown in Figure 6. The syngas conversion increased slightly when going from 0K to 0.36K at each temperature; however, there was essentially no effect on conversion with increasing potassium loading beyond 0.36K.

For the sake of simplicity the reaction was assumed to be first order in H_2 and zero order in CO (equation 2).

$$-R_{CO+H_2} = kP_{H_2}$$

Rate constants at each temperature for each potassium loading are shown in Table 1. There is approximately 5% relative error for the rate constant of the duplicate runs using 0K loading. Arrhenius plots for the different catalysts are shown in Figure 7. Activation energy as a function of potassium loading is shown in Figure 8. In general, the activation energy ranged between 64 kJ mol^{-1} and 82 kJ mol^{-1} . The activation energy decreased from 79 kJ mol^{-1} for the catalyst with no potassium to 64 kJ mol^{-1} for the catalyst with 0.36K; however, additional potassium caused the activation energy to increase up to 82 kJ mol^{-1} for the 2.2K catalyst. The activation energy for the catalyst without K was essentially the same for the duplicate runs; however, additional runs which repeat the runs with 0.36K and 2.2K should be completed before any conclusions can be reached about the effect (if any) of potassium on activation energy. No reason that the activation energy should have a minimum with respect to potassium loading is apparent. It may be that we are only seeing the effects of experimental error from the catalysts being incompletely activated (activity always increased after completing the series of temperature reductions and then returning to the original conditions). This is an important aspect and work continues on this.

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Table 1						
	k(mol h ⁻¹ g-Fe ⁻¹ kPa ⁻¹)					
T (°C)	0K	0K	0.36K	0.72K	1.44K	2.18K
230	1.32 x 10 ⁻⁴	1.18 x 10 ⁻⁴	1.93 x 10 ⁻⁴	1.58 x 10 ⁻⁴	1.36 x 10 ⁻⁴	1.23 x 10 ⁻⁴
250	2.79 x 10 ⁻⁴	2.56 x 10 ⁻⁴	3.37 x 10 ⁻⁴	3.33 x 10 ⁻⁴	2.88 x 10 ⁻⁴	2.80 x 10 ⁻⁴
270	5.31 x 10 ⁻⁴	4.90 x 10 ⁻⁴	6.17 x 10 ⁻⁴	5.67 x 10 ⁻⁴	5.64 x 10 ⁻⁴	5.38 x 10 ⁻⁴

Figure 1. Conversion profile for 100Fe/4.6Si.

Figure 2. Conversion profile for 100Fe/4.6Si/0.36K.

Figure 3. Conversion profile for 100Fe/4.6Si/0.71K.

Figure 4. Conversion profile for 100Fe/4.6Si/1.44K.

Figure 5. Conversion profile for 100Fe/4.6Si/2.2K.

Figure 6. Syngas conversion as a function of K loading at each temperature.

Figure 7. Arrhenius plot for the different K loadings.

Figure 8. Activation energy as a function of the K loading.

D. Fischer-Tropsch Synthesis: Influence of Startup Media on Activity and Selectivity over Magnesium Iron Promoted Catalysts

Introduction

Fischer-Tropsch synthesis process converts CO and H₂ to liquid fuels, and the feedstock, a mixture of CO and H₂, can be produced from coal gasification. As a cleaner raw material source than coal, natural gas can also be used for Fischer-Tropsch synthesis. One of the advantages of FTS is that the process can be designed to produce either gasoline, diesel and/or chemicals. There are two types of operation modes, the low temperature, which is for production of high wax, and the high temperature FTS, which is designed for production of gasoline and alkenes.

In an FTS process, the hydrocarbon is produced from CO and H₂, which can be expressed as

where n is defined as $n = 1/(1-\alpha)$ or it can be rearranged as $\alpha = 1 - (1/n)$ (1).

When an iron catalyst is used for FTS reactions, the water gas shift (WGS) reaction can also occur. This side reaction consumes CO and water produced in the FTS process and produces additional hydrogen.

Potassium has long been used as a promoter for iron catalysts to increase the alkene yield and to decrease the CH₄ selectivity (2). It is also believed that potassium can also increase FTS and water-gas shift reaction activity (3).

Although catalyst play the most important role in FTS reactions, it is believed that startup media also had an innegligible influence on the activity and selectivity of the FTS reactions. The purpose of this study was to investigate the effect of the startup media, two different media were used, i.e., the liquid C-30 oil and solid granular parawax. Iron FTS catalysts promoted with

1.44% alkalis of magnesium and potassium were used in this study. A simulated synthesis gas of 40% hydrogen and 60% carbon monoxide was used in a one-liter CSTR slurry reactor. Liquid oil, water, heavy wax and gas samples from the FTS reactions were collected and analyzed with gas chromatographs (GC). Reaction conversion, product selectivity and other results were calculated by a database system.

Experimental

Preparation of alkali metal promoted catalysts

Iron catalyst promoted with Mg were prepared and tested in this study. Promoter was added at a 1.44:100 of promoter to iron atomic ratio. Precipitated iron catalysts were prepared with tetraethyl orthosilicate, iron nitrate. Ferric nitrate solution was first prepared by dissolving $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in distilled and deionized water, and the amount of orthosilicate needed to make Si:Fe of 4.6 was added. The mixture was stirred vigorously until the tetraethyl orthosilicate has hydrolyzed. Tetraethyl orthosilicate and iron nitrate mixture was then added to a CSTR precipitator vessel together with ammonium hydroxide. By maintaining the slurry pH at 9 and an average residence time of 6 minutes, a base catalyst material with an iron to silicon molar ratio of 100:4.6 was obtained. The slurry was then filtered with a vacuum drum filter and washed twice with deionized water. The final filtration cake was dried in an oven with flowing air at 110°C for 24 hours. The catalyst was crushed to approximately 60 μm and calcined in a 350°C oven under an air flow for 4 hours.

In this study, the iron catalyst was impregnated with an aqueous nitrate solutions of magnesium for alkali metal promoted catalyst. Magnesium nitrate was added to obtain a promoter to iron atomic ratio of 1.44:100. The catalysts was dried at 110°C overnight with good mixing following the impregnation. Thus, catalyst promoted with magnesium was prepared for FTS studies.

In-situ catalysts activation

The iron catalyst needs to be activated with either H₂, CO or synthesis gas. Activation procedures can have a significant effect on the selectivity and activity of iron catalyst (6, 7). It was reported that catalysts activated with CO yielded higher long-chain hydrocarbons than syngas and H₂ activated catalysts. In addition, activation conditions may also influence the performance of the iron catalyst. In this study, the potassium promoted iron catalysts were pretreated with CO at 270°C, 1.2 MPa for 24 hours. The reduction of Fe₂O₃ with CO occurs in two steps:

In addition, CO₂ may be formed by the Boudouard reaction:

Previous work in our lab showed that approximately 50 % to 75% more carbon was present in the catalyst mass than was needed to form Fe₅C₂ (8). Gradual oxidation of Fe₅C₂ to Fe₃O₄ was observed when iron catalyst was used in FTS. The results showed that at the end of the run an unpromoted iron catalysts had been completely oxidized to Fe₃O₄.

Reactor system

A one-liter continuous stirred tank reactor (CSTR) was used in this study. A sintered filter was installed to remove the wax samples from the catalyst slurry. The wax sample was extracted through the internal filter and collected in the hot trap (200°C). A warm trap (100°C) and cold trap (0°C) were used to collect oil, light wax and water samples. Tail gas from the cold trap was analyzed with an HP quick GC.

Gas mixer equipped with a CO and an H₂ mass controller was used to provide a simulated synthesis gas. After the catalysts was activated with CO, syngas was introduced at a

rate of 10 NL/hr/gram-catalyst. Then the gas space velocity was varied in the range of 3 to 60 sl/hr/g-Fe to collect kinetic data. Other reaction conditions were maintained at 270°C, 1.2 MPa and a stirrer speed of 750 rpm.

Product sampling and analysis

Daily gas, water, oil, light and heavy wax samples were collected and analyzed. Table 1 gives the summary of the instruments for gas and liquid product analysis. A heavy wax sample was taken from the 200°C hot trap connected to the filter. Vapor phase above the slurry phase passed to the warm (100°C) and the cold (0°C) traps outside the reactor. The light wax and water mixture was collected from the warm trap and an oil plus water sample from the cold trap. Tail gas from the cold trap was analyzed with an online HP Quad Series Micro GC. Molar compositions of C₁-C₇ olefins and paraffins were thus obtained. Hydrogen and carbon monoxide conversions were calculated based on the gas product GC analysis results and the gas flow measured at reactor outlet. Hydrogen, carbon monoxide and syngas conversion were obtained using the following formula:

$$\text{Conversion} = \frac{(N_{\text{in}} - N_{\text{out}})}{N_{\text{in}}} \times 100\%$$

The Oil and light wax samples were mixed before analyzed with an HP 5790A GC. The heavy wax was analyzed with an HP5890 Series II Plus GC while the water sample was run with an HP5890 GC.

Results and Discussion

Effect on Fischer-Tropsch synthesis activity

Two parallel Fischer-Tropsch reactions were carried out in a CSTR using two different startup media, i.e., C-30 oil (liquid oil) and parawax (granular solid polymer). Figure 1 shows

the CO conversion results from the two reactions. With C-30 oil, higher CO conversion was obtained than in a parawax medium. As the reaction proceeds, the difference in CO conversion between the two startup media becomes more pronounced. Initial conversion were at about 37% in both media, after 150 hours of reaction, CO conversion in C-30 oil stablized at 56% while the conversion in parawax decreased to 32%. This results suggest that in FTS reaction system, heavier startup media may have a detrimental effect on the catalyst activity due to the negative effect by the parawax in the mass transport process in the solid-liquid-gas slurry.

Figure 2 gives the results of FTS rate, which is calculated by the following equation:

$$\text{FTS rate} = \text{Rate [CO]} - \text{Rate [CO}_2\text{]} \text{ (mol/hr/g-Fe)}$$

Regardless of the space time, C-30 oil produced a higher FTS rate than parawax. At a short space time C-30 oil generated twice as much hydrocarbon as parawax but the difference in hydrocarbon rate was insignificant at a higher space time.

Effect on Fischer-Tropsch synthesis selectivity

Figure 3 gives the methane selectivity and the alpha values from the FTS reactions using two different startup media. Methane selectivity from the FTS using C-30 oil was significantly higher than that in a parawax. A 7.12% methane selectivity was obtained in a C-30 oil while only a 4.87% was obtained in a parawax medium. In the meantime, C-30 oil showed a slightly lower alpha value than parawax.

Olefin ratio was calculated from the following equation:

$$\text{Olefin ratio} = \frac{\text{Olefin}}{(\text{Olefin} + \text{Paraffin})} \times 100\%$$

Olefin ratios of C_2 to C_{20} were shown in Figure 4 and it was found that two lines were overlapped in the whole range of the data. The results indicates that the startup media did not have any influence on olefin ratio of the FTS product.

Figure 5 gives the results of hydrocarbon fractions from the FTS reactions. It is shown that C-30 oil generated more gas (C_1 - C_4) and gasoline (C_5 - C_{11}) products and less diesel (C_{12} - C_{18}) and C_{19+} products than parawax. As shown in both Figure 3 and Figure 5, C-30 oil produced a slightly heavier products or higher alpha value than parawax.

Effect on product partial pressure and water gas shift activity

Water partial pressure was given in Figure 6 and it shows that at a low space time, C-30 oil produced a higher water partial pressure than parawax while at a higher space time, the opposite result was obtained. Figure 7 shows the partial pressure of CO_2 at different space time, C-30 oil always yielded a higher CO_2 partial pressure than parawax, indicating that water-gas shift reaction activity was affected by the startup media. Heavy medium inhibited the WGS reaction and as the space time increase, the detrimental effect became more and more pronounced.

Figure 8 shows the partial pressure of hydrocarbon at different space time. Similar to CO_2 partial pressure, hydrocarbon partial pressure from FTS using C-30 oil was higher than that in a parawax startup medium. This suggests that heavy startup medium inhibits the mass transport between the gas reactants and the surface species on the solid catalyst surface; thus a lower hydrocarbon yield was resulted in a parawax medium than that in C-30 oil.

Figure 9 gives the result of water gas shift quotient, which is calculated from the following equation:

$$\text{Water gas shift quotient} = \frac{P_{[CO_2]} \cdot P_{[H_2]}}{P_{[CO]} \cdot P_{[H_2O]}}$$

Water-gas shift quotient measures the water gas shift reaction extent. Similar to the CO_2 partial pressure, WGS quotient from reaction in C-30 oil was higher than that in parawax medium. At a low space time, the two media showed little difference in WGS quotient, but the difference between the two media becomes more and more greater at higher space time. It is also found that the WGS quotient remained stable in parawax medium regardless of the space velocity while the WGS quotient increased appreciably as the space time increase.

Conclusion

Startup media showed an innegligible influence on FTS reactions over iron FTS catalysts promoted with magnesium. Although startup media had little effect on olefin ratio, alpha value and gasoline faction of the hydrocarbon products, they had a significant influence on CO conversion, methane selectivity, hydrocarbon fractions other than gasoline, partial pressure of CO_2 , water, and the water-gas shift quotient. The effect of startup media depends on the space time applied in the FTS reactions. Greater influence on CO conversion, water-gas shift activity, hydrocarbon and CO_2 partial pressure was observed at a high space time than at a low space time. This study suggests that C-30 oil yielded a better CO conversion, hydrocarbon rate but higher CO_2 and methane byproduct and slightly lighter hydrocarbon products. Thus a heavy parawax startup medium is not recommended for FTS reactions in a CSTR due to the detrimental effect on mass transport property.

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Table 1. Analyzers for FTS Products

Analyzer	Sample	GC Detector
HP Quad Series Micro GC	Gas	TCD
HP 5790A GC	Water	FID
HP5890 GC	Oil+light Wax	TCD
HP5890 Series II Plus	Heavy Wax	FID

Figure 1. CO conversion v.s. time on stream

Figure 2. FTS rate v.s. space time

Figure 3. Methane selectivity and alpha value

Figure 4. Olefin ratio v.s. carbon number

Figure 5. Hydrocarbon fractions

Figure 6. Water partial pressure

Figure 7. Carbon dioxide partial pressure

Figure 8. Hydrocarbon partial pressure

Figure 9. Water-gas shift qotient

E. Two Alpha Fischer-Tropsch Product Distribution. A Role for Vapor Liquid Equilibrium?

Abstract

The simple polymerization mechanism for the Fischer-Tropsch synthesis produces products which follows an Anderson-Schulz-Flory distribution. Thus, plotting the logarithm of the mole fraction versus carbon number will produce a straight line whose slope is related to alpha which is determined by the chain termination and propagation probabilities. In contrast, the products from laboratory and large commercial plants exhibit a two-alpha plot. Vapor-liquid calculations show that product accumulation cannot be responsible for the two-alpha plot when the alpha value is large enough to produce liquid products at the reaction temperature. Only in the case where alpha is small and all products are in the vapor phase, allowing evaporation of the startup solvent and a “drying out” of the reactor can a product accumulation produce a two-alpha plot.

Introduction

By 1950, it was recognized that a simple polymerization mechanism should describe the Fischer-Tropsch synthesis product distribution, the so-called Anderson-Schulz-Flory (ASF) distribution (1-3). Thus, a plot of the logarithm of the molar concentration versus the carbon number would produce a straight line plot whose slope is related to alpha, the chain propagation probability. While this description has become widely accepted, it was also recognized at that time that the actual products, when higher carbon-number products were included, could not be described by a single alpha value. The so-called two-alpha distribution of products from several larger-scale plants in Germany and the U.S. were demonstrated in a plots by Anderson (4). In each of these and subsequent plots it has been shown that the break occurs in the range of carbon numbers 8 to 14.

Several models have been proposed to account for the two, or even more, alpha values (5). One that is frequently cited is the operation of two or more chains that undergo propagation independently (6-8). Another reason frequently cited for the two alpha distribution is the impact of diffusion and reincorporation of higher carbon number alkenes (9-14). It has become apparent that the ^{14}C -distribution in the products when labeled alcohols or alkenes are added to the synthesis gas fed to a continuous stirred tank reactor (CSTR) are impacted by accumulation of heavier products in the liquid in the reactor (15). Bell, among others, has shown that the initial gas phase products are depleted of higher carbon number products during the Fischer-Tropsch synthesis in a CSTR (16). For a catalyst that exhibits a constant conversion for some period and then declines in activity, the accumulation effects can provide a two alpha plot since the increasing gas flow carries accumulated products from the reactor in higher concentrations than they are formed (17). It was therefore of interest to learn whether a two alpha plot could be obtained when a catalyst with constant activity was utilized in a slurry reactor. Results of calculations for vapor-liquid equilibrium models corresponding to the operation of a Fischer-Tropsch catalyst with a single alpha value was utilized in a CSTR are provided in this manuscript.

Continuous Stirred Tank Reactor

The continuous stirred tank reactor provides the advantage that all catalyst particles have the same average catalyst life (based on usage), all catalyst particles are exposed to the same synthesis gas composition, and the reaction temperature is uniform in the catalyst slurry. Thus, the typical CSTR for Fischer-Tropsch synthesis is operated under constant temperature, pressure and reactant compositions. A certain amount of paraffin is charged to the reactor as starting solvent to provide a slurry phase. Reactant gases, i.e., CO and H_2 , continuously flow into the reactor at constant rates. Vapor phase products, i.e., unconverted CO and H_2 , CO_2 , water, and

volatile hydrocarbons, continuously flow out. Liquid phase products are either removed continuously or allowed to accumulate in the reactor for some time interval. In the latter mode of operation, the excess reactor liquid is drained periodically, as necessary, so that the reactor is operated at a nearly constant liquid level. The drained liquid is added to the vapor phase product to obtain the total reaction product for the sampling period.

For the development of VLE model for Fischer-Tropsch synthesis, it is convenient to divide a CSTR reactor into two operational parts, i.e., reaction and separation, as illustrated schematically in Figure 1, where,

F_{CO} , F_{H_2} , F : molar flow rate of feed CO, feed H_2 , and total flow after reaction,

respectively

X_{CO} : CO conversion to hydrocarbons

x_i , y_i , z_i : individual hydrocarbon molar fraction in reactor slurry, vapor stream, and the combined streams after reaction, respectively

k_i : vapor-liquid equilibrium constant

L : moles of reactor liquid

V : molar flow rate of vapor stream

Fischer-Tropsch Reaction

For the Fischer-Tropsch reaction, it is assumed that CO and H_2 react stoichiometrically to produce hydrocarbons (exclusively paraffins for simplicity) and water following a single α ASF distribution and constant catalyst activity. Also, the fraction of CO converted to hydrocarbons (X_{CO}) is assumed to be constant through any reaction time period. Therefore, with constant reactant flow rates, the total flowrate of the stream after reaction (F) is constant. In addition, the each component in the reactor effluent (z_i) is constant with time. The water gas shift reaction,

which is significant with an iron catalyst, is not included explicitly in this model because it is an equal molar reaction that does not impact the total reactor effluent flow. This reaction does not affect hydrocarbon product distribution if the gases are insoluble, or of limited solubility, in the reactor liquid.

Based on the above assumptions, the Fischer-Tropsch reaction can be written as

and the composition of each hydrocarbon produced by the reaction

$$Z_i = (1-\alpha)^2 \alpha^{i-1} F_{\text{co}} X_{\text{co}} / F \quad (2)$$

Vapor-Liquid Separation

In the vapor-liquid separation component, the input is the stream leaving the reaction component. Here, the input stream is separated into liquid and vapor, which are assumed to be in thermodynamic equilibrium at reaction temperature and pressure (Eq. (3)). Equations (4) and (5) are used to describe the material balance for the separation process.

$$y_i = k_i x_i \quad (3)$$

$$\frac{dL}{dt} = F - V \quad (4)$$

$$\frac{d(Lx_i)}{dt} = Fz_i - Vy_i \quad (5)$$

The above equations can be solved numerically. For an infinitesimally small time interval, Δt , equations (3) - (5) can be combined to give

$$x_i = \frac{Fz_i \Delta t + (Lx_i)_{prev}}{L + k_i (F\Delta t - L + L_{prev})} \quad (6)$$

Equation (6) allows the calculation of the composition, x_i , and amount, L , of liquid in the reactor at any time interval within the constraint of Equation (7).

$$\sum x_i = 1 \quad (7)$$

With a knowledge of the initial reaction conditions, the liquid composition, vapor composition, vapor flow rate, and the amount of liquid in the reactor can be calculated at any time-on-stream.

Model Simulation

Based on the above model, the simulation is performed using a computer program developed in our lab. For simplicity of simulation, it was further assumed that hydrocarbon products are linear paraffins from C_1 to C_{100} whose relative concentrations follow a single α ASF distribution. Also for simplicity, CO , H_2 , and H_2O are assumed to be insoluble in reactor liquid. All vapors are assumed to be ideal gases and the liquid is assumed to be an ideal solution; their compositions are related by Raoult's law:

$$y_i = k_i x_i = \frac{P_i^s}{P} x_i \quad (8)$$

In the simulations, unless noted otherwise, the saturation vapor pressures of the Caldwell and Van Vuuren paraffins in Equation (8) are calculated using Equation (9) obtained from the literature (18). In this correlation, the unit for vapor pressure is atm and the unit for temperature is Kelvin.

$$P_i^s = 176.0452 \exp(-427.218(\frac{1}{T} - 1.029807 \times 10^{-3})) \quad (9)$$

The paraffin vapor pressure was also estimated using Antoine's equation whose constants are obtained from API Project 44 (19). The difference between vapor pressure from these two sources and their impact on FT product distribution will be discussed later. A temperature

dependent correlation from the literature (20) is used to estimate the partial molar volumes of paraffins in the FT liquid. Other conditions for simulation are Newton's method for iteration of Equation (6), accuracy of the sum of liquid molar fraction of 0.0001 (Eq. (7)), and time interval of 0.01h for each numerical calculation.

Before reaction, a certain amount of C_{28} paraffin is added to the reactor as start-up solvent. This volume is used as the liquid volume to be maintained in the reactor. The catalyst volume is ignored in this simulation. The reaction effluent enters the separator, with vapor products leaving continuously and liquid products accumulating for some time interval. The amount of liquid in the reactor is examined at each time interval. If the liquid level is higher than that to be maintained, the extra volume is drained instantaneously so that the liquid level is constant throughout the simulation. The liquid drained from the reactor, if there is any, is added to the vapor stream as the total reaction products generated during that sampling period. Vapor products collected include water, unconverted H_2 and CO, and hydrocarbons. The flowrate of the vapor stream and its compositions are normalized to those of pure hydrocarbons for further calculations. Since C_{28} paraffin is used as the start-up solvent, its composition in both liquid and vapor are substantially higher than they should be in the Fischer-Tropsch product. Therefore, C_{28} is removed from vapor product as it does not represent what is produced by the reaction. Its composition in the vapor is determined from the amount of C_{27} and C_{29} using single α distribution rule. The same method is used for the liquid which is drained from the reactor and is added to the vapor stream to obtain the total reaction product.

The following seven (7) parameters are required as input to the simulation program: reaction temperature ($^{\circ}C$), reaction pressure (atm), H_2 flowrate (SL/h), CO flowrate (SL/h), CO conversion (mole%), amount of C_{28} starting solvent (g), and the single α value.

Simulation Results

Two sets of reaction conditions are used to illustrate the effect of VLE on the FT product distribution. The common conditions are temperature (270°C), pressure (12.9 atm), hydrogen flow rate (F_{H_2} ; 23 SL/h), CO flow rate (F_{CO} ; 33 SL/h), conversion of CO to hydrocarbons (X_{CO} ; 40%), and the amount of C_{28} starting solvent (300g). The only difference is single α value; $\alpha=0.85$ represents normal operating condition with liquids accumulation and $\alpha=0.65$ which represents a drying out condition due to excessive evaporation of the starting solvent.

Figures 2 through 4 shows the hydrocarbon product distribution with an α value of 0.85 when the reactor is operated under normal conditions without drying out. In Figure 2 and the liquid phase plots thereafter, the composition of starting solvent (C_{28}) is not shown since it is not representative. The composition of a hydrocarbon in both liquid phase (Figure 2) and vapor phase (Figure 3) increases with time-on-stream before leveling off. The higher the carbon number, the longer time-on-stream it takes to attain the “steady-state” composition. After 5000 hours on stream, both liquid and vapor compositions become stable and are no longer affected by reaction time. For vapor phase composition, there is always a negative deviation from the ASF distribution for about C_{20+} products, due to the thermodynamic effect. When the drained reactor liquid is added to the vapor stream to obtain the total reaction product, as shown in Figure 4, the product distribution approaches a single α distribution, although there is still a negative deviation before steady state. Also shown in Figure 4 are two dashed lines for liquid and vapor phases at 100 h to illustrate how they are combined to generate the total reaction product distribution. Once the reactor reaches steady state, the total reaction product distribution is represented by a single α distribution and without deviation. Longer reaction times up to 10,000 hours do not

change this distribution. It appears that, with a single α chemistry, vapor/liquid separation and/or accumulation is not responsible for the two α observation.

Figures 5 and 6 show the simulation results with $\alpha=0.65$ when the reactor is drying-out at 508 h due to excessive evaporation of the start-up solvent. The vapor stream is the only product collected since the reactor liquid level decreases with time-on-stream, and hence no liquid can be drained from the reactor. As shown in Figure 5, the hydrocarbon fraction in the reactor liquid decreases with carbon number except when the reactor is close to drying-out, in contrast to normal operation (Figure 2) in which liquid fraction increases with carbon number and then decreases after reaching a maximum. Figure 6 shows the vapor phase composition, together with the theoretical ASF plot (dotted line). It is interesting to note that after some time on stream (e.g., 400 h), the vapor composition begins to show positive deviation from the ASF distribution. Obviously, this is due to the flashing-off of previously-accumulated heavier hydrocarbons, in agreement with earlier observations (17). Misinterpretation of this phenomena may lead to the conclusion of a two α product distribution. It should be noted that, with single α chemistry, positive deviation is possible only under drying-out conditions. Under the extreme situation when the reactor is dry (508 h, liquid level 0.1% of initial level in this simulation), an abnormal phenomena occurs. The plot at this time on stream indicates that the α value can be larger than unity over a range of carbon numbers, which is impossible from the chemical reaction stoichiometry.

As mentioned previously, a correlation from the literature is used to calculate the paraffin vapor pressure for vapor/liquid separation. Data from other sources may lead to different product distribution. Figure 7 compares the differences for the paraffin vapor pressure at 270°C from two sources, the one used in this simulation and the other one from API Project 44 (19). For carbon numbers higher than about 40, the vapor pressure deviates from each other, and the

deviation becomes greater with increasing carbon number. As a result, predicted product distribution in both vapor phase and liquid phase depend on the data used. For the example shown in Figure 8, vapor pressure from API Project 44 predicts higher concentration of C_{30+} paraffins in the vapor phase, and a lower concentration in liquid phase. However, when the reactor reaches “steady-state”, the total reaction product distribution is represented by a single α straight line. The dependence of vapor and liquid on vapor pressure is canceled out when the drained liquid is added to the vapor to produce the total reaction product. It is therefore reasonable to predict that as long as the reactor is operated under normal conditions, the total reaction product distribution is independent of the vapor-liquid equilibrium constant (k value), although vapor and liquid compositions will vary.

Conceptual Illustration

The above discussion is based on computer simulation involving 100 components with assumptions such as ideal gases, ideal solution, and vapor/liquid separation at equilibrium. In fact, whether two α observation in FT synthesis can, or cannot, be attributed to vapor-liquid separation can be understood conceptually from separation principles.

A binary system shown in Figure 9 is used to illustrate the composition change with time. Pure component A continuously flows into the tank initially containing A_0 amount of A and B_0 amount of non-volatile component B. The objective is to examine if there is any chance that the amount of A in the output (vapor + drained liquid) be more than its input, due to accumulation of A in the liquid phase over time. A positive answer will lead to the vapor/liquid separation being responsible for the two α product distribution in the FT synthesis.

For easier discussion, it is assumed that the liquid phase density is constant so that its volume is directly proportional to its mass. The vapor phase and liquid phase are not necessarily

in equilibrium, nor do they need to be an idea mixture. This binary separation process can be described as:

- 1) During any time interval Δt_i ($t_i - t_{i-1}$), F amount of A flows in, V_i amount of A flows out, and Δ_i is the amount of A leftover in the liquid phase.
- 2) Vapor flows out continuously, but the liquid level might increase due to accumulation of A. The liquid is drained to the level of L_0 instantaneously or at time t_n , if L_n is higher than L_0 .

These two liquid draining cases will be discussed separately in the following section.

Liquid Allowed to Accumulate over a Time Period This is the most common operation practice for FT synthesis in a CSTR. Typically, exit vapor is collected in a condenser vessel during the sampling period, e.g., each 24 hours. The reactor liquid level is allowed to increase during this period before draining the reactor to the desired level. The drained reactor liquid is then added to the vapor condensate to obtain the total reaction product for this period. Therefore, the product distribution is actually the average of the sampling period. For the binary system discussed here, the sampling period is divided into n time intervals, each being of differential scale theoretically. The amount of A in vapor and liquid at each time interval is shown in Table 1. At the end of the sampling period, t_n , the reactor liquid is drained to the initial level of L_0 . The total amount of A in output (F_{out}) is the sum of A in the drained liquid and the amount of A in vapor, shown as follows:

Total component A collected in vapor phase:

$$V = \sum V_i = nF - \sum \Delta_i = F_{in} - \sum \Delta_i$$

Total component A drained from liquid phase:

$$L = (L_n - L_0)C_n = (\sum \Delta_i) (A_0 + \sum \Delta_i) / (L_0 + \sum \Delta_i)$$

Total A sampled

$$\begin{aligned}
F_{out} &= V + L \\
&= F_{in} - \Sigma\Delta_i + \frac{(\Sigma\Delta_i)(A_0 + \Sigma\Delta_i)}{L_0 + \Sigma\Delta_i} \\
&= F_{in} - \frac{B_0 \cdot \Sigma\Delta_i}{L_0 + \Sigma\Delta_i}
\end{aligned} \tag{10}$$

In Equation (10), F_{in} and F_{out} are the input and output of A during the sampling period, respectively. The amount of A in output depends on the following four cases:

- 1) $\Sigma\Delta_i > 0, F_{out} < F_{in}$, accumulation of A in liquid phase, negative deviation
- 2) $\Sigma\Delta_i = 0, F_{out} = F_{in}$, no accumulation of A in liquid phase, single α observation
- 3) $\Sigma\Delta_i < 0$ & $(-\Sigma\Delta_i) < L_0, F_{out} > F_{in}$, drying-out, false two α observation
- 4) $\Sigma\Delta_i < 0$ & $(-\Sigma\Delta_i) \rightarrow L_0, F_{out} \rightarrow \infty$, almost dry, hump observed, $\alpha > 1$

Case 1 is an unsteady state process for component A which accumulates in the separation tank. In FT synthesis, product distribution will show negative deviation from ASF distribution in this case. Case 2 is a “steady state” when the amount of A that accumulates during the sampling period equals the amount drained so that there is no net accumulation of A. These two cases are under normal operating conditions corresponding to Figure 4 in FT synthesis. In cases 3 and 4, the negative accumulation of A indicates that more material is collected in output than added in the input. This is possible only when the previously accumulated A in the tank is carried out by the flowing vapor. In FT synthesis, product distribution will exhibit positive deviation from ASF distribution. When the reactor is nearly dry (Case 4), F_{out} is much larger than F_{in} , which explains the “hump” in Figure 6.

Liquid Sampling Instantaneously (constant liquid level)

In this case, liquid level is kept constant by draining extra liquid instantaneously at each time interval. The liquid level is kept at the amount of L_0 after liquid draining. Table 2 shows

the material balance of component A at each time interval. Similar to the above example where liquid is allowed to accumulate, the amount of A in output cannot be higher than its input unless under drying out conditions.

Summary

From the above computer simulation and the conceptual discussion, it is concluded that under normal operating conditions, the observation of two α values for the Fischer-Tropsch synthesis cannot be due to VLE of reaction products. A positive deviation from ASF distribution is possible only when the reactor is drying-out. This false two α distribution should not be interpreted as the responsibility of VLE for normal operation.

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Table 1			
Amount of Component A at Any Time Interval when the Liquid is Allowed to Accumulate			
Time	A in Vapor	Amount of Liquid Phase	Concentration of A in Liquid Phase
0		L_0	A_0/L_0
t_1	$V_1 = F - \Delta_1$	$L_1 = L_0 + \Delta_1$	$C_1 = \frac{A_0 + \Delta_1}{L_1} = \frac{A_0 + \Delta_1}{L_0 + \Delta_1}$
t_2	$V_2 = F - \Delta_2$	$L_2 = L_0 + \Delta_1 + \Delta_2$	$C_2 = \frac{A_0 + \Delta_1 + \Delta_2}{L_2} = \frac{A_0 + \Delta_1 + \Delta_2}{L_0 + \Delta_1 + \Delta_2}$
t_3	$V_3 = F - \Delta_3$	$L_3 = L_0 + \Delta_1 + \Delta_2 + \Delta_3$	$C_3 = \frac{A_0 + \Delta_1 + \Delta_2 + \Delta_3}{L_3} = \frac{A_0 + \Delta_1 + \Delta_2 + \Delta_3}{L_0 + \Delta_1 + \Delta_2 + \Delta_3}$
.....			
t_i	$V_i = F - \Delta_i$	$L_i = L_0 + \Delta_1 + \Delta_2 + \dots \Delta_i$	$C_i = \frac{A_0 + \Delta_1 + \Delta_2 + \dots \Delta_i}{L_i} = \frac{A_0 + \Delta_1 + \Delta_2 + \dots \Delta_i}{L_0 + \Delta_1 + \Delta_2 + \dots \Delta_i}$

Table 2			
Amount of Component A at Any Time Interval when Liquid is Drained Instantaneously			
Time	A in Vapor	Concentration of A in Liquid Phase	Total A Collected (vapor + drained liquid)
0		A_0/L_0	
t_1	$V_1 = F - \Delta_1$	$C_1 = \frac{A_0 + \Delta_1}{L_0 + \Delta_1} = 1 - \frac{B_0}{L_0 + \Delta_1}$	$F_1 = V_1 + \Delta_1 C_1$ $F_1 = V_1 + \Delta_1 \left(\frac{A_0 + \Delta_1}{L_0 + \Delta_1} \right) = F - \frac{\Delta_1 B_0}{L_0 + \Delta_1}$
t_2	$V_2 = F - \Delta_2$	$C_2 = \frac{\Delta_2 + \left(\frac{A_0 + \Delta_1}{\Delta_1 + L_0} \right) \cdot L_0}{L_0 + \Delta_2}$ $= 1 - \frac{L_0 B_0}{(L_0 + \Delta_1)(L_0 + \Delta_2)}$	$F_2 = V_2 + \Delta_2 C_2$ $F_2 = F - \Delta_2 + \Delta_2 \left(1 - \frac{L_0 B_0}{(L_0 + \Delta_1)(L_0 + \Delta_2)} \right)$ $= F - \frac{\Delta_2 L_0 B_0}{(L_0 + \Delta_1)(L_0 + \Delta_2)}$
t_3	$V_3 = F - \Delta_3$	$C_3 = 1 - \frac{L_0^2 B_0}{(L_0 + \Delta_1)(L_0 + \Delta_2)(L_0 + \Delta_3)}$	$F_3 = F - \frac{\Delta_3 L_0^2 B_0}{(L_0 + \Delta_1)(L_0 + \Delta_2)(L_0 + \Delta_3)}$
.....			
t_i	$V_i = F - \Delta_i$	$C_i = 1 - \frac{L_0^{i-1} B_0}{(L_0 + \Delta_1)(L_0 + \Delta_2) \dots (L_0 + \Delta_i)}$	$F_i = F - \frac{\Delta_i L_0^{i-1} B_0}{(L_0 + \Delta_1)(L_0 + \Delta_2) \dots (L_0 + \Delta_i)}$

Figure 1. Schematic diagram of VLE mode for Fischer-Tropsch synthesis in a CSTR.

Figure 2. Hydrocarbon molar fraction in reactor liquid with $\alpha=0.85$.

Figure 3. Hydrocarbon molar fraction in vapor phase with $\alpha=0.85$.

Figure 4 Hydrocarbon molar fraction in total reaction product with $\alpha=0.85$ (solid line). Dashed lines are liquid phase and vapor phase compositions at 100 h.

Figure 5 Hydrocarbon molar fraction in liquid phase with $\alpha=0.65$

Figure 6 Hydrocarbon molar fraction in vapor phase with $\alpha=0.65$
(Dotted line is ASF plot)

Figure 7 Comparison of paraffin saturation vapor pressure from different sources (270 °C)

Figure 8 Effect of vapor pressure source on hydrocarbon molar fraction with $\alpha=0.85$

Figure 9. Schematics of a binary separation system.

F. Fischer-Tropsch Synthesis: Induction and Steady-State Activity of High-Alpha Potassium Promoted Iron Catalysts

Abstract

Iron Fischer-Tropsch synthesis (FTS) catalysts with different potassium loadings showed different induction periods during which the conversion increased from a low initial level to a peak value before declining to attain a lower stable activity at the same reaction conditions. A lower K loading produced a slightly higher peak conversion and a shorter induction period. Although the induction period and the peak conversion were slightly dependent on the K loading for the iron catalyst, the stabilized conversions and the stabilization periods were independent of potassium content. The C₂-C₄ olefin to paraffin ratio of the gaseous products and the CO₂ selectivity did not change significantly as the potassium content increased from 5 to 10%. An increase in reaction temperature produced a new induction period and a higher conversion than was obtained before the reaction temperature was increased. The H₂:CO ratio also had an important influence on FTS conversions. Increasing the H₂:CO ratio in the feed gas lowered the H₂ utilization. A higher H₂:CO ratio feedstock gas produced lower FTS catalyst activity compared to a low H₂:CO ratio gas.

Keywords: Catalyst, iron; Fischer-Tropsch Synthesis; Promoter, K; induction period; catalyst activation

Introduction

In a FTS process, the hydrocarbon is produced from CO and H₂ by a reaction which can be expressed as

where the average value of n is defined as $\bar{n} = 1/(1-\alpha)$ or it can be rearranged as $\alpha = 1 - (1/\bar{n})$

where α is the ratio of chain termination to chain propagation [1]. When an iron catalyst is used for FTS reactions, the water gas shift (WGS) reaction can also occur. This side reaction consumes CO and water formed by the FTS reaction and produces additional hydrogen and carbon dioxide.

Potassium has long been used as a promoter for iron catalysts. It provides an increase in the alkene yield and a decrease in the fraction of CH_4 that is produced [2,3]. Potassium can also increase the catalytic activity for FTS and water-gas shift (WGS) reactions [4]. Activation of low α FTS with iron catalysts that are similar, except they have K to Fe atomic ratios less than 2, have been described earlier [5].

Dry reported the effect of K_2O on iron catalysts utilized in a fixed bed and a fluidized bed reactor that operated at different temperatures [3]. According to Dry, the low temperature FTS catalytic activity decreased as the loading of K_2O increased but the high temperature reaction showed the opposite effect. As shown in Figure 1, at 200°C , the relative catalyst activity decreased from 64 to 29 when the relative K_2O content increased from 0 to 2.6. At 330°C , the catalytic activities first increased and then stabilized at a certain level as the relative K_2O content was above 2 to 3. For use at high temperature conditions, Figure 1 indicates that the catalytic activity can be enhanced by potassium when its loading was lower than 3 relative to Fe, but a further increase in K_2O loading does not enhance the iron catalytic activity.

The influence of potassium on iron catalysts has also been investigated by other researchers [e.g., 6-8]. It is believed that strong bases of Group I metals have significant effects on both FTS activity and product selectivity. Bell and coworkers found that potassium enhances

the adsorption of CO but decreases the adsorption of H₂; therefore, potassium decreases olefin hydrogenation [14,15]. As the most effective promoter, potassium salts are widely used in iron catalysts; however, the readiness to form an alkali compound with common catalyst supports, or structural promoters such as alumina or silica, complicates the situation.

Although potassium enhanced the FTS activity and heavy product fraction, high potassium loadings may cover too large of a fraction of the surface of the iron catalyst, resulting in a limited promotion effect or even a decrease in FTS conversions. In our study, a potassium loading resulting in K to Fe atomic ratio of greater than 5 failed to further enhance the CO conversion.

Bonzel and Kerbs [9] claimed that potassium lowered the methane formation rate and increased the carbon deposition rate. It was also found that the deposited carbon was covered by potassium compounds rather than carbon sitting on top of the promoter. Huang et al. [6] studied potassium promoted iron catalysts with XPS and found that two-thirds of the catalyst surface was covered by K₂O and SiO₂. Wang, et al. [7] applied the temperature programmed reduction (TPR) technique to study the effects of potassium. They suggested that potassium facilitates the desorption process of carbon monoxide and strengthens the Fe-C bond. Thus, potassium enhanced the selectivity of long-chain products; i.e., it resulted in a high alpha product distribution. Copper is widely used as a promoter for iron FTS catalyst. It was believed that copper can facilitate the activation process. Copper can also minimize the sintering of iron catalysts by lowering the reduction temperature [3].

“In 1944, Hofer made an attempt to correlate the more reliable of the existing data of interest in connection with the Fischer-Tropsch synthesis [L. J. E. Hofer, “The Preparation and Properties of Metal Carbides,” Report of Investigations 3770, U.S. Bureau of Mines, Washington. DC, July 1944]. Some 20 years later, Hofer reported that up to then (1966) little

work had been done on the action of CO on iron oxide [L.J.E. Hofer, "Nature of the Carbides of Iron," Bulletin 631, U.S. Bureau of Mines, Washington, DC, 1966]. During the 1940s, testing of iron catalysts prepared by six German organizations was conducted; these utilized the best activation procedure practiced by each organization and these varied widely [Anon., "Report on the Petroleum and Synthetic Oil Industry of Germany," Ministry of Fuel and Power, His Majesty's Stationery Office, London, 1946, pp 96-100.] While some utilized reduction in hydrogen, others indicated that activation in CO was preferred. Some of these early studies indicated that the catalyst activity and/or stability depended upon the amount of free carbon that was incorporated into the catalytic material during the induction period [L.J.E. Hofer, E. M. Cohn and W. C. Peebles, J. Am. Chem. Soc., 71, 189 (1949); H. Pichler and H. Merkel, "Chemical and Thermomagnetic Studies on iron catalysts for Synthesis of Hydrocarbons," Technical Paper 718, U.S. Bureau of Mines, Washington, DC, 1949 (based on thesis by H. Merker)]. Dry [M. E. Dry in "Catalysis-Science and Technology," (J. R. Anderson and M. Boudart, Eds.), Vol. 1, 160-255 (1981)] summarized much of the work on catalyst activation that was conducted during the commercialization of Fischer-Tropsch synthesis at Sasol; however, much of this work was applicable to the high temperature conditions and not the lower temperatures utilized in this study. More recent work has utilized conditions that are applicable to low temperature Fischer-Tropsch synthesis but much of this has been accomplished at low conversion conditions or at short times on stream [Bukur, Dragomir; X. Lang, et al; IEC Res. 28 (1989) 1130-1140; Niemantsverdriet, J.W.; A. van der Kraan; J. Catal. 72 (1981) 385-388; Sancier, K.M.; W.E. Isakson, H. Wise; Adv. Chem. Ser., 178, 129-45 (1979); Pennline, Henry; M. Zaroachak, J. Stencel, J. Diehl; IEC Res. 26 (1987) 595-601; Sault, Allen G.; J. Catal. 140 (1993) 121-135; Sault, Allen G.; A. Datye; J. Catal. 140 (1993) 136-149; Ameise, J. A., J. B. Butt and L. H. Schwartz; J. Phys. Chem., 82, 558, (1978); Pijolat, M, V. Perrichon and P.

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In this study, three potassium promoted iron catalysts were prepared and tested at low temperatures to investigate the effect of potassium at a high level of K to Si atomic ratio of 0.05 to 0.10 on the selectivity and activity of Fischer-Tropsch synthesis. Influences of reaction conditions and gas compositions were also studied in this work.

Experimental

Preparation of Catalyst

In this study three catalysts, containing 0.05, 0.075 and 0.10 atomic ratio of K relative to iron, have been utilized. Precipitated iron catalyst precursors were precipitated from a ferric nitrate solution that was prepared by dissolving $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in distilled and deionized water, and then an amount of tetraethyl orthosilicate needed to make a Si/Fe atomic ratio of 4.6 was added. The mixture was stirred vigorously until the tetraethyl orthosilicate had hydrolyzed. A stream of the tetraethyl orthosilicate and iron nitrate mixture was added to a continuous stirred tank reactor (CSTR) precipitation vessel and a separate stream of 30% ammonium hydroxide was added at a rate to maintain a pH of 9.0. By maintaining the slurry pH at 9 and an average residence time of 6 minutes, a base catalyst material with an iron to silicon atomic ratio of 100:4.6 was obtained. The slurry from the CSTR was filtered using a vacuum drum filter and washed twice with deionized water. The final filter cake was dried for 24 hours in an oven at 110°C with flowing air. The catalyst was crushed to approximately $60\ \mu\text{m}$ sized particles and then calcined at 350°C in an air flow for 4 hours.

The 100Fe/4.6Si catalyst base powder was impregnated with the proper amount of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ to give an atomic composition of 100Fe/4.6Si/2.0Cu. The amount of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ added will depend on the iron content of the base catalyst following calcination. In addition to copper, potassium was also added as a promoter for the iron catalyst. Although most researchers use the carbonate, it is believed other potassium salts, such as nitrate, hydroxide, fluoride, silicate or permanganate, produce equal results [3]. In this study, the iron catalyst was impregnated with an aqueous K_2CO_3 solution to give the desired K-content in the final catalyst. The catalyst was dried at 110°C overnight with good mixing following the impregnation. Thus, catalysts with three different potassium loading of $\text{K/Fe} = 0.05, 0.075$ and 0.10 (atomic ratio) were prepared for FTS studies.

In-situ Activation of Catalysts

The iron catalyst needs to be activated with H_2 , CO or synthesis gas. Activation procedures can have a significant effect on the selectivity and activity of iron catalyst [8,10]. It was reported that catalysts activated with CO yielded higher amounts of long-chain hydrocarbons than catalysts activated with syngas or with H_2 . Hydrogen activation followed by CO activation was reported by Bell [15] and by Anderson [16]. In addition, activation conditions may also influence the performance of the iron catalyst during the course of the run.

In this study, the potassium promoted iron catalysts were pretreated with 24NL/h CO at 270°C and 1.2 MPa for 24 hours. The CO flowed through a catalyst slurry containing 10% solids suspended in 300 mL of Ethylflow (a mixture of decene trimers). The reduction of Fe_2O_3 with CO occurs in two steps:

In addition, CO_2 may be formed by the Boudouard reaction:

Previous work in our lab showed that approximately 50 % to 100% more carbon was present in the activated catalyst mass than was needed to form Fe_5C_2 [10]. Gradual oxidation of Fe_5C_2 to Fe_3O_4 was observed when this iron catalyst was used in FTS. It is believed that reaction system becomes more oxidizing and magnetite is usually formed at a high CO conversion [16].

Reactor System

A one-liter CSTR was used in this study (Figure 2). A sintered metal filter was installed to remove wax samples from the catalyst slurry. The wax sample was extracted through an internal filter and collected in a hot trap held at 200°C. A warm trap (100°C) and cold trap (0°C) were used to collect light wax and the water plus oil samples, respectively, by condensing from the vapor phase that was continuously withdrawn from the reactor vapor space.

CO and H_2 mass flow controllers were used to provide a simulated synthesis gas of the desired composition. After the catalysts was activated with CO, syngas was introduced at a rate of 3.1 NL/hr/gram-Fe. Reaction conditions were 230°C, 1.2 Mpa, $\text{H}_2/\text{CO} = 0.67$, and a stirrer speed of 750 rpm.

Product Sampling and Analysis

Daily gas, water, oil, light and heavy wax samples were collected and analyzed. Table 1 gives a summary of the instruments for gas and liquid product analysis. A heavy wax sample was taken from the 200°C hot trap connected to the filter. The vapor phase above the slurry passed continuously to the warm (100°C) and the cold (0°C) traps outside the reactor. The light wax and water mixture was collected from the warm trap and an oil plus water sample from the cold trap. Tail gas from the cold trap was analyzed with an online HP Quad Series Micro GC, providing molar compositions of $\text{C}_1\text{-C}_7$ olefins and paraffins as well as for H_2 , CO and CO_2 . Hydrogen and carbon monoxide conversions were calculated based on the gas product GC

analysis results and the gas flow measured at the reactor outlet. Hydrogen, carbon monoxide and syngas conversion were obtained using the following formula:

$$\text{Conversion} = 100\% \times (N_{\text{in}} - N_{\text{out}}) \div N_{\text{in}} \quad (6)$$

The oil and light wax samples were mixed before analysis using an HP 5790A GC. The heavy wax was analyzed with an HP5890 Series II Plus GC while the water sample was analyzed using an HP5890 GC.

Results and Discussion

Potassium Effect on Fischer-Tropsch Synthesis Activity

In this study, a CSTR reactor was used under the conditions of 230°C and 175psig (1.20 MPa). Simulated synthesis gas was prepared by mixing CO and H₂ to produce a H₂:CO ratio of 0.67. Gas feed flow rate was controlled at 3.1 NL/h/g-iron. To study the effect of potassium on iron catalyst activities, two series of catalysts were used to produce low and high wax Fischer-Tropsch synthesis products. Low wax (low alpha) iron catalysts were prepared to obtain a potassium to iron atomic ratio of 0.07 and 0.02 while high alpha catalysts had ratios of 0.05, 0.75 and 0.10.

The results (Figure 3) show that potassium has a significant effect on FTS catalyst activity when potassium loading was relatively low. Carbon monoxide conversions increased from 14% to 25% as the potassium to iron atomic ratio increased from K/Fe = 0.0 to 0.02. However, potassium, when added at levels higher than about K/Fe = 0.050 it did not affect the CO conversion. All three higher potassium-containing catalysts used in this study yielded a stabilized CO conversion of 40%. This shows that the potassium promotion effects for synthesis at 230°C for an iron FTS catalyst activity reached a maximum at a K loading of K/Fe = 0.050 or less. This contrasts to the results shown in Figure 1 since it is anticipated that similar activity patterns should be obtained at 200°C and 230°C.

Figure 4 gives the relation of potassium loading and FTS alpha values, which was calculated using all gas, oil and wax analysis data. A lower level of K loading significantly increased the alpha value. An increase in K loading from $K/Fe = 0.0$ to 0.02 raised the alpha value from 0.71 to 0.85 . A further increase to a K/Fe loading of 0.050 increased the alpha value to 0.91 ; however, a further increase in potassium loading did not increase the alpha value further.

Induction Period

The induction periods for three potassium promoted iron catalysts were obtained under the same conditions of 1.2 MPa and 230°C . A mixture of known CO and H_2 composition was used as a simulated synthesis gas. Figures 5 and 6 show the CO and H_2 conversion results obtained from these tests. All three higher K-containing catalysts used in this study showed a similar behavior for both hydrogen and carbon monoxide conversions. For hydrogen conversion, all catalysts showed an induction period in which the catalysts effected increasing conversion from a low initial point to a peak value before declining to a lower but stable level. The lower potassium loaded catalyst, $K/Fe = 0.05$, produced a slightly higher maximum conversion, and at a shorter induction period. The peak hydrogen conversion for the $K/Fe = 0.050$ catalyst was as high as 50% while the $K/Fe = 0.10$ yielded a 45% peak conversion (Figure 5). While the induction period and the peak conversion values for hydrogen are slightly dependent of the K loading, the stabilized conversions and the stabilization periods are independent of the potassium content. All three higher potassium promoted catalysts yielded the same stabilized hydrogen conversion at about 400 hours of total on-stream time.

Carbon monoxide conversions showed a behavior that is similar to hydrogen conversions using these K-promoted catalysts (Figure 6). The $K/Fe = 0.0144$ catalyst showed an induction period of 25 hours while the $K/Fe = 0.05$, 0.075 and 0.10 catalysts yielded induction periods of 80 , 120 and 150 hours, respectively. When high alpha catalysts were used, stable CO

conversions were obtained after about 400 hours of reaction time. Figure 6 showed only a slight difference in stabilized CO conversions for catalysts with different potassium loadings. The $K/Fe = 0.075$ catalyst yielded a 40% CO conversion while the $K/Fe = 0.05$ and 0.10 catalysts produced a CO conversion of 36% and 38%, respectively.

Selectivity

Table 2 shows the productivity and selectivity of the FTS reactions catalyzed by these high-alpha iron catalysts. Hydrocarbon productivity, CO_2 selectivity and the water gas shift reaction were not significantly influenced by the potassium content at the three higher loadings. Only a slight improvement in methane selectivity, water gas shift reaction and hydrogen productivity was observed when potassium content increased from K/Fe of 0.05 to 0.075. A further increase in potassium content did not enhance the productivity and the selectivity of FTS. Gas (C_2-C_4) analysis results indicate that the percentage of olefins for each carbon number were in the range of 82 to 87% for all three catalysts (Figures 7 and 8). The data (Table 2) also indicate that, as potassium content increased from K/Fe of 0.075 to 0.10, long-chain hydrocarbons (C_{19+}) yield increased significantly from 17.7% to 44.9%. The amount of the gas fraction with increasing potassium content (C_1-C_4) decreased by 61% and gasoline (C_5-C_{11}) fraction decreased by over 50% when increased from 0.05 to 0.07 K/Fe . These results are consistent with the findings by other researchers [3,14,15].

Dry reported that formation of methane is inversely proportional to the concentration of water and carbon dioxide [3], although others believed that CO_2 and water favor the formation of methane [13]. Figures 9 and 10 show the influence of high loadings of potassium on CO_2 and CH_4 selectivity for low temperature synthesis. Similar to the CO conversion profile, CO_2 selectivity also shows an induction period. The CO_2 selectivity for all three catalysts went through a rapid initial period of increase; however, the induction period for CO_2 is shorter than it

is for hydrocarbon formation. The CO₂ selectivity declined from its peak value of 42% to a stable level of 39%. Potassium had little effect on CO₂ selectivity for iron catalysts with K/Fe = 0.05 to 0.10. Figure 10 shows an initial decline in methane selectivity during the first 200 hours of the run. The content of potassium had little effect on the methane selectivity. All three catalysts yielded a stable methane selectivity of 1.5% after the first 200 hours of run. The results shown in Figures 9 and 10 suggest that the surface structure and/or composition changes in the first 250 hours of the reaction so that it favors the formation of CO₂ and inhibits the formation of methane. This is opposite the expectation since a slower CO₂ content produces a lower H₂/CO ratio and this is expected to produce less methane, in contrast to the higher methane fraction.

Reaction Conditions

After both hydrogen and the carbon monoxide conversions were stabilized, the FTS reaction temperature was changed from 230 to 250°C using the K/Fe = 0.10 promoted catalyst. As shown in Figure 11, both conversions went through a new induction period and then rapidly reached a stable conversion level. A 20°C temperature increase resulted in a hydrogen conversion change from 36% to a stable level of 50%. Similarly, CO conversion increased from 37% to 47%.

In addition to reaction temperature, total pressure and the H₂:CO ratio also had an important influence on FTS conversions. A test was conducted using an iron catalyst (K/Fe = 0.075) to study the effect of H₂:CO ratio on the catalyst activity. Initial reaction conditions were 175psig, 230°C and H₂:CO ratio of 0.67. After FTS conversions became stable after 500 hours of reaction time, the pressure was increased to 350psig and the H₂:CO ratio to 1.7. Figure 12 show that a change of the H₂:CO ratio did not yield stable conversions for H₂ and CO in the initial 200 hours of reaction following the changes in reaction conditions. Immediately after the H₂:CO ratio was changed, the H₂ conversion decreased significantly from 40% to less than 30%,

and then the H₂ conversion declined linearly from 30 to 22% before it approached a stable level. Although carbon monoxide conversion showed an initial increase, it then decreased at a similar rate as the H₂ conversion did.

The results show, as expected, that an increase of the H₂:CO ratio in the feed gas lowered the H₂ utilization rate. Higher H₂:CO ratio feedstock gas and/or the higher partial pressures lowered the FTS catalyst activity, apparently due a slower replenishment of the iron carbide surface than when a lower H₂:CO ratio gas was used. CO₂ selectivity decreased from 40% to 30% immediately after the gas ratio and pressure were changed, suggesting that water gas shift reaction can be inhibited due to the higher H₂ content in the gas (H₂:CO = 1.7); however, this may be due to changes of the surface composition. The data in Figure 12 also showed a new induction period after the reaction temperature changed from 230 to 270°C. A new stabilized conversion may be expected that is similar to the result given by Figure 11.

Conclusion

Promoted iron FTS catalysts showed a significant increase in CO conversion up to about K:Fe ratio of 5:100. An increase in K loading K/Fe = 0.0144 to 0.020 increased the alpha value from 0.71 to 0.85; a further increase to K/Fe = 0.050 increased the alpha value to 0.91. Catalysts with different potassium loadings showed different lengths of induction period, in which the FTS reaction showed increasing conversion from a low initial value to a peak value before declining to a stable activity level. Lower potassium loadings produced a higher maximum conversion and a shorter induction period. Although the induction period and the peak conversion values were dependent of the catalysts with higher K loading, the stabilized conversions and the stabilization period were independent of potassium content. All three of the higher level potassium promoted catalysts yielded a stabilized hydrogen conversion at about 400 hours of total on-stream time.

An increase in potassium content to K/Fe = 5:100 substantially enhanced the long-chain hydrocarbon yield with a concurrent decrease in the gas fraction (C₁-C₄) by nearly 50% and the gasoline(C₅-C₁₁) fraction by over 40%. Further increase in potassium iron ratio from K/Fe = 0.075 to 0.10 did not further enhance the production of the heavy fraction. Similar to the CO conversion profile, CO₂ selectivity also shows an induction period. The CO₂ selectivity for all three catalysts went through a rapid initial period of increase and then declined from its peak value of 42% to a stable level of 39%. Potassium had little effect on CO₂ selectivity for K/Fe ratios in the range of 5:100 to 10:100 for the potassium promoted catalysts. Methane selectivity declined gradually during the first 250 hours of run. All three higher potassium-containing catalysts yielded a stable methane selectivity of 1.5% after the first 250 hours of run. The surface structure and/or composition changes in the first 250 hours of reaction increases the formation of CO₂ but inhibits the formation of methane. All three potassium promoted catalysts yielded a stable CO₂ selectivity of 38-39% and methane yield of 1.5 mole %.

Increase in reaction temperature resulted in a new induction period and a new higher activity than that before the reaction temperature was increased. In addition to reaction temperature and pressure, H₂:CO ratio also had an important influence on FTS conversions. Increase of the H₂:CO ratio in the feedstock gas lowered the H₂ utilization rate. Higher H₂:CO ratio feedstock gas lowered the FTS catalyst activity presumably due to the lower iron carbide formation rate than that when a low H₂:CO ratio gas was used. CO₂ selectivity decreased immediately after the H₂:CO ratio increased, suggesting that water gas shift reaction be inhibited due to the higher H₂ content in the gas of H₂:CO ratio of 1.7.

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Table 1		
Analyzers for FTS Products		
Analyzer	Sample	GC Detector
HP Quad Series Micro GC	Gas	TCD
HP 5890 GC	Water	FID
HP 5790A GC	Oil + Light Wax	TCD
HP 5890 Series II Plus	Heavy Wax	FID

Table 2			
Productivity and Selectivity for Potassium Promoted Catalysts			
Catalyst	5.0%	7.5%	10.0%
Conversion			
CO	38	41	39
H ₂	40	40	39
Syngas	39	40	39
Productivity			
Hydrocarbon, g/hr/g-Catalyst	0.28	0.29	0.28
Hydrocarbon, g/h/Nm ³ -	145	153	148
Syngas	0.279	0.329	0.318
Methane, mol/h	0.181	0.213	0.210
Ethene, mol/h	0.032	0.040	0.040
Ethane, mol/h	0.196	0.023	0.225
Propene, mol/h	0.029	0.003	0.035
Propane, mol/h	0.113	0.144	0.124
Butene, mol/h	0.022	0.053	0.027
Butane, mol/h			
Water-Gas Shift			
K _p ^a	2.0	2.3	2.1
H ₂ :CO usage ^b	0.72	0.66	0.67
Selectivity			
CO ₂ , mol% ^c	38	40	39
CH ₄ , mol% ^d	1.43	1.44	1.61
Olefin ratio ^e			
C ₂	85	85	84
C ₃	87	87	87
C ₄	84	87	82
Product Composition (Wt.%)			
C ₁ -C ₄	30.06	11.64	14.74
C ₅ -C ₁₁	31.28	15.43	21.64
C ₁₂ -C ₁₈	27.41	55.29	18.71
C ₁₉₊	11.25	17.65	44.92
a. $K_p = [P_{H_2}P_{CO_2}]/[P_{CO}P_{H_2O}]$ b. $Usage = r_{H_2}/r_{CO}$ c. CO₂ mole% = CO₂ formed/CO converted. d. CH₄ mole% = CH₄/all hydrocarbons. e. Olefin ratio = olefin/[olefin + paraffin].			

Figure 1. Potassium Effect on Relative Activity (draw from data in reference17)

Figure 2. Schematic of the CSTR reactor system.

Figure 3. Potassium Effect on Fe Catalyst Activity
(230°C, 1.3MPa, H₂/CO=0.7 and 3.1 NL/gFe/hr)

Figure 4. Potassium Effect on Alpha Values

Figure 5. Potassium Effect on H₂ Conversion

Figure 6. Potassium Effect on CO Conversion

Figure 7. Olefin Ratio (C_2)

Figure 8. Olefin Ratio (C₄)

Figure 9. Potassium Effect on CO₂ Selectivity

Figure 10. Potassium Effect on CH₄ Selectivity

Figure 11. Effect of Temperature on FTS Conversions

Figure 12. Effect of Gas Composition and Temperature on FTS Conversions

G. Study of deactivation of iron based Fischer-Tropsch synthesis catalysts

Abstract

Attempts to correlate the catalytic activity of unpromoted and potassium-promoted iron Fischer-Tropsch catalysts to their bulk phase compositions as determined using Mössbauer spectroscopy are reported. The CO-conversion of both catalysts declined with time-on-stream. Samples of the unpromoted catalyst were primarily Fe_5C_2 and this phase gradually decreased to become essentially pure Fe_3O_4 after 450 hours time-on-stream. In contrast, the potassium-promoted catalyst was primarily Fe_{2+}C after pretreatment and remained this phase during 400 hours of synthesis. Thus, both Fe_5C_2 and Fe_{2+}C phases are about equally active for Fischer-Tropsch synthesis but exhibit much different stability during the course of the synthesis reaction.

Introduction

Iron-based Fischer-Tropsch (FT) catalysts undergo a series of phase transformations during activation and use (1). Activation with carbon monoxide or syngas typically results in the conversion of Fe_2O_3 to Fe_3O_4 and ultimately to one or more iron carbides (2). During FT synthesis, iron carbides can be oxidized to Fe_3O_4 if the $\text{H}_2\text{O}/\text{H}_2$ or CO_2/CO ratios are high enough (1). There has been considerable debate about the active phase of the FT synthesis. Some studies have indicated an active oxide species (3) while most have supported a carbide species (2,4). Mössbauer spectroscopy has proven to be an effective technique for the analysis of iron-based FT catalysts. *In situ* Mössbauer studies have been reported (5,6); however, these studies have been performed at low pressure and low conversions. Studies performed at industrially relevant conditions have generally involved removing the catalyst from the reactor followed by passivation (7) which, if not performed properly, will oxidize the catalyst (4).

The early work directed toward defining the role of different carbide species that are present during CO hydrogenation have been reviewed (8,9). It has been suggested that the ϵ and

ϵ' -carbide (Fe_2C and $\text{Fe}_{2.2}\text{C}$, respectively) are responsible for catalysis following CO dissociation (10). Hägg carbide formation has been considered to decrease the activity of the catalyst (6). On the other hand, it has been claimed that the deactivation of iron catalysts in FT synthesis is associated with the transformation of the highly active Hägg carbide to a less active epsilon-carbide and to the formation of a highly ordered graphite on the surface of the catalyst (11).

Tau et al. (12) utilized an in-situ Mössbauer cell to follow changes in a 10% Fe- Si_2O_3 (Alon-C) and 10% Fe- SiO_2 (Cab-O-Sil catalysts. Using Niemantsverdret's nomenclature (13), the progressive carburization in 10% CO/ H_2 at 285°C, following reduction in H_2 at 450°C, produced the following progression: $\text{Fe} \rightarrow \text{Fe}_x\text{C} \rightarrow \kappa\text{-Fe}_{2.5}\text{C} \rightarrow \epsilon'\text{-Fe}_{2.2}\text{C}$. The authors cautioned that this sequence was not followed for an unsupported iron catalyst (13) nor for a supported catalyst that was similar to the one they used (14). Their composition was not consistent with the usual order of stability of the carbides where the $\epsilon'\text{-Fe}_{2.2}\text{C}$ form, when heated, loses carbon to form the κ -form and then the θ -form. After 30 min time the bulk of the iron is about 74% carburized to a mixture of $\kappa\text{-Fe}_{2.5}\text{C}$ and $\epsilon'\text{-Fe}_{2.2}\text{C}$ (15). They reported that at longer synthesis times, the $\epsilon'\text{-Fe}_{2.2}\text{C}$ form predominates.

Gatte and Phillips (16) evaluated the modeling routine used to obtain the iron phases from Mössbauer spectra and concluded that this is fraught with difficulties. In spite of this, they conclude that there is ample evidence to support the conclusion that at least one phase of octahedral carbide, normally called ϵ' carbide, forms during Fischer-Tropsch synthesis; however, they cautioned that the spectra of ϵ' -carbide probably consists of at least two sextuples.

Herein are reported Mössbauer results obtained for an unpromoted and potassium promoted precipitated iron catalyst that was activated and used for synthesis in a slurry phase, continuous stirred tank reactor at high conversion and under industrially relevant conditions. Strict measures were observed to prevent oxidation of the catalyst samples. The results reported

here compare the iron phases present initially and as the two iron catalysts are utilized for FT synthesis.

Experimental

Catalysts was prepared by a previously described procedure (2). An aqueous solution of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Johnson Matthey Co., 98+% metals basis, 1 M) at a feeding rate of $157 \text{ cm}^3/\text{min}$ was precipitated with concentrated NH_4OH (VW, reagent grade, 28-30 wt.%) of $71 \text{ cm}^3/\text{min}$. The pH of the slurry was 9.3 and the residence time in the reactor was 300 s. This resulted in a total slurry volume of 34.4 liters. After the initial filtration, the filtrate was washed by re-slurring the filtrate in the amount of distilled, de-ionized water required to bring the total volume of the re-slurried material back to 34.4 liters for each of the two washings. Each of the filtrations was done with rotary drum filters. The washed filter cake was dried in air at 373 K overnight. The dried catalyst was ground using mortar and pastel to particles of $\sim 0.15 \text{ mm}$ and then treated in stagnant dry air at 623 K for 4 h. A comparable promoted catalyst was obtained by impregnating the calcined material with sufficient potassium nitrate solution to yield a finished catalyst with $\text{Fe}:\text{K} = 100:0.71$.

Activation and FTS Reaction

All FTS runs were conducted in a 1 L continuous stirred tank reactor (CSTR). The catalyst precursor (64.44 g) was suspended in C-30 oil (Ethylflow, a decene trimer obtained from the Ethyl Corp.; 290 g) and it was pretreated with CO at 543 K at 1.22 MPa for 24 h. The CO flow (58.7 sl/h g-Fe) was started at ambient conditions (298 K and 0.1 MPa), the pressure was raised to 1.22 MPa, and the reactor was ramped to 543 K at 2 K/min and maintained at this temperature for 24 h. Following the activation treatment, the reactor was brought to reactions conditions, which were 543 K, 1.22 MPa, H_2/CO ratio of 0.68, and a total flow ($\text{CO}+\text{H}_2$) rate of 3.1 SL/h g-Fe .

Reaction products were analyzed using several chromatographs. Gas products were analyzed using a Hewlett-Packard Quad-Series Refinery Gas Analyzer Micro Gas Chromatograph (QRGA). The analysis of the aqueous phase collected beyond the reactor used a Hewlett-Packard 5790 GC with a thermal conductivity detector and a Porapak Q column. Oil and wax were combined and analyzed with a Hewlett-Packard 5890 GC with a flame ionization detector and a 60 m DB-5 column. The reactor wax was analyzed on a Hewlett-Packard 5890 High Temperature GC with an flame ionization detector and a 30 m alumina clad HT-5 column.

Catalyst samples were extracted from the autoclave during reaction using a dip tube blanketed with an inert gas. All subsequent handling of the used catalysts was carried out under an inert gas within a glove box. A total of 20 samples were withdrawn from the reactor during the 452 hour run for the unpromoted sample and 17 samples during 400 hours for the potassium promoted catalyst.

Mössbauer Spectroscopy Measurement

The Mössbauer experiments used a constant acceleration spectrometer. The radioactive source comprised 50-100 mCi of ^{57}Co in a Pb matrix. The samples in the reactor wax form were loaded into Plexiglass compression holders presenting a thin sample to the beam. All spectra were analyzed by a least-squares fitting procedure, which attempts to describe the spectra as a series of Lorentzian peaks corresponding to the Mossbauer spectra of known Fe compounds. The fraction of the Fe atoms in each of the known phases is reported as the contributions of each of these known phases to the experimental spectrum.

Results

Unpromoted Iron Catalyst

Table 1 contains a description of the unpromoted iron samples that were used and the Mössbauer data showing the catalyst composition as a function of time-on-stream. Samples 1, 3,

10, and 20 are the used samples after various FTS reaction times. The Fe_5C_2 phase was established from the measured hyperfine parameters, although the measured fraction ratio ($\text{Fe}_\text{I}:\text{Fe}_\text{II}:\text{Fe}_\text{III}$) did not conform to the expected ratio of (2:2:1). In large-crystal samples of the carbide, the ratio frequently differs from (2:2:1) due to the variable concentration of carbide carbon. Here, however, the deviation is more profound and indicates that crystallization is not complete. In spite of this, Fe_5C_2 is the only iron carbide that can be discerned from the Mössbauer measurements.

Table 1. Mössbauer structural analysis results for unpromoted iron sample

Sample	1	2	3	4
FTS reaction time (hr)	0	23	168	452
Fe_5C_2 (atom %)	94	83	42	0
Fe_3O_4 (atom %)	6	17	58	100

Unpromoted iron catalyst samples for Mössbauer spectroscopy were withdrawn immediately after activation and at 23 h, 168 h and 453 h of FT synthesis. The distribution of iron in the catalyst after activation with carbon monoxide was 94 % $\chi\text{-Fe}_5\text{C}_2$ and 6 % Fe_3O_4 . Exposure to syngas initiated oxidation of the $\chi\text{-Fe}_5\text{C}_2$ to Fe_3O_4 . After 23 hours of FT synthesis, 83 % of the iron was present as $\chi\text{-Fe}_5\text{C}_2$ and the balance was Fe_3O_4 . The amount of iron present as $\chi\text{-Fe}_5\text{C}_2$ had decreased to 18 % after 168 hours of FT synthesis. The only detectable phase after 453 hours of FT synthesis was Fe_3O_4 .

Syngas conversion and carbide-phase versus time-on-stream for the unpromoted iron catalyst are shown in Figure 1. Syngas conversion after 24 hours of FT synthesis was above 84% as is in excellent agreement with a similar catalyst whose results were reported earlier (17). The catalyst activity declined steadily throughout the run with an average rate of deactivation of

0.16 % h⁻¹ and when the conversion is corrected for catalyst withdrawal the decline is even more rapid.

Potassium Promoted Iron Catalyst

The Mössbauer spectrum of the potassium-promoted sample taken at the earliest time-on-stream is more complex than the others and indicates that the sample contains 42 atomic% of a superparamagnetic phase (Figure 2). The Mössbauer line widths are relatively sharp for the spectra recorded for the potassium-promoted samples that were withdrawn later in the run (Figure 3). The data for five samples are summarized in Table 2. If this portion of the sample follows the pattern of another sample; the low temperature spectrum, still to be obtained, will show that the superparamagnetic contribution is due to both Fe₃O₄ and iron carbide phases. The data for sample 3 suggest that the carbiding of the promoted iron catalyst is incomplete at the end of 24 hours and continues during the early stages of the synthesis. However, after about 100 hours-on-stream, the iron is present essentially as carbide phases. Thus, the latter four samples could be fitted to four sextets (sub-spectra), as shown by the deconvolution curves. For sample 3, an additional collapsing spectrum, which originates from the superparamagnetic fine clusters, is necessary. It is reasonable to assign the major sextet (HMF 168-170 kG) to ϵ -Fe₂C. The minor sextet (HMF 217-221 kG) is assigned to a phase with an excess of Fe and this phase may be designated as ϵ -Fe₂₊C.

Table 2. Mössbauer structural analysis for potassium-promoted iron samples.

Sample	Time-on-stream, h	HNF ^a	Atomic Aeral Fraction, %	Phase
3	48	491	6	A-site Fe ₃ O ₄
		457	9	B-site Fe ₃ O ₄
		219	6	Fe ₂₊ C
		170	36	Fe ₂₊ C
		Unknown	42	Superparamagnetic
5	97	490	3	A-site Fe ₃ O ₄
		453	5	B-site Fe ₃ O ₄
		228	6	Fe ₂₊ C
		168	86	Fe ₂₊ C
8	167	491	1	A-site Fe ₃ O ₄
		457	2	B-site Fe ₃ O ₄
		219	3	Fe ₂₊ C
		170	93	Fe ₂₊ C
11	259	493	2	A-site Fe ₃ O ₄
		454	3	B-site Fe ₃ O ₄
		217	2	Fe ₂₊ C
		168	93	Fe ₂₊ C
16	394	490	2	A-site Fe ₃ O ₄
		453	2	B-site Fe ₃ O ₄
		221	3	Fe ₂₊ C
		168	93	Fe ₂₊ C

a. HNF = hyperfine magnetic field.

The conversion with time-on-stream and the fraction of the iron present as the carbide phase are shown in Figure 4. The CO conversion is high for both the promoted and unpromoted iron catalyst at the early time-on-stream. For both catalysts, the activity remains nearly constant for a brief time and then begins to decline to a low (<20%) level at later times-on-stream. While there is uncertainty about the amount of catalyst withdrawn for each sample and the impact that this has on the contact times, and therefore the CO conversion, it appears that the CO conversion for the promoted iron catalyst declines slightly more rapidly than for the unpromoted sample. The relative activity decline for these two catalysts is similar to the ones reported earlier (17).

Discussion

Based on data generated from several catalysts, a model of the working FT catalyst was developed. In this model, the initial catalyst was essentially comprised of a mixture of iron carbides. As the reaction progressed, the carbide fraction decreased to attain a value of about 30-40% (18). During this phase change, the conversion did not decrease appreciably. To account for the nearly constant activity while the iron phases changed, a model was proposed. This model had the core of each catalyst particle, initially consisting of an iron carbide phase, oxidizing to form Fe_3O_4 and an outer layer that remains as a carbide form; thus, the surface of the catalyst remained essentially the carbide form while the ratio of oxide/carbide increased as the core consisting of Fe_3O_4 expanded to approach a “steady state” carbide/oxide ratio. The constant conversion while the bulk carbide/oxide ratio changed seems to dictate that the surface composition remain essentially constant throughout the run.

The results with the unpromoted iron catalyst do not agree with this model. Instead, it appears that the catalyst particles convert from the carbide to the oxide form in parallel with the decline in conversion. Thus, it appears that a steady-state surface carbide phase/core Fe_3O_4 phase is not formed for the unpromoted iron catalyst. One explanation to account for this is that the rate of iron carbide oxidation is dependent upon the particle size for the unpromoted catalyst.

The results for the potassium-promoted iron catalyst provide a third model for the iron Fischer-Tropsch catalyst as it is used for longer times-on-stream. Initially, the catalyst activity is high and the catalyst is incompletely carbided. As the time-on-stream increases with the unpromoted catalyst, it is oxidized to the Fe_3O_4 phase in parallel with the decline in CO conversion. On the other hand, the potassium-promoted iron catalyst continues to form the iron carbide phase during the initial time-on-stream and the material remains as the carbide phase even though the activity declines with time-on-stream much like the unpromoted iron catalyst.

These results make it clear that relating the catalyst composition to the catalytic activity of an iron Fischer-Tropsch synthesis catalyst will be a demanding task. It appears that the carbide phase is more active than the oxide phase. Furthermore, the data for the promoted and unpromoted show that the initial activity of the χ -Fe₅C₂ phase is as great as the ϵ or ϵ' -carbide (Fe₂C to Fe_{2.2}C) phases. The present data do not allow us to decide whether it is the presence of potassium or the stability of the iron carbide phases that allows the ϵ or ϵ' -carbide (Fe₂C to Fe_{2.2}C) phases to remain as the conversion declines to a low level while the χ -Fe₅C₂ oxidizes as the conversion decreases.

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Figure 1. The changes in CO conversion (!) and total iron carbide phases (") for a precipitated, unpromoted iron catalyst, activated in CO, during synthesis.

Figure 2. Mössbauer data (experimental points) and fitted spectra (A, superparamagnetic contribution, ϵ -Fe₂C).

Figure 3. Mössbauer data (experimental points) and fitted spectra (see text for identification).

Figure 4. CO conversion and Fe_{2+}C percentage as a function of time-on-stream.

H. Deactivation and Regeneration of Alkali Metal Promoted Iron Fischer-Tropsch Synthesis Catalysts

Abstract

Iron Fischer-Tropsch synthesis (FTS) catalysts promoted with potassium or beryllium showed a superior deactivation property. Potassium promoted iron FTS catalyst showed a low deactivation rate of 0.59% CO conversion/week after passing an initial conditioning period of 300 hours. Beryllium promoted iron catalyst produced an even more stable activity than potassium. A deactivation rate as low as 0.43% CO conversion/week was obtained from beryllium promoted catalyst. Higher temperature generated a shorter conditioning period for potassium promoted catalyst. The FTS activity began to decrease when the bulk phase of the catalyst changed from 100% carbide to iron oxides. Although the initial activity changed rapidly, little change occurred in the bulk phase of the catalyst. For potassium promoted catalyst, FTS activity, CO₂ selectivity, hydrocarbon productivity and water gas shift activity showed the same conditioning period of 300 hours of time on stream after passing a peak value at about 120 hours of reaction time. A higher water gas shift activity, higher CO₂ and CH₄ selectivity by beryllium promoted catalyst than those by potassium were also found in an FTS process. Beryllium promoted catalyst also showed a superior regenerability when either H₂ or CO was utilized. When rejuvenated with CO a better activity recovery was achieved than that with H₂.

Introduction

Hydrocarbons of various chain length can be produced from CO and H₂ in Fischer-Tropsch synthesis process, which can be expressed as

When an iron catalyst is used for FTS reactions, the water gas shift (WGS) reaction can also occur. This reaction consumes CO and water formed by the FTS reaction and produces additional hydrogen and carbon dioxide.

Potassium has long been used as a promoter for iron catalysts. It provides an increase in the alkene yield and a decrease in the CH₄ selectivity (1,2,3). Potassium can also increase the catalytic activity for FTS and water-gas shift (WGS) reactions (4). The influence of potassium on iron catalysts has been investigated by other researchers (e.g., 5-8). It is believed that alkali metals have significant effects on both FTS activity and product selectivity. As the most effective promoter, potassium salts are widely used in iron catalysts; however, the readiness to form an alkali compound with common catalyst supports, or structural promoters such as alumina or silica, complicates the situation. Although potassium enhanced the FTS activity and heavy fraction product distribution, high potassium loadings may cover too large of a fraction of the surface of the iron catalyst, resulting in a limited promotion effect or even a decrease in FTS conversions. Bonzel and Kerbs (9) claimed that potassium lowered the methane formation rate and increased the carbon deposition rate. It was also found that the deposited carbon was covered by potassium compounds rather than carbon sitting on top of the promoter. Huang et al. (6) studied the potassium promoted iron catalysts with XPS and found that two-thirds of the catalyst surface was covered by K₂O and SiO₂. Wang, et al. (7) applied the temperature programmed reduction (TPR) technique to study the effects of potassium. They suggested that potassium facilitates the desorption process of carbon monoxide and strengthens the Fe-C bond. Thus, potassium enhanced the selectivity of long-chain products; i.e., it resulted in a high alpha product distribution. Copper, as a secondary promoter, can facilitate the activation process.

Copper can therefore minimize the sintering of iron catalysts by lowering the reduction temperature (3).

Experimental

Catalyst

Two iron FTS catalysts with an atomic ratio of K:Fe=10:100 and Be:Fe=1.44:100 were prepared and utilized in this study. Precipitated iron catalysts were prepared using $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ tetraethyl orthosilicate, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, and K_2CO_3 or $\text{Be}(\text{NO}_3)_2$ was used as the promoter precursor. Details of the preparation procedure was given elsewhere (5). The iron catalyst needs to be activated with H_2 , CO or synthesis gas. Activation procedures can have a significant effect on the selectivity and activity of iron catalyst (8,10). It was reported that catalysts activated with CO yielded higher amounts of long-chain hydrocarbons than catalysts activated with syngas or with H_2 . In addition, activation conditions may also influence the performance of the iron catalyst during the course of the run. In this study, the potassium promoted iron catalysts were pretreated with CO at 270°C and 1.2 MPa for 24 hours. The CO flowed through a catalyst slurry in 300 ml of Ethylflow oil. The reduction of Fe_2O_3 with CO occurs in two steps:

Reactor System

A one-liter continuous stirred tank reactor (CSTR) was used in this study. A sintered metal filter was installed to remove the wax samples from the catalyst slurry. The wax sample was extracted through the internal filter and collected in the hot trap held at 200°C. A warm trap (100°C) and cold trap (0°C) were used to collect light wax and the water plus oil samples, respectively, by condensing from the vapor phase that was continuously withdrawn from the

reactor vapor space. CO and H₂ mass flow controllers were used to provide a simulated synthesis gas of the desired composition. After the catalysts was activated with CO, syngas was introduced into the CSTR with a stirrer speed of 750 rpm. Reaction conditions were 1.2 Mpa, H₂/CO = 0.67, 230°C for potassium promoted catalyst and 270°C for beryllium promoted catalyst.

Product Sampling and Analysis

Daily gas, water, oil, light and heavy wax samples were collected and analyzed. A heavy wax sample was taken from the 200°C hot trap connected to the filter. The vapor phase above the slurry passed continuously to the warm (100°C) and the cold (0°C) traps outside the reactor. The light wax and water mixture was collected from the warm trap and an oil plus water sample from the cold trap. Tail gas from the cold trap was analyzed with an online HP Quad Series Micro GC, providing molar compositions of C₁-C₇ olefins and paraffins as well as for H₂, CO and CO₂. Hydrogen and carbon monoxide conversions were calculated based on the gas product GC analysis results and the gas flow measured at reactor outlet. The oil and light wax samples were mixed before analysis with an HP 5790A GC. The heavy wax was analyzed with an HP5890 Series II Plus GC while the water sample was analyzed using an HP5890 GC.

Results and Discussion

Activation, conditioning and deactivation of potassium promoted catalyst

In this study, a potassium promoted iron FTS catalysts with an atomic ratio of Fe:K=100:10 was used. Reaction was carried out at 230°C, 1.2 MPa at a space velocity of 3.1 sl/h/g-iron. The results (Figure 1) show that a conditioning period, in which CO conversion increased from below 10% to a peak value of 45% at 120 hours of time on stream and then gradually decreased to a stable level at 300 hours of reaction time. As indicated in the figure, a deactivation rate of 0.827% per day was observed from the peak CO conversion during the

conditioning period. Then a very low deactivation rate of 0.0834% per day was obtained following the initial conditioning period. Although CO conversion increased rapidly during the initial conditioning phase, Mossbauer spectroscopy analysis shows that the bulk phase iron carbide did not change. Almost all iron was converted during the in-situ catalyst activation prior to the FTS reaction. As carbon monoxide conversion decreased from the maxima, Fe_3O_4 started to appear in the bulk phase of the catalyst. This result suggests that as both the FTS and WGS reactions proceed, increasing carbon dioxide and water partial pressure changed the reaction system to a more oxidizing environment and thus cause the formation of iron oxide, which subsequently cause the CO conversion decrease. A stabilized activity may be obtained after the iron oxides-carbides phase or the three-phase reaction system thermodynamic equilibrium was reached. Figure 1 also shows that a temperature increase caused a new conditioning period, in which CO conversion reached a maxima of 75% before it stabilized at about 57%. This new conditioning period (250°C) appeared more sharply than that over the fresh catalyst at 230°C, suggesting that at a higher temperature, the new equilibrium on the catalyst surface is easier to be established than that at a lower temperature.

Selectivity and productivity of potassium promoted iron catalyst

Figure 2 gives the CO_2 and CH_4 selectivity over the potassium promoted catalyst. Methane selectivity decreased from 3.5% at 24 hours of reaction time to a stable level of 1.6% in 300 hours of time on stream. While methane selectivity decreased monotonously, carbon dioxide went through a conditioning period similar to that of CO conversion. The CO_2 selectivity started from 23% at 24 hours of time on stream and decreased from its maxima of 43% to a stabilized level of 39% in 300 hours of time on stream. Hydrocarbon rate showed a similar trend to that of CO conversion and CO_2 selectivity, as indicated in Figure 3. The rate

rapidly increased from below 0.1 g/h/g-iron to a peak value of 0.32 g/h/g-iron before reaching a stabilized level of 0.28 g/h/g-iron in 300 hours of time on stream.

Water gas shift activity over potassium promoted catalyst

When iron catalyst was utilized in an FTS process, water gas shift as expressed by equation [2] is always an important reaction involved. This property makes the iron catalyst more suitable for a carbon-rich syngas produced from coal. A water gas shift coefficient was calculated by the following equation to evaluate the WGS activity:

$$K_{WGS} = \frac{P_{[H_2]} \cdot P_{[CO_2]}}{P_{[CO]} \cdot P_{[H_2O]}} \quad [5]$$

Figure 4. gives the results of WGS coefficient and an initial conditioning period similar to the ones for CO conversion and CO₂ selectivity was found. The water gas shift activity rapidly increased from an initial value of 1.2 and then gradually decreased from its maxima of 2.8 to a stable level of 2.3. It indicates that potassium promoted iron catalyst showed a similar FTS and WGS activity trend.

Deactivation and Regeneration of beryllium promoted iron catalyst

A beryllium promoted iron catalyst with an atomic ratio of Fe:Be=100:1.44 was prepared and tested in this study. FTS was carried out at 270°C, 1.2MPa and 10 sl/h/g-iron. Table 1 gives the summary of results from the FTS reaction over beryllium promoted iron catalyst. At 270°C, a CO conversion of 51% and a CO₂ selectivity of 45% were obtained; however, a higher methane selectivity of 8.14% than that over the potassium promoted catalyst at 230°C. In addition, a higher hydrocarbon rate and higher water gas shift activity were produced over beryllium promoted catalyst at 270°C. Figure 5 gives the results of CO conversion and deactivation rate from the FTS reaction over the beryllium promoted iron catalyst. After passing

an initial conditioning period, CO conversion stabilized at 50% in the first 500 hours of time on stream. As indicated in Figure 4, a deactivation rate as low as 0.0062% during the first 500 hours of time on stream, suggesting that a superior stability was achieved over beryllium promoted iron FTS catalyst.

The reaction was operated at a series of low space velocity at 500 hours and thus the catalyst deactivated significantly. Regeneration with hydrogen was carried out at the same temperature as the FTS but zero gauge pressure for 24 hours. As shown in the figure, CO conversion increased from 37.03% to 45.35% after hydrogen regeneration. Another regeneration with CO further improved the activity by almost 10% to 55.20%. This rejuvenated activity was maintained in the next 150 hours of time on stream. These results indicated that beryllium promoted catalyst showed a good regenerability and CO is a more efficient regeneration reagent than H₂.

Conclusion

Potassium promoted iron FTS catalyst showed a low deactivation rate of 0.083% per day after passing an initial conditioning period of 300 hours. Higher temperature generated a shorter conditioning period. The FTS activity began to decrease when the bulk phase of the catalyst changed from 100% carbide to iron oxides. Beryllium promoted iron catalyst produced an even more stable activity than potassium. A deactivation rate as low as 0.0062% per day was obtained from beryllium promoted catalyst. Although the initial activity changed rapidly, little change occurred in the bulk phase of the catalyst, suggesting only the surface change may attribute to the activity change in the initial conditioning period. For potassium promoted catalyst, FTS activity, CO₂ selectivity, hydrocarbon productivity and water gas shift activity showed the same conditioning period of 300 hours of time on stream after passing a peak value

at about 120 hours of reaction time. Methane selectivity, however, showed a monotonous decrease from an initial maxima to a stable level of 1.6%.

Beryllium promoted iron catalyst showed a better deactivation property than potassium promoted catalyst, even operated at a higher reaction temperature than that over the potassium promoted catalyst. A higher water gas shift activity, higher CO₂ and CH₄ selectivity by beryllium promoted catalyst than those by potassium were also found in an FTS process. Beryllium promoted catalyst also showed a superior regenerability when either H₂ or CO was utilized. Carbon monoxide rejuvenation generated a better CO conversion recovery than hydrogen.

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Table 1	
Productivity and Selectivity for Beryllium Promoted Catalysts	
Conversion (%)	
CO	51.21
H ₂	61.98
Syngas	55.53
Product distribution (%)	
C ₁	10.11
C ₂ -C ₄	35.61
C ₅ -C ₁₁	31.80
C ₁₂ -C ₁₈	11.56
C ₁₉ +	10.92
Hydrocarbon rate, g/hr/g-iron	1.08
Water-Gas Shift	
K _p ^a	1.76
H ₂ :CO usage ^b	0.81
Selectivity (%)	
CO ₂	45.00
CH ₄	8.14
a. $K_p = [P_{H_2} P_{CO_2}] / [P_{H_2O} P_{CO}]$. b. $Usage = r_{H_2} / r_{CO}$.	

Figure 1. Deactivation rate over potassium promoted iron FTS catalyst.

Figure 2. Methane and carbon monoxide selectivity over potassium promoted iron FTS catalyst.

Figure 3. Hydrocarbon rate over potassium promoted iron catalyst.

Figure 4. Water-gas shift coefficient over potassium promoted iron FTS catalyst.

Figure 5. CO conversion over beryllium promoted iron catalyst.

I. OVERVIEW OF REACTORS FOR LIQUID PHASE FISCHER-TROPSCH SYNTHESIS

Abstract

The following overview is divided roughly into three sections. The first section covers the period from the late 1920s when the first liquid-phase synthesis was conducted until about 1960 when the interest in FTS declined because of the renewed view of an abundance of petroleum at a low price. The second period includes the renewed activity that resulted from the oil shortage due to the Arab embargo in 1972 and covers from about 1960 to 1985 when the period of gloomy projections for rapidly increasing prices for crude had faded away. The third section covers the period from when the interest in FTS was no longer driven by the projected supply and/or price of petroleum but by the desire to monetize stranded natural gas and/or terminate flaring the gas associated with petroleum production (1985 to date). These sections are followed by a brief overview of the current status of the scientific and engineering understanding of slurry bubble column reactors.

Introduction

Petroleum refining adjusted its production from kerosine to gasoline following the introduction and rapid acceptance of the auto for personal transportation. During these early years of petroleum usage, the United States was the principal exporter of petroleum crude and refined products (1). During World War I, the Allies had sufficient petroleum supplies for the war effort that was becoming increasingly mechanized; however, Germany was very poor in oil resources and this greatly handicapped their effort. Following the end of WWI, German officials were determined to develop an independent source of transportation fuels that was based on their abundant brown coal resource. The introduction of the Haber process for the high-pressure synthesis of ammonia provided Germany with a leadership role in high-pressure processes,

especially those involving hydrogen. The importance and the scientific advances associated with the ammonia synthesis were recognized and Fritz Haber was awarded the Nobel Prize in 1918.

After much research and development work, the first commercial success in 1925 was with the direct hydrogenation of coal (especially German brown coal) at high-pressure, high-temperature conditions to produce liquids that could be utilized as transportation fuels. This was the Bergius Process and its discoverer, Friedrich Bergius, was awarded the Nobel Prize in 1931. Bergius was led to this effort by his desire to be an entrepreneur and a desire to free Germany from dependence upon external oil supplies for their transportation fuels. I.G. Farbenindustrie (Farben) purchased the rights to the Bergius process. Farben was attracted to this process requiring several conditions, at least in part, because of the expertise they had developed with other high-pressure processes. By 1925, Carl Bosch had risen to a high leadership position in Farben following his successful efforts to commercialize first the ammonia synthesis process, discovered in 1908 by Nobel Laureate Fritz Haber, and then the successful conversion of synthesis gas to methanol. In this work, Farben had become recognized for its ability to produce and utilize hydrogen at high pressures. For his leadership role in developing high-pressure processes and the materials of fabrication that was needed for the processes, Bosch was awarded the Nobel Prize together with Bergius in 1931. In addition to the technical contributions, Bosch was involved in extensive negotiations with the German government that would provide them with the support necessary to conduct the development of their synfuels industry. In addition to his business activities in Germany, Bosch was active at the international levels. The details of his negotiations with the organization that is now Exxon are described in some detail in various sources (e.g., 2,3). In addition, Bosch was in a delicate situation as he negotiated with Nazi government officials as he sought to establish Farben as the lead organization for government

contracts for the production of fuels by both the direct and indirect coal liquefaction processes since he did not join the party.

The first major work on the hydrogenation of carbon monoxide was by Sabatier and his coworkers, and this work was recognized by P. Sabatier being awarded the Nobel Prize in 1912. In 1923, Franz Fischer and Hans Tropsch discovered the production of liquid hydrocarbons from synthesis gas ($\text{CO} + \text{H}_2$) that could be produced by gasifying coal. Following its discovery, the major advances in the Fischer-Tropsch synthesis (FTS) technology and scientific understanding emanated from Germany. The advances in FTS were concentrated initially in the Kaiser-Wilhelm-Institut (KWI) and then in the German companies selected by the government to commercialize the processes associated with FTS. The companies were supported by the government with a guarantee of a minimum price for the products.

The historical accounts of FTS are far too extensive to be covered adequately in a book, let alone a review paper. Hence, the following will provide a limited survey of the development of the reactors that were used to conduct the reaction in the liquid phase.

“Since 1921 the KWI had been engaged in intensive investigations of the area of gas synthesis, with the goal of producing liquid hydrocarbons. One of the reasons for this activity was the fact that Rhineland-Westphalian heavy industries, a source of financial support for the Institute, were interested in finding ways of utilizing their excess coke-oven off-gases (3).” Fischer and Tropsch were studying as one possible starting point the catalytic preparation of "Synthol," a mixture of liquid hydrocarbon- and oxygen-containing oils described in prewar patents issued to BASF (4,5). Schuster (6) later identified Mittasch and Schmidt as the inventors of these products derived from the reaction of carbon monoxide with hydrogen under high pressure. Much of the initial work was directed toward mechanistic aspects of the process (the

"formate theory"). Nevertheless, Fischer and his co-workers failed to develop a satisfactory scientific explanation of the synthesis, remarking simply in their first publication (7):

‘We wish therefore to conclude this section regarding the theory of Synthol formation by noting that for the time being we are giving first priority, relative to other possible explanations, to the notion of synthesis through carbon monoxide addition to alcohols, albeit without claiming that we have definitely proven this to be the mechanism.’

The initial mechanism that was widely accepted involved the formation of the metal carbide followed by the hydrogenation of the carbide to produce hydrocarbons. This mechanism became associated with Fischer even though he probably had less to do with its acceptance than others working in the area. By 1950, the bulk carbide mechanism had been shown to be invalid and was replaced by a mechanism that involved a surface oxygenate intermediate. This mechanism received strong support from the results of studies at the U.S. Bureau of Mines and the ^{14}C tracer studies of Emmett and coworkers. By 1980, the results produced using a variety of surface sensitive instruments led to the abandonment of the oxygenate mechanism and the revival of the carbide mechanism which now limited carbide formation to a surface carbon species. This surface carbide mechanism was so strongly supported that it was reproduced on the cover of an issue of Chemical & Engineering News on October 21, 1981. More recently the results of ^{14}C tracer studies indicate that the oxygenate mechanism is more appropriate, at least for the iron catalyst.

In their explanation of the course of the reaction leading to Synthol, Fischer and Tropsch assumed that methane and formaldehyde arose as intermediates, which is a reason why Fischer and coworkers (including the young doctoral candidate Otto Roelen) carried out an extensive series of experiments related to methane combustion and the formation and decomposition of

formaldehyde (8). Despite these efforts, Fischer and his coworkers never succeeded in detecting more than traces of the presumed intermediates (9).

Primarily because of the influence of the management of I. G. Farbenindustrie with the German government and because its ownership of the Bergius direct liquefaction process, the early plants to produce synfuels were for the Bergius process, and not FTS (10,11).

Three reactor types have been utilized for FTS: fixed bed, fluid bed and slurry bubble columns (Figure 1). The fluid bed reactor must be a two phase, solid and gas, system for FTS; if this is not the case liquid will lead to solid agglomeration and loss of the fluid phase. The slurry phase will always be a three-phase system for FTS. Biardi and Baldi (12) have recently reviewed briefly three-phase catalytic reactors and conclude that trickle bed and slurry reactors are the most important. Another review considers the advantages and prospects for FTS in a fixed-bed and slurry reactor but does not conclude that either is the preferred one (13). Reactive distillation tray columns are receiving much attention for some applications (e.g., 14,15) and, in at least a variation, have been applied to FTS. However, the tray columns never received widespread application. The early commercial plants that were operated in Germany utilized fixed bed reactors; however, other reactor types were investigated. The Brownsville, Texas plant utilized a fixed fluid-bed reactor. While the Brownsville plant encountered and overcame many operational problems, it remained for Sasol to develop the circulating fluid-bed reactors to the point where its operation was reliable. More recently Sasol has replaced the circulating fluid bed reactors with fixed fluid bed reactors. Sasol also operates fixed-bed and slurry reactors but on a smaller scale than the fluid-bed reactors; currently, 90% or more of the Sasol production utilizes fluid bed reactors.

Period I: 1929 to 1965

Work in Germany

Conversions in the liquid phase were initiated in Germany shortly after the discovery of the reaction. The developments progressed from the initial fixed-bed effort at atmospheric pressure to work in a bubble column reactor operated at atmospheric pressure to a large pilot plant that was operated during the 1940-1950s period. The German efforts were extensive and involved work by several companies. These companies added to the complexity faced by a reviewer because of their joint ventures with organizations located outside Germany. Thus, a complete and detailed coverage of the German work is outside the scope of the present manuscript.

Kaiser-Wilhelm-Institut für Kohlenforschung (KWI)

The Institute, founded in 1913 with Franz Fischer as the director, was established to concentrate its efforts on fundamental studies of coal and its conversion (16). The onset of WWI within months following Fischer's arrival and Germany's need for synfuels led the institute toward more practical accomplishments. Both direct and indirect coal liquefaction studies were undertaken. The indirect approach eventually led to the low-pressure synthesis of predominantly hydrocarbon products, the Fischer-Tropsch synthesis (FTS). The exothermicity of the reaction and the need to provide a uniform temperature in the reactor were quickly recognized.

Fischer and coworkers turned to synthesis in the liquid phase soon after they discovered the FTS reaction. Fischer and Peters (17) evaluated the use of a bubble column reactor (Figure 2) that was operated at atmospheric pressure for the hydrogenation and oligomerization of acetylene and for the hydrogenation of carbon monoxide using a supported nickel catalyst. They indicated that the use of the catalyst in liquid media for these exothermic reactions is advantageous for laboratory and commercial operations because it makes possible close control

of temperature and eliminates overheating as is encountered in fixed-bed reactors. In November 1930 the pilot plant staff attempted to run the F.-T. in the liquid phase, and they were successful in solving the heat flow problem. Fischer and Küster (18) reported results to identify the influence of temperature and pressure on the synthesis. A horizontal stirred silver-lined autoclave was utilized for these studies (Figure 3). The authors found that higher temperatures were needed for liquid phase synthesis because there was no hotspot as was the present for fixed-bed operations. They utilized a catalyst with a composition of 9Co:2Th:1Cu:0.25Ce with an equal mass of Kieselgur as support. However, the typical catalysts of that day had an activity that was too low to have practical commercial interest. They also reported that pressures near atmospheric were preferred since “Synthol” (alcohols, acids, aldehydes, ketones, etc) was formed at higher pressures.

Fischer and Pichler (19) indicated that four approaches were suitable for removing the heat of reaction and for maintaining a uniform temperature in the reactor: (1) circulating oil outside the tube with the catalyst, (2) suspending the catalyst in oil, (3) circulating superheated water outside the catalyst space (e.g., 180°C and 10 atm.) and (4) the suspension of the catalyst in superheated water. Interestingly, they referred to middle-pressure synthesis not as Fischer-Tropsch synthesis but the Fischer-Pichler middle-pressure synthesis. They utilized four catalysts (Ni, Co, Fe and Ru) in a study of middle pressure synthesis in an aqueous phase utilizing a stirred-horizontal autoclave, similar to the one in Figure 3, to effect the synthesis. They found that only Co and Ru were suitable for synthesis since Ni formed the carbonyl and was carried from the vessel while the iron catalyst was too active for the water-gas-shift reaction. The best catalyst was Ru, which was active below 200°C. The amount and kind of products for both Ru and Co were similar to those of the dry synthesis. It was noted that water was effective in removing the heat of reaction and in providing a uniform temperature; this was based on the fact

that the fixed bed catalyst in a reaction tube of the diameter they used would have not produced useful products (i.e., higher hydrocarbons). They indicated that work in the aqueous phase was not suited for scale-up because: (1) the results are not better than operating in the dry phase, (2) a larger reactor volume is needed, (3) the apparatus is more expensive due to the need for an acid resistant reactor liner, (4) considerable expenditure of energy is necessary for stirring to provide the vigorous agitation and (5) the reaction products are not easily removed from the reactor.

Thus, Fischer and coworkers were successful in using liquid-phase synthesis to control the temperature but the reaction velocity with their catalysts was too slow to be of commercial interest. In 1931, they returned to the gas-phase reaction and experiments were conducted with the so-called “moving catalyst” where the catalyst was transported through the heated zone with a screw conveyor. This research also led to results that were unsatisfactory (20).

I. G. Farbenindustrie A. G. (Farben)

Farben utilized two general types of liquid-phase operations: (1) a fixed bed of solid catalysts with liquid and syngas circulating concurrently over the catalyst and (2) a suspension of fine catalyst particles due to the fine bubbles formed when the syngas passed through a ceramic bottom plate with slurry circulation through an external vessel for heat removal. In some versions, they also utilized stirring as a means to maintain the catalyst suspension. Only the fixed-bed version developed beyond the laboratory scale.

The foam process was one variation of the liquid phase synthesis (21-26). During 1939 to 1944 Farben was developing a liquid-phase operation in which iron powder, prepared from iron carbonyl, was mixed with oil and the gas contacted with the liquid suspension (27,28) using a process scheme as outlined in Figure 4.

Michael (28) reports that laboratory reactors of 3 m height and 6.6 and 16.5 cm i.d. were utilized. These reactors were fitted with an internal central tube along the axis of the reactor.

Because the gas bubbles rose in the annular space between the reactor wall and the inner tube, the density of the slurry in the annular space was lower than the essentially gas free slurry inside the smaller tube. The difference in density caused rapid circulation of the slurry within the reactor. In today's language, the inner tube would be a downcomer tube. When they constructed a pilot plant reactor identical to the laboratory reactors except that the volume was 300 L (2.0 m diameter), difficulties were encountered. If the circulation was interrupted for some reason, the catalyst would settle and, upon re-starting, the gas flow was insufficient to cause the catalyst to become uniformly suspended. The concentration of the catalyst at the lower portion of the annular space of the reactor provided a density that was greater than the slurry in the downcomer so that circulation could never be re-started. For this reason, a pump was installed and, for convenience of maintenance, placed outside the reactor vessel as shown in Figure 4. A reactor of this design with a 0.5 m diameter and 8 m tall (1.5 m^3 volume) was constructed and operated satisfactorily. A larger 1.5 m diameter and 8 m tall (14 m^3 volume) reactor was constructed but was not operated because of a shortage of synthesis gas because of wartime problems.

It was found to be difficult to operate the suspended catalyst because the formation of high molecular weight products of limited solubility caused the catalyst particles to agglomerate and settle (21,29). Frequently they experienced thick deposits of iron catalyst around the wall of the reaction vessel, and especially in the upper portions of the reactor.

Duftschnid Process.

One Farben development (30-32) consisted of an oil recycle process in which a cooling oil was passed concurrently with the synthesis gas over granules of an iron catalyst (fused or sintered iron that was doubly promoted with aluminum and potassium oxides, or with titanium, manganese and potassium oxides). Cooling was effected by recycling the oil heated by the exothermic reaction through an external heat exchanger. The process was operated at a pressure

of 20 to 25 atm (2.02-2.53 MPa). and a temperature of 260 to 300°C in the first stage, and 280 to 330°C in the second stage when used. The throughput of synthesis gas ($H_2/CO = 0.8$ for this example) was controlled to yield about 0.5 kg of total product per liter of catalyst per day. The yield of C_3+ hydrocarbons was about 150 grams per cubic meter of synthesis gas ($H_2/CO = 1$ for this example) and was distributed as follows: 16% C_3 and C_4 (85% olefins), 40% gasoline boiling to 200°C (50% olefins), 20% gas oil (25% olefins), 20% paraffin wax and 4% alcohols, largely methanol and ethanol. The crude gasoline had a research octane number of 62 to 65 and the gas oil a cetane number above 70. Some of these patents were assigned to the Standard Catalytic Company. The Standard Catalytic Company was established by six U.S. petroleum companies to develop processes for the production of synthetic fuels, and included an agreement with Farben. Following WWII, legal actions divided the holdings of the Standard-Farben company. Jersey received complete possession of 544 patents and ownership of Standard Catalytic Company. Jersey retained half-ownership of another 254 patents.

Benson et al. (33) report that, after the preliminary work by F. Duftschmid, et al., as described above, a pilot plant with a reactor of 0.2 m diameter and 6 m height (about 0.75 m³) was constructed during 1936 and 1937 and that it was operated, first at pressures of 100 atm (10.1 Mpa) and then at 15 to 20 atm (1.5 to 2.0 MPa). In 1938, a larger plant with a 0.5 m diameter and 6 m height (4.7 m³) was operated. The recirculation rate was high, 9-12 reactor volumes of catalyst/oil was recirculated each hour (34). At the end of the war they were planning a 40,000 ton/year (860 bbl/d) plant for this process (34).

The Duftschmid process was consider to be different from the one developed by Ruhrchemie (described below) since the entire bed of solid catalyst is immersed in oil (33). However, Farben obtained a patent (35) in which oil was sprayed onto the catalyst in a fixed bed (Figure 5). The liquid passed in the same direction as the gas. They indicated that, while it was

desirable to always have a thin layer of liquid present on the surface of the catalyst, it may be advantageous to temporarily interrupt the trickling in order to cause a brief increase in the temperature of the catalyst, in effect, a catalyst rejuvenation step.

An early German liquid-phase reactor involved an arrangement of trays, each containing catalyst particles, that were contained in a cylindrical vertical reactor that was fitted at the top with a reflux condenser and an arrangement for removal of liquid at the bottom of the reactor (Figure 6) (32,36). Experiments were conducted in a 7-tray reactor, 4.5 cm diameter and 60 cm tall, with up-flow of the reactant gas.

Another variation of the liquid-phase fixed-bed reactor was developed as shown in Figure 7 (30). A catalyst, K, is placed in an inner tube, which is surrounded by an outside tube. In the example, the reactor was 15 cm in diameter and 5.8 m tall; it was surrounded by a shell that was 20 cm in diameter. An inert liquid from FTS is circulated by a pump, P, through a preheater, H, where it is heated to 240°C and then added through L to the reactor shell held at 120 atm (12.1 MPa). Syngas is preheated by passing through T and then enters through N located below the reactor. Products and recycle solvent exit the top of the reactor and pass through a cooler, S, where liquid products, including water, condense and enter a holding vessel, B. Water and product are withdrawn through D and the oil is recycled. In the example about 6 L of liquid products are formed per hour while 0.75 m³ of oil is recycled per hour. If the separation vessel, B, has about the volume of the reactor, the recycle volume/reactor volume would be about 10 and the material being withdrawn would contain only about 10% liquid products. It would therefore appear that separation would present major operational problems at the commercial scale. In addition to the reactor configuration shown (Figure 7 (1, 1A)), two other versions were shown: in one the location of the catalyst bed is reversed (Figure 7,(2,2A)) and in the other

multiple catalyst tubes are located within the shell (Figure 7 (3, 3A)). The U.S. patent covering this reactor configuration (30) was assigned to Standard Catalytic Company.

Ruhrchemie

A general license for the FT process developed at KWI was assigned to Ruhrchemie AG in Oberhausen-Holten on October 27, 1934. Independent of this licensing agreement, Ruhrchemie had started construction of a pilot plant on their own and had acquired the services of Otto Roelen, who was glad to leave the KWI since his relationship with Fischer was not entirely satisfactory (16). Roelen is credited with much of the experimental success at both KWI and Ruhrchemie. In addition to his excellent experimental capabilities, Roelen had outstanding scientific and technical abilities. His keen intellectual curiosity led him to discover the oxo process by concluding, correctly and in contrast to the views of others, that the recirculation of ethene to the FT reactor led to the formation of additional C_3 -products, especially C_3 -oxygenates. This observation led him to the discovery of the oxo process.

Their reactors had a vertical tube 6 m in height that was inside a larger tube where oil circulated to remove the heat of reaction (Figure 8). The reactor volume of one was 55 L and a second reactor had 85L of slurry volume. Because significant quantities of oil were carried over, even with a wider head at the top of the larger reactor, a reflux condenser was operated to return heavier oil to the reactor. Heavy products were withdrawn from the reactor through a filter stick immersed in the slurry. Initially a ceramic plate was used to generate small gas bubbles of feed gas, but the catalyst settled and plugged the plate when the operation had to be interrupted, even temporarily. The plate was replaced by a simple copper capillary tube which never blocked and, based on the conversion, operated to produce fine bubbles of syngas just as well as the ceramic plate.

They indicated that, on a large commercial scale operation, it would be better to limit the conversion in the stage I reactor and to use reactors in series. This operational mode was claimed to limit methane formation and to extend catalyst life.

The usage ratio (the ratio H_2/CO converted), when CO conversion was in the 70-75% range, as when operating a single stage, was usually 1.4-1.5; however, if the reactor was operated at lower conversion levels the usage ratio could be reduced to about 0.9. With two stages together, the usage ratio was 1.24-1.28, which was essentially that of the feed syngas. They had an objective of making the feed and usage ratio the same for each reactor in the series, but apparently never attained this goal. We have reported that this goal can be easily accomplished with a low H_2/CO ratio syngas when using an iron catalyst but that it may be more difficult to accomplish with a high H_2/CO ratio (37).

Ruhrchemie (38) worked to develop a modified liquid-phase process in which finely divided cobalt-thoria-magnesia-kieselguhr catalyst was suspended in oil boiling between 240 and 300°C. During the synthesis, water was injected into the slurry where it vaporized to maintain control of the slurry temperature. The presence of a high water partial pressure, as must be present in this operation, implies that oxidation of their cobalt catalyst did not occur to an extent that it was a problem. An alternative explanation is that the activity of the catalyst was so low that the change could not be detected. With $H_2/CO = 2$, 10 atm (1.01 MPa) and 2.5 L/gCo/hr at 190-210°C, 172 g of liquid and solid hydrocarbons per cubic meter were produced, with 90% of the liquid product boiling below 300°C. By the end of the war, the work had not progressed to the large-scale pilot plant stage (39).

Ruhrchemie workers also developed a version of the oil recirculation process. Their process utilized a fixed bed of catalyst that was sprayed continuously with an oil that was added through a device that was designed to provide a uniform distribution of oil across the radial

dimension of the catalyst. The intent was to have the oil maintain the catalyst free of wax and to remove the heat of reaction by the latent heat of vaporization of the added oil (34). It was not made clear how the added oil could wash the wax from the catalyst through the bottom of the reactor and, at the same time, evaporated to maintain the temperature.

Rheinpreussen

This company began work on the liquid-phase synthesis about 1937. Most of the work was under the direction of H. Kölbel and the work conducted up to 1945 was summarized by him (34). The composition of most of the catalysts used by Kölbel and coworkers in this early work, as well as in the later pilot plant studies, had a composition of Fe:Cu:K₂O = 100:0.2-0.5:1.0 and was activated 10-20°C above the synthesis temperature. They used a suspension of 10-20% Fe, a syngas with H₂/CO = 0.5 and a space velocity of 75/hr, a very low value. The early experiments were conducted in a vessel with 15cm id and 3-4 m height with cooling coils either inside or outside. They reported a usage ratio of 0.5, as it was reported that no water was present in the products. In this and other work, Kölbel reported that diesel and the product olefins, and even paraffins, reincorporated extensively to produce heavier products. Excluding the mass of product formed from the diesel recycle fluid, 180 g product was formed from a m³ of synthesis gas. With this catalyst they reported that no methane was not formed. The synthesis products were obtained by withdrawing oil and catalyst, filtering, and returning the remaining catalyst slurry to the reactor, all operations being conducted under synthesis gas (34).

The claim of paraffin reincorporation is astounding but the data that are reported seem consistent with this claim. Kölbel reported that the great freedom available when operating in the fluid phase process is the reason why the large variation of the primary products, with respect to the variables (temperature, gas composition, catalyst, pressure, residence time, etc.) cannot be approached with other reactors (Table 1) (40). In addition, it is possible that doing the synthesis

in the slurry reactor causes liquid hydrocarbons which were added (recycled is allowed with the German wording) to the reactor, through molecular (reincorporation) of the liquid hydrocarbon that is added back to the reactor, to form hard paraffins (41,42). For this reason, treating the primary product in a secondary process, such as, in general, cracking is not needed. Kölbel explains that this is why this type of process allows one to change the molecular size.

Kölbel and Ackermann (43,44) obtained patents for an apparatus for carrying out gaseous catalytic reactions in liquid medium. The reactions included Fischer-Tropsch synthesis. It was stated that the "[Fischer-Tropsch] synthesis according to known processes is feasible without trouble in a reaction space of up to 20 cm [7.9 in] diameter. With increasing horizontal diameter of the reaction space the amount of gas conversion decreases and it is always more difficult to maintain a constant gas conversion. The larger the horizontal diameter of the reaction space, the more the liquid substance leans toward changing from stationary state to a state of vertical rotation. [Vertical rotation occurs when] the liquid flows downwardly along the surface of the wall and flows along the bottom to the middle of the reaction space, whereby it is drawn out by the gas bubbles leaving at the middle of the bottom. The compressed central gas stream flows along with the liquid toward the top whereby the firmly compressed gas bubbles combine to form large elongated gas bubbles. Only at the upper reversal point of the liquid, in the vicinity of the surface of the column of liquid, the gas spreads out horizontally across the transverse section and the large gas particles are partially decomposed (Figure 9)."

As Kölbel and Ackermann illustrate (Figure 9), the liquid flows upwardly in the interior of the reactor tube and flows downward along the wall side of the reactor. They indicated several disadvantages that accrue from this situation, including: (1) decreased gas conversion, (2) occurrence of secondary reactions, (3) increased catalyst damage, and (4) increased catalyst aging.

These authors state that, for reactions like Fischer-Tropsch synthesis where the gas composition changes with conversion and where the products admix with the unconverted gas, "...the gas conversion should be complete as possible on passing the gas through once..." The authors indicate that, prior to their patent, none of the available operations permit "...maintaining the liquid medium and the suspended catalyst stationary and nevertheless permitting the gas bubbles in uniform size and distribution to pass vertically through the liquid medium at equalized velocity..." The authors indicate that the disadvantages of the liquid and catalyst circulation, as shown in Figure 9 (Figure 1), can be overcome in a cylindrical reactor with a horizontal diameter of more than 30 cm and up to 3 m or more and more than 1.5 m in height, and a gas head space above the liquid at least as large as the reactor diameter. To provide within the reaction zone a stationary catalyst and liquid condition, the large reactor shell is subdivided into similar, vertical shafts which are open at top and bottom that have liquid-tight casings and a diameter of at least 5 cm (Figure 10). The shafts should terminate above the expanded liquid level; i.e., in the free-board gas space. Because of the flows in the bottom of the reactor, it is stated that each of the shafts, in the center as well as at the wall region, receive the same amount gas. While there is circulation of the liquid in the sump (bottom of reactor in Figure 10), "...there are formed in the shafts extremely stationary liquid columns whose expansion depends on the amount of gas."

The authors indicate that in certain cases, as in the Fischer-Tropsch reaction, it may be an advantage to allow the temperature to rise toward the top of the reactor, and provisions are described which would allow for this to occur. Thus, as the partial pressure of the reactants decrease, the higher temperature will be able to compensate, completely or partially, by having the rate increase to compensate for the partial pressure decrease.

Kölbel and coworkers operated a large demonstration plant with a reactor that was 1.55 m in diameter and 8.6 m in height. Until the start-up of the slurry reactor by Sasol, the Rheinpreussen-Koppers demonstration plant was the largest slurry reactor that had been operated successfully. Kölbel states that at the time that most work was conducted using the demonstration plant (1952-53), the operation was confined almost exclusively to the production of gasoline (45). The results of the operation of this plant and the smaller laboratory scale slurry phase reactor produced data that have become the "standard" that is used to compare with other slurry phase studies. As indicated above, a typical catalyst used by Kölbel in this plant would have a composition of Fe:Cu:K₂O = 100:0.1:0.05-0.5; thus, it would be consistent with the objective of producing gasoline range material, and not high molecular weight reactor-wax. The catalyst used by Kölbel would be similar to a low-alpha iron catalyst described in Mobil patents (46,47) and government reports for the Mobil work (48,49) and, except for a much lower copper content, the one used for La Porte run II (50).

At the conversion level shown in Table 2, only 178 g of hydrocarbons were produced per m³ gas (from the original paper in German, it is not possible for even a native German to tell whether this volume of gas refers to the amount of gas fed or to the amount of gas converted). Even if it is taken as the amount fed, at the 90% conversion level, more than 178 g. of hydrocarbons should have been produced. For example, in the Mobil runs more than 200 g hydrocarbon were produced. Sasol workers indicate that they could not repeat Kölbel's results in their early studies (51). Kölbel et al. report that through polymerization of lower olefins, about 18 g of alkylate gasoline can be produced for each m³ of syngas that was converted. When this was mixed with the reformed gasoline (112 g/Nm³ CO+H₂), 130 g/Nm³ CO+H₂ of finished gasoline could be produced. For a CO conversion of 91%, the H₂ + CO conversion was 89%; the feed gas ratio was H₂/CO = 0.67. With this gas ratio, based upon our results, the only way that

Kölbel could have obtained such similar high CO and CO + H₂ conversions would be to operate so that the single pass conversion was 50-60% and to recycle the unconverted gas. It has not been widely appreciated that much of the work that Kölbel reports has been conducted under conditions designed to produce gasoline; in this mode the demand on wax/catalyst separation is minimal. Thus, much of Kölbel's work can be viewed as being conducted under conditions that make the operation of a slurry reactor much easier than the current goal of operating to maximize the reactor-wax fraction to subsequently hydrocrack to produce diesel fuel.

Kölbel stressed that the low viscosity and surface tension of the liquid was crucial for maintaining the small bubble size needed to maintain gas-liquid mass transfer. Kölbel maintained the view that it was necessary to establish upper limits upon the solids content of the slurry in order to maintain a low viscosity. Kölbel and coworkers obtained very low methane for the distribution of the other products that they reported. This is illustrated in Figure 11 where the Kölbel data are compared by the author with data obtained by others using bubble column slurry reactors (49). In spite of the question regarding mass balance, Kölbel and coworkers provided a strong scientific and engineering basis for further work.

Another reactor type was constructed along the lines of a modern multi-tray bubble cap distillation tower. Thus, a reactor is fitted with a number of trays that contain catalyst and are fitted with bubble caps arranged to allow vapors, unconverted feed gases and vapor phase products, to be distributed to keep the catalyst in suspension (Figures 12 and 13) (52). Some bubble caps are fitted with downcomers that allow nonvolatile liquid to descent to the bottom of the reactor. In an example, 0.34 lb (0.184 kg) of catalyst was suspended in one gallon (3.79 L) of oil (about 6% slurry) and charged to a reaction chamber containing 50 bubble trays. Other variations were provided (Figures 14 and 15) (31). In these versions, the cooling liquid could be

added at several levels in the reactor to maintain a better control of temperature during startup and synthesis.

The Netherlands

International Hydrocarbon Synthesis Co [N. V. Internationale Koolwaterstoffen Syntheses Maatschappij. The Hague, The Netherlands]

This company was reported to employ a form of the recycle technique that utilized vapor-phase synthesis in the first stage and this stage was followed by a liquid-phase operation that utilized a catalyst suspended in oil. The two reactors were separated by a product condensation unit (53). However, the reference given for this work appears to apply only for an oil recirculation liquid-phase process that has the features of those described above (54). This company obtained many patents covering FTS during the 1930s but only a limited number apply to liquid-phase synthesis.

United Kingdom

The Fuel Research Station at Greenwich first utilized fixed bed reactors that had a reaction space up to 50 liters volume and in 1947 began work on the fluidized bed reactor. In 1949 work began on the liquid-phase technique. Hall et al. (55) compared fixed bed, fluid bed and liquid-phase reactors and in 1952 concluded that the maximum selectivity and flexibility could be obtained with the liquid-phase system. The decision was made to construct a pilot plant, based primarily on the fact that the liquid-phase reactor was the only one that could be operated with the CO-rich gas produced in a slagging coal gasifier. Pilot-scale operations were initiated at Greenwich and transferred to Warren Spring Laboratory in 1958. A plant was to produce up to 385 L of product/day and to operate at pressures up to 20 atm (2.02 MPa) and reaction temperatures to 300°C was operated. The reactor had a 9.75 inch (23.5 cm) internal

diameter and was 28 ft tall (8.5 m), allowing a reactor volume of 273 L. Initial problems were encountered in the settling method they used for wax separation from the catalyst slurry and from carbon formation which increased the viscosity of the reactor contents to the point of near-gellation.

The operation of the British plant was terminated about the time that they had solved most of the operating problems and considered themselves to be at a point where they could operate to produce reliable data. Low catalyst activity and rapid catalyst aging were problems that limited the usefulness of the data produced during the period of operation of the plant.

Dreyfus, a British citizen who assigned U.S. patents to the Celanese Corp., described a liquid phase synthesis for Fischer-Tropsch synthesis (56,57). In his version a catalyst was immersed in a liquid medium which boils at about the temperature of the desired reaction. Syngas is bubbled through the liquid containing the catalyst and fitted with a reflux condenser to maintain the liquid phase. While the inventor indicated that the reaction could be conducted at high pressure, he indicated that it had the greatest value when applied to the synthesis of hydrocarbons under atmospheric pressure. Cobalt catalysts were utilized at a temperature of about 180-200°C and an iron catalyst at a temperature of about 250°C. The example utilized a cobalt catalyst that was promoted with thoria. Excess liquid products are drawn off by an overflow at the desired level, fitted with a liquid seal.

Dreyfus also described the use of liquid-phase synthesis in the range of sub-atmospheric to about 5 atmospheres (5.05 MPa) of pressure (57,58). A feature of this patent was the use of a metal active for Fischer-Tropsch synthesis that was present in a reduced form and at a low concentration. A salt of a reducible metal (especially Co, Ni or Fe) that is soluble in the reaction medium was indicated. A salt of a fatty acid is especially preferred since is very soluble in the

organic medium. Promoters may be included as part of the catalyst system. The metal is reduced in a few hours at the reaction temperature, e.g., 200°C prior to the synthesis.

United States Liquid Phase Work

U.S. Bureau of Mines

The U.S. Bureau of Mines constructed and operated a pilot plant that utilized oil-recycle in a reactor with a 3 inch (7.6 cm) and 8 ft. (2.44 m) tall (33). After several runs during 1946-47 with co-current downflow of gas and liquid over cobalt catalysts, a run was made with the cobalt catalyst completely submerged in liquid and co-current upflow of gas and liquid. After it had been demonstrated that the unit could be operated with the cobalt catalyst, the later runs were made with an iron catalyst. The composition of the cobalt catalyst was Co:ThO₂:MgO:kieselguhr = 100:7:12:200. The cobalt catalyst was reduced at atmospheric pressure (0.101 MPa) in the reactor. The temperature was raised to 360°C as rapidly as possible using a hydrogen flow of 10 ft³/h (1.05 m³/hr) and then the hydrogen flow was increased to 200 to 400 ft³/h (21 to 42 m³/hr) and the reduction continued for 4 h. Since the catalyst bed occupied about 0.25 ft³ (0.026 m³), the GHSV was about 800 to 1600 h⁻¹ during the reduction at 360°C. Following reduction, the hydrogen flow was reduced to 5 ft³/h (0.53 m³/hr) and the temperature reduced to 150°C. Nitrogen replaced hydrogen at this point and the pressure was increased to 40 psig (0.28 MPa). Oil was then admitted to the reactor. After the oil was added, syngas flow of GHSV = 100 h⁻¹ was started. The temperature was slowly increased from 150°C while increasing the pressure in small increments, which decreased the rate of evaporation of the cooling oil. The temperature was maintained below 175°C, maintaining a gas contraction of less than 50%, during 48 hours. The temperature was increased to 180°C during the next 24 h., after which the induction was considered complete. The conditions were then adjusted as required to obtain maximum productivity.

The Bureau of Mines also operated a larger 8 inch (20.3 cm) diameter reactor in the oil-recycle mode (Figure 16) (59). These units were operated with a precipitated and a fused iron catalyst that has a very low activity compared to the high surface area precipitated iron catalyst. The fused catalyst was used because it was hard and seemed to have the physical strength needed for slurry operation. Some experimental operating problems made it difficult to maintain constant temperature during significant portions of the runs. While it was demonstrated that this mode of operation was viable, little else was obtained that merit further consideration here.

Standard Oil (Jersey) (Now Exxon Mobil)

In the 1920s it became necessary for Farben to seek funding and partners that were located outside of Germany. One company that was targeted by Bosch, then head of the company, was Exxon. When the top management of Exxon visited the research facilities where Farben was working on the Bergius process and other high pressure hydrogenation and hydroconversion processes, they were sufficiently impressed to enter quickly into a joint effort that was centered on hydrogenation. In the early 1930s Exxon abandoned research on hydrogenation although they had spent more than \$30 million on experimental and commercial plants and an additional \$35 million payment in Jersey stock to Farben. Larson et al. (60) conclude that, "Perhaps the most important result of the early work in hydrogenation was the interest it stimulated among Jersey researchers in catalysis and catalytic processing...Catalysis research also aroused the company's interest in the synthesis of hydrocarbons from carbon monoxide and hydrogen derived from natural gas or coal... [Thus,] Jersey sought still other methods [than direct hydrogenation] for making motor fuels of high quality. For example, it investigated the Fischer-Tropsch hydrocarbon synthesis process, developed by Ruhrchemie, A.G., which converted brown coal into liquid fuel. In 1938 and 1939, patents for this process outside Germany were transferred by Ruhrchemie to Hydrocarbon Synthesis Corporation, in

which Standard Oil Development [now Exxon Mobil] took 680 shares, Shell and Kellogg 425 each, and I. G. Farben 170. Both Great Britain and France considered the building of plants using this synthetic process for providing aviation gasoline, but they had been unable to accomplish anything definite by the time the war broke out in Europe in 1939."

It was recognized soon after the discovery of the Fischer-Tropsch synthesis that a reactor employing the catalyst in direct contact with a cooling oil was an attractive approach to maintain temperature control of the exothermic reaction. U.S. patents were obtained by Farben, Standard Oil Development Company and Standard Catalytic Company.

A procedure designed to facilitate removal of the reaction product was to pass the preheated synthesis gas into a 50-bubble tray tower at the rate of 105 m³/hr. A suspension containing about 0.34 kg of finely divided nickel catalyst activated with magnesium and aluminum oxides per 3.8 L of sulfur-free paraffin was charged through the tower at the rate of 20 L/min. The reaction produced about 385 L of liquid hydrocarbons for each 105 m³ of gas charged (61).

Texaco

Most of Texaco's attention during this period was directed toward fluid-bed operations such as was utilized at the Brownsville plant. The Brownsville plant was developed by a group of companies and utilized a fixed-fluid bed reactor. The driving force for this plant was Dobie Keith who founded Hydrocarbon Research, Inc. (62). During WWII, Keith was assigned the responsibility for developing the barrier for the separation of the uranium isotopes and the construction for the gaseous diffusion plant at Oak Ridge. He developed an interest in the Fischer-Tropsch synthesis during his work on the Manhattan Project. Three drivers for the Brownsville plant were: (1) the anticipated shortage of petroleum crude, (2) the lack of a pipeline to deliver natural gas to markets, and (3) the development of plants that could be used to produce

oxygen for preparing the syngas. The discovery of the vast quantities of mid-East oil removed the major driving force for the plant just as many of the operating difficulties for the plant were overcome. The scale of the operation was small by today's standards: 900 bbl/day of diesel, 200 bbl/day of fuel oil and 300,000 lb/day of chemicals (63).

Texaco obtained a patent which provided much insight into the operation of a slurry bubble column reactor (Figure 17) (64). While the process equipment and its operation are described in much detail, neither experimental data nor examples are given; thus, it is not certain whether the patent presents a detailed conception or whether it describes equipment that was constructed and operated. The reactor can be viewed as a grouping of tubes inside a shell. The catalyst slurry is circulated through the tubes while the cooling fluid is circulated in the space between the tubes and the shell. Moore cautioned that the height/cross-sectional area should be large and provide an example where the height may range from about 10 to 40 feet (3.1 to 12.2 m) and have an inside diameter of 1 to 6 inches (2.54 to 15.2 cm). Moore taught that the flow of gas should be sufficient such that the "flooding velocity" is exceeded and that diluent gases may be used to accomplish this objective. It was indicated that a light olefin product, e.g., propene, may be used as the diluent and that a portion of the olefin may enter into the conversion, presumably by chain initiation, reincorporation or by hydrogenation. The gas feed rate may be adjusted to give turbulent flow within the tubular reactor tubes. The recycled slurry and dispersed gas flow can be adjusted to give rise through the reactors in "tubular flow." Presumably, tubular flow can be considered to be equivalent to plug flow, as this term is used today. A variety of catalyst formulations were presented, including supported or unsupported cobalt and iron. Separation of wax from the slurry was accomplished external to the reactor and could be operated so that separation was accomplished continuously or by filtering the entire catalyst inventory at one time. The entire recovered catalyst could be regenerated and returned

to the reactor or, as an alternative, regeneration could be effected by discontinuing the CO feed while continuing the H₂ feed to the reactor while the system was held at some elevated temperature.

In another variation, the liquid-phase synthesis is effected in a reactor similar to the one in the above patent but materials are added to alter the surface tension to permit the formation of a froth or foam (65). This was claimed to increase the rate of synthesis by materially increasing the area of the liquid-gas interface. In one variation, water is introduced into the reactor above the entrance of the catalyst/slurry oil entrance. The steam will evaporate and form a foam which will fill the reactor. The foam, after leaving the reactor, is broken and the slurry is separated from the products and recycled.

Another variation of the Texaco liquid-phase synthesis (66) is similar to the Duftschmid process. As shown in Figure 18, a solvent is injected between the catalyst layers of alternating catalyst and noncatalyst solids. Above each stage in the reactor, there is a device for injecting a fluid which, by partial evaporation, effectively removes the heat of the synthesis reaction.

Gulf

Cornell and Cotton (67) patented a reactor that was dramatically different from the others described above. First, the reactor was oriented with its length horizontally rather than vertically (Figure 19). A catalyst bed is located within a tube in a tube (cross-section shown in Figure 20). Located above the catalyst bed and at locations along the length of the reactor are openings to allow syngas to be fed (12) and fans to provide the pressure needed to force the liquid and syngas through the catalyst bed. Along the bottom of the vessel a number of openings allow for the removal of liquid products. Tubes (29) are located below the catalyst bed so that a coolant can be added and withdrawn through openings 31 and 32. A portion of the liquid phase is recirculated around the catalyst through the space between the tube shell containing the catalyst

and the outer shell which depends upon the pressure difference across the catalyst bed that is generated by the series of blowers at near the top of the reactor. This reactor configuration would have intellectual appeal, especially where the height of a reactor is important, as it may be if the reactor is located on a barge. However, it appears that the operation of this plant in a steady-state condition would be an exceptionally demanding task.

In viewing the reactors described for this period, one should keep in mind that the Brownsville plant, at about 7,000 bbl/day, was very large for its time. However, today one thinks of 20-50,000 bbl/day plants so that a design that was reasonable to consider for this period may be impractical when projected to the reactor size needed today.

Period II - 1960-1985

UOP

UOP workers (68) made a comparison of the entrained bed reactor, designed by Kellogg (69) and operated commercially by Sasol, a tube-wall reactor developed by U.S. DOE (70), a slurry reactor, designed by Kölbel (45) and operated on a semi-commercial scale at Rheinpreussen-Koppers, and the ebullating bed reactor, developed by the US Bureau of Mines (33) and utilized by Chem Systems Inc. (71).

It was concluded that, since the FT reactor represents only a small part of the total cost of an indirect liquefaction plant, the value of the products is of primary importance in the selection of a particular reactor (72). These authors also concluded that in spite of uncertainties in the yield structures that have been reported for some reactor systems, the differences in comparing the above reactor systems are large enough to indicate clear advantages for the slurry reactor as it has the lowest investment and catalysts costs. It was expected to give the highest gasoline yields and thermal efficiencies (72). While the slurry reactor seems to be the one currently being

considered by most organizations, it appears that it will be operated to maximize wax yield which will be cracked to diesel fuel with the goal of minimizing the gasoline yields.

Exxon

The patent history indicates that Exxon has exhibited a renewed interest in converting synthesis gas to hydrocarbons. The early work during this period contains numerous examples of syngas conversion at ambient pressures. More recently the data reflect a more sophisticated evaluation of catalysts and a long string of patents that relate to improvements in equipment and its operation. The latter are a result of the operation of a sizable fully integrated pilot facility (200 bbl/day) at their Baton Rouge Laboratory for their AGC-21 process. Because the Exxon work overlaps Periods II and III, and, since there is no logical break in the reports, their work during both periods will be covered in this section.

Slurry Bubble Column Reactor Design

Modified Gas Inlet System. Patents provide claims of methods to improve the axial distribution of catalyst and the mixing of particulate catalyst in the slurry. The methods include adding a secondary gas into the column at locations above, as well as the commonly practiced addition below, the gas distributor plate. The basis of this design is that since solids distribution along the axis of a column is a function of gas velocity in the column, by increasing gas velocity, solids distribution will decrease in the lower part of the column and increase in the upper part. A key to the method disclosed in patents is that introducing a disproportionate share of the gases at an inlet point source close to but above the distributor inlet will reduce the concentration of solids in that particular portion of the reactor and result in an increase in solids concentration in other portions of the reactor. The overall result is a more even distribution of solids in an axial direction.

Downcomers. The patents make a variety of claims regarding the utilization of downcomers to effect catalyst redistribution and/or catalyst rejuvenation. The downcomer is specified as a vertical conduit which is open at both ends, fully submerged in the slurry with the bottom near the bottom of the reactor and the top near the top surface of the slurry. A patent issued to Behrmann et al. (73) claims a method for redistributing catalyst in a slurry reactor by use of a downcomer. The bottom of the downcomer is shielded by a baffle plate to divert gases from rising from the bottom and gas free slurry enters at the top and passes down the conduit and out at the bottom. Most, if not all, Exxon patents utilize downcomers with some attachment to the bottom of the conduit and this feature presumably relates to some finer technical and/or legal features. The preferred cross sectional area of the downcomer should be no more than 2% of the total cross sectional area of the entire reactor. An example is provided using the same equipment described under Pedrick et al. (74) in which the bubble column was run both with and without a downcomer in operation. In both cases rejuvenation tubes were operated in an equivalent manner. The results showed that axial distribution of the catalyst was more uniform when the downcomer was in operation, as shown in Figure 21.

A patent issued to Chang (75) claims a slurry bubble column reactor design incorporating a peripheral downcomer. The reactor comprises a double walled vessel wherein the inner vessel serves as the main reactor zone and the peripheral circumferential top rim of the inner vessel wall, having attached to it an inverted channel having an apex and two edges, being attached to the inner wall along the outer edge of the inverted channel. The second edge of the inverted channel extending over the main reaction zone creating a gas space within its inverted contour with a gas vent extending upward from the inverted channel. A liquid by-pass pipe extends from below the top of the liquid level interface through the inverted channel between the attachment of the inverted channel to the inner reactor wall and the apex of the channel

providing a means through which slurry flows into the peripheral downcomer section. This design is shown in Figure 22 wherein the outer edge 8A of the inverted channel is attached to the top of the inner vessel wall. The innermost edge is in contact with the slurry in the main reaction zone. Gas disengaging from the slurry trapped in the inverted channel exits into the gas disengagement space 5 through line 12 and slurry exits through line 13 onto the top of inverted channel outside the apex 10 through line 13 into the downcomer section 4. The higher density in the downcomer section promotes flow from the top of the vessel to the bottom. A more complete description of this invention can be obtained by referring to the patent specification.

Heat Transfer System. This is illustrated by a patent issued to Stark (76) which claims a method for removing heat from a FT reactor which comprises passing pentane through the tube-side of cooling tubes, vaporizing the pentane to a pressure greater than the pressure in the reaction zone and recovering the vaporized cooling medium. In a preferred embodiment of this invention the vaporized pentane is sent to an expander where the high pressure energy is recovered. The low pressure vapor leaving the expander is fed to a condenser where it is liquified and then pumped up to pressure and fed back to the reactor. The recovered energy can be used to drive compressors for an air separation plant or turbogenerators to generate electricity. A goal is to replace steam so that if a leak develops the cooling fluid will be an inert which will not damage the catalyst whereas steam would in nearly all cases be harmful to the catalyst.

Tube-in-Shell Reactor. A patent issued to Koros (77) claims a slurry FT reactor wherein the slurry catalyst is disposed in a plurality of vertically arranged tubes having a length/diameter ratio of at least 10 with each tube surrounded by a common heat transfer medium disposed within the shell of a shell and tube reactor, the heat transfer medium not in fluid communication with the slurry liquid. The description of the operation of a reactor comprising a 5.76 in (14.6 cm) ID x 50 ft (15.2 m) long pipe mounted in a 12 inch pipe cooling jacket was provided.

Liquid heights varied between 12 and 32 feet (3.66 and 9.75 m) with linear gas velocities up to 7.9 cm/sec. For a 2.1/1 H₂/CO synthesis gas mixture at a superficial velocity of 5 cm/sec, 2200 GHSV, reactor pressure of 285 psig (1.96 MPa), and steam jacket pressure of 140 psig (0.96 MPa), CO conversions in excess of 50% were obtained. The temperature of this run was not given.

Reactor Operation

Setting Operating Conditions. A patent issued to Herbolzheimer and Iglesia (78) claims a method for operating a solid-liquid-gas bubble column having a diameter >15 cm for FT synthesis over a supported cobalt catalyst in which the solids are fluidized by the gas. The invention comprises:

- (a) injecting gas at an average gas velocity >2 cm/sec;
- (b) fluidizing the particulate catalyst having an average diameter >5 µm in an expanded liquid column >3 meters in height and a particle settling velocity U_s and a dispersion coefficient D , such that (H expanded slurry height):

$$0.5 (U_s - U_L) \leq \frac{D}{H}, \text{ where } H > 3m$$

where

$$U_s = \frac{1}{18} d_p^2 \frac{\rho_s - \rho_l}{\mu} g f(C)$$

(C_p , catalyst concentration profile; ρ is density, μ , viscosity of wax; C , volume fraction of slurry; g , gravitational constant; d_p , particle diameter)

- (c) operating at plug flow at a gas velocity U_g , expanded liquid height H , and dispersion coefficient D such that

$$U_g \geq 0.2 \frac{D}{H} \text{ where } H > 3 \text{ m, } U_g > 2 \text{ cm/sec.}$$

In one example using a Co-Re/TiO₂ catalyst having a density of 2.7 g/cm³, a liquid density of 0.7 g/cm³, and a wax viscosity of 0.01 g•cm/sec, the particle settling velocity is:

$$U_s (\text{cm/sec}) = 1.1 \times 10^{-4} [d_p (\mu\text{m})^2]$$

For a 60 μm average particle, $U_s = 0.39$ cm/sec. For a liquid velocity of 0.5 U_s , and a column height of 3 m, a gas velocity of 2 cm/sec provides a Peclet number of 10, which is the minimum gas velocity allowed that would maintain suspension of the solids in the column and maintain a plugflow operation in the column.

This patent and its European counterpart have attracted enormous attention, both technically and in the courts. It appears that enforcement of the patent would prohibit the use of a cobalt catalyst in a slurry bubble column reactor for any conditions that would have appeal for a commercial operation.

Catalyst Activation and Rejuvenation. A patent issued to Mitchell (79) claims a method for activating a fresh, reduced cobalt containing FT catalyst by treating the catalyst with H₂ in hydrocarbon liquids for a period sufficient to increase catalyst productivity. A patent having an identical specification issued to Mitchell (80) claims a process using the method of catalyst activation that is run under FT conditions. The method applies specifically to treating catalysts that had been previously reduced ex situ and exposed to the atmosphere before introduction into

a slurry system. Such catalysts are suspended in a slurry and treated with H_2 at hydrocarbon synthesis temperature and pressure with temperatures no lower than $40^\circ C$ below hydrocarbon synthesis temperature. Another patent issued to Mitchell (81) claims a method for rejuvenating partially deactivated catalysts which is essentially the same procedure described above. An example for activating a 12% Co-1% Re on a 94% TiO_2 -5% Al_2O_3 catalyst by reducing the catalyst with H_2 was given. Following reduction, catalyst was passivated with a CO/H_2 stream. This passivated catalyst was combined with wax in a slurry reactor and treated with H_2 . Synthesis gas productivity over the treated catalyst increased to 100% relative to 25-60% productivity for the non- H_2 treated catalyst. The effect of several periods of catalyst rejuvenation during a 50 day run on catalyst productivity following this method is shown in Figure 23.

A patent issued to Pedrick et al. (74) claims a method by which reversibly deactivated particulate hydrocarbon synthesis catalyst in a gas-slurry reactor is rejuvenated and more uniformly distributed in the reactor. A hydrogen rich gas, injected into the bottom of a vertical draft tube which is fully immersed in the slurry, forces the catalyst up the draft tube while concomitantly reactivating the catalyst, which is discharged from the top into the upper portion of the slurry phase. The examples contained results from a series of balances made during a run in a 4 ft (1.2 m) diameter by 35 ft (10.7 m) high reactor that show both activation and axial redistribution of the catalyst. During the run, various combinations of draft tubes fed with H_2 , which were commonly referred to as rejuvenation tubes, and draft tubes fed with tail gas, were employed. The maximum flue-gas fed draft tube plus rejuvenation tube cross-sectional area for any of the run conditions was 2.6% of the cross sectional area of the reactor. A feed gas mixture comprising 56% H_2 /26% CO /13% CO_2 /5% CH_4 , by volume, was fed to the reactor containing a 12% Co-1% Re on a 94% TiO_2 -5% Al_2O_3 slurry catalyst at 210 - $230^\circ C$ and 20 atm (2.02 MPa).

When operating the reactor with two-2 inch (5.08 cm) diameter and two-4 inch (10.2 cm) diameter flue-gas fed draft tubes and one-3 inch (7.62 cm) diameter rejuvenation tube, the superficial velocities in the respective locations were:

inlet,	12-14 cm/sec;
outlet,	10.5-12.1 cm/sec;
draft tubes,	58-60 cm/sec;
rejuvenation tubes,	40-70 cm/sec.

Under these conditions the axial dispersion of the catalyst in the reactor improved significantly (Figure 24) and productivity increased from 41 to 69 (vol CO/hr/vol slurry). The overall reactor temperature differentials from the bottom to the top of the reactor for the individual balances using both lift and rejuvenation tubes was only a couple of degrees.

The effect of rejuvenation tubes on catalyst activity is shown in runs where both flue gas fed draft tubes as well as rejuvenation tubes were used. In a run sequence described in Figure 25, the decline in activity of catalyst was followed for a period of 3 days after which one 3 inch (7.62 cm) rejuvenation tube was brought on line. Immediately upon addition of H_2 an exotherm was observed followed by an immediate increase in catalyst activity recovering its initial activity in 1-2 days, after which it remained constant. After line-out, adding another rejuvenation tube provided no additional benefit. The exotherm in the rejuvenation tube was also used as a method to determine the degree of aging of the catalyst.

The beneficial effect of heating the rejuvenation tube to a temperature higher than the surrounding slurry was also demonstrated. Although the temperature in the rejuvenation tube is typically a few degrees higher than the surrounding slurry, through insulation of the tube and heating with steam, even higher temperatures can be attained. During one period in which the rejuvenation tube was heated sufficiently to raise the temperature an additional 5.6°C, CO

conversion in the reactor increased from 26 to 36% over a 24 hr period whereas in a prior balance period without external heating being applied to the rejuvenation tube, CO conversion had dropped from 32 to 26% over a 12 hr period, as shown in Table 3 (82).

Exxon patents have covered a variety of procedures to effect catalyst rejuvenation that utilize operations within as well as external to the reactor. A number of patents pertain to catalyst rejuvenations that mirror the operations utilized for fluid cracking units. An example is a patent issued to Hsia (83) claims a FT process comprising a slurry reactor design coupled with a continuous rejuvenation reactor. Deactivated catalyst is reactivated and rejuvenated using an external rejuvenation reactor vessel to which catalyst from the synthesis reactor is continuously fed via a downcomer from the top of the slurry bed in the synthesis reactor to the bottom of a slurry bed in the external rejuvenation reactor vessel (see Figure 26). Likewise, rejuvenated catalyst is fed to the synthesis reactor via a downcomer from the top of the slurry bed in the rejuvenation reactor to the bottom of the slurry bed in the synthesis reactor. Slurry flow from synthesis reactor vessel to the rejuvenation vessel and the flow of rejuvenated catalyst back to the synthesis reactor vessel are driven by gravity since both vessels are under the same pressure. A drawing is included but no examples are given.

Removal of Catalyst Fines. A patent issued to Hsu and Robbins (84) claims a method for removing $<1\ \mu\text{m}$ particles adhering to catalyst particles containing a Group VIII metal supported on an inorganic refractory oxide. The removal of fines is important for wax separations. The method comprises dispersing the particles to which the $<1\ \mu\text{m}$ particles adhere in a liquid comprising a Fischer-Tropsch derived wax, agitating the dispersion and concentrating the $<1\ \mu\text{m}$ particles in the supernatant liquid and separating the $<1\ \mu\text{m}$ particles by decanting this layer from the larger particle containing phase. Although examples are given in which the liquid used in the particle classification step includes solvents other than Fischer-Tropsch derived wax, the claims

only apply to the latter (see Table 4). Catalysts stirred with FT wax at 130°C gave initially a filtration rate of 0.024L/cm²/min which decreased to 0.20 cm³/cm²/min after stirring for 44 hours. Using the method of this invention of extended stirring and separating the decant after 3 cycles, the filtration rate improved to 0.06L/cm²/min.

Apparatus for Substantially Plug-Flow, Slurry Phase Synthesis

Koros (77) has patented a slurry apparatus that permits a substantially plug-flow slurry-phase operation in an arrangement of multiple tube reactors in a shell. Thus, the concept of the mechanical part of the tube and shell reactor resembles a Sasol Arge reactor; however, numerous additional features are incorporated to permit slurry-phase operation.

In Figure 27, the syngas is added through 12 and is dispersed through sparger 14 into the liquid slurry medium, held at a level so as to maintain a gas-liquid interface, with the gas held in the space between 15, the slurry-gas interface and 18, a distributor tray.

A series of reactor zones, 20, are arranged within the shell, such as the ones shown by the example in Figure 28.

The reactor tubes are held in place by lower, 22, and upper, 28, tube sheets. The space between the distributor plate, 18, and the lower tube sheet, 22, may or may not contain catalyst in addition to the slurry liquid. A detail of the distribution zone is provided in Figure 29. The bubbly liquid from area 9 enters the tube/bubble cap 19A/19B. The bubble cap is aligned vertically with the reaction zone tube 20. The bubble cap is sized to give a pressure drop and injection velocity sufficient to decrease the size of the bubbles and to suspend the catalyst in the reaction zone (injection velocity about 20 to 100 ft/sec (6 to 30 m/sec)). The gas to liquid transfer rates are at least equal to the conversion rate of the syngas gas.

Preferred slurry materials are stated to be Fischer-Tropsch waxes and C₁₆-C₁₈ hydrocarbons. The concentration of solids are usually about 10-50 wt.%, preferably 30-40 wt.% solids.

Catalyst/slurry addition/withdrawal may be effected through line 32. The region between tube sheets, 28 and 30, allows interconnection between the upper ends of the reaction zones for gas, liquid and catalyst. Tube sheet 30 holds filter cartridges, 31, which may be manufactured from sintered metal mesh, woven metal fibers, glass fibers, cloth or fibrous carbon, which can retain the catalyst particles while allowing the wax to pass. The filter cartridges are aligned vertically above each reaction zone. A gas-liquid disengagement zone lies above the filter cartridge tube sheet, and liquid product, separated from catalyst, can be withdrawn through tube 40 and/or 33. A demister, 41, separates gas from liquid droplets; residual gases are withdrawn through tube 42.

During operation the catalyst, 21, is preferably located in the reaction zone although some catalyst may be found in the liquid zones above or below the upper and lower tube sheets.

The catalyst most preferred is cobalt on titania (primarily in the rutile form) with less than about 70 m²/g. Preferred promoters are stated to be rhenium and hafnium.

It is stated that "...catalyst particle size is not critical..." but is preferably in the 20-150 micron size range.

The example described the operation of a single reactor (6" o.d., 5.76" i.d., 15.24 cm o.d.; 14.63 cm i.d.) about 50 ft. (15.2 m) tall mounted inside a 12" (30 cm) pipe to serve as a cooling jacket. Feed gas to the reactor was preheated.

The catalyst was prepared by impregnating cobalt onto titania extrudates which were crushed and screened to give ca. 30 micron diameter particles (presumably the catalyst contained promoters). The catalyst was reduced in hydrogen in a fluidized bed, and then the slurry wax

was introduced. Following a prescribed procedure of start-up, they attained a CO conversion in excess of 50% at GHSV = 2800. Following a brief reactor upset, the unit was restarted at a higher steam jacket pressure (140 psig; 0.96 MPa) and higher reactor pressure (285 psig, 2.0 MPa at the reactor gas outlet). The reactor maintained CO conversion of 60-70% (2800-3600 hr⁻¹) for nearly seven days of synthesis. This material was stated to be a "...very active HCS catalyst." Methane selectivities were in the range of 2.7 to 3.2%. Assuming the steam jacket pressure represents steam/water, this corresponds to 354°F (178°C); presumably the reactor side would not be at a much higher temperature.

Mobil

The initial runs in the pilot plant (Figures 30 and 31) at Mobil Oil (48,49), based upon the catalyst compositions in Mobil's patents, utilized a catalyst with a composition that resembles the one reported for Kölbel's work and the catalyst used for the La Porte Run II (low, not high, Cu content). Mobil's data from work funded by DOE have become the "standard" for both economic (e.g., 85) and technological evaluations (e.g., 856). The first three runs in the Mobil plant were conducted using a catalyst that produced low molecular weight materials; during the third run a potassium salt was added at 81 days-on-stream and this decreased the methane + ethane production from about 13 to 18 wt.% without significantly lowering the CO conversion; however, operational upsets prevented a valid assessment of the impact of the added alkali (49). The later runs were in the high molecular weight product mode (wax mode). In most runs, Mobil operated with about a 20 wt.% slurry catalyst loading. In run 8, the aging rate of the iron catalyst operated at 250°C, 1.48 MPa and 1.4 NL/gFe-hr was such that half the activity would be lost during 24 days; later in the run the catalyst half-life was 13 days when the temperature and pressure were increased. Mobil workers indicate that the catalyst used in this run was not acceptable because of its high aging rate. In run 9, a surprisingly low methane + ethane make

(about 5.4 wt.%) was obtained. The catalyst was the "same" as had been used in a prior run where this was not observed; the only difference noted was that the low methane + ethane catalyst had a lower surface area. An operational upset terminated the effective operation at day 10. In run 10, Mobil workers reported that the catalyst could not be fully activated at synthesis conditions.

Run 12 was operated for 17 days at constant conditions and "This period represented the finest example of low methane + ethane [4.1 wt.%] mode operation we have ever produced in the pilot plant." Wax production was about 60 wt.%. An operational upset occurred on day 17 and afterwards catalyst settling and low catalyst activity were problems that could not be overcome.

Run 13 was a repeat of run 12 and good operation was accomplished for 35 days-on-stream, after which catalyst settling became a problem. Viewing the pictures of the catalyst, Mobil was utilizing particles in the 1-5 micron range, and the final catalyst particles were considerably larger following removal from the reactor. It is not clear whether this is due to catalyst particle growth or, more likely, cementing together several particles by reactor wax. It is not clear, if wax caused the particle size increase, whether this occurred in the reactor itself or was an artifact introduced during catalyst collection and subsequent treatment.

As stated above, the Mobil data have replaced the Kölbel data as the "standard" for slurry F.-T. operation. Data for reactor wax yield of 46 wt.% are shown in Figure 32. This data has been utilized by Bechtel Corp. for their analysis of slurry F.-T. operations. They consider the data to consist of three regions: methane (α_1) that is higher than ASF; C₂-C₄ (α_2) and reactor wax (α_3). Theoretical curves for reactor wax make of 9.49 wt. % (low alpha data), 46.02 (intermediate alpha data) and 75.95 (high alpha data) are shown in Figure 33.

Thus, the Mobil data, in spite of operational problems, represents the best data that is available in the open literature in sufficient detail that its quality can be adequately judged.

Gulf Oil (Now Part of Chevron)

During this period Gulf Oil conducted a major effort to develop processes that would enable them to convert natural gas to transportation fuels and to petrochemicals. Much of this work was devoted to the development of active catalysts and to the operation of fixed-bed reactors. An outgrowth of this effort was the development of the Gulf-Badger FTS process. Much, if not at all, of the rights to the Gulf FTS technology was obtained by Shell following the incorporation of Gulf Oil into Chevron. Gulf did some work using a slurry bubble column reactor and that is described in the following.

A 1985 patent (87) obtained by Gulf Oil claimed a process for the conversion of synthesis gas using a finely divided catalyst (ca. 10-110 microns) dispersed in a fluid medium. The catalyst consisted essentially of cobalt and ruthenium on a support.

The process is outlined in Figure 34 and does not differ significantly from one used by Kölbel and coworkers (45). In the reactor, the catalyst particles are suspended in a liquid medium having sufficient viscosity to ensure that the particles remain in suspension and having a volatility that is low enough to avoid loss due to vaporization within the reactor. The catalyst is present in the slurry at concentrations from about 2 to 40 wt.%. The catalyst bulk density can be in the range of 0.25 to 0.90. The gas flow enters at a rate sufficient to suspend all of the catalyst particles in the system without settling. The gas flow rate will be selected depending upon the slurry concentration, catalyst density, suspending medium density and viscosity, and particular particle size utilized. Suitable gas flow rates include, for example, from about 2 to 40, preferably from about 6 to 10 cm/sec. The pressure range covered is from about 1 to 70 atm. Light hydrocarbon products, such as C₂₀ and below, are withdrawn overhead through a line designated

32 in Figure 34. A portion of the heavier products and catalyst slurry is withdrawn through line 38 and is passed to a separation zone. A concentrated catalyst/slurry fraction is returned to the reactor while a portion of the catalyst/slurry may be passed through a regeneration zone 54 before being returned to the reactor. Heavy products with low catalyst concentration are revolved through line 44. Separation by filtration can be utilized for separating catalyst from the suspending liquid (vessel 40).

The data obtained in the slurry reactor were compared to a run in the fixed bed reactor with the same catalyst formulation. Gas entered the reactor at the bottom through a stainless steel screen in the form of small bubbles. Hydrocarbon was removed from the top through a heated line. The pressure was 160 psig (1.08 MPa) and the gas flow with $H_2/CO = 1.95$ was 1826 cm/s. Initially the temperature was 225°C but was increased and held at several higher temperatures to obtain additional conversion data. The increase in conversion with increasing temperature gives an activation energy of 20.5 kcal/mol (85.7 kJ/mol). At 225°C, methane is 8.4 wt.% of the product and increases to 15.6 wt.% at 240°C. As the temperature increases, the C_5+ fraction gradually decreases (Figure 35) and the C_5-C_{20} fraction increases, indicating that the alpha value decreases with increasing temperature; however, there is not sufficient data to obtain reliable values of alpha (Table 5).

Period III 1985-2000

Sasol

Sasol has reported general, but few specific, details about the development and operation of their slurry reactor operations. Sasol's work on a small scale began in the early 1980s (51). In 1990, a slurry bed with a diameter of about 1 m was commissioned and the results confirmed their early expectations. In a bold move, Sasol decided to construct a commercial scale slurry reactor (5 m diameter, 22 m high) rather than two 5,000 tube tubular-fixed-bed reactors for the

expansion of their low temperature operation. The commercial reactor was commissioned in May 1993 and has been reported to operate successfully since that time.

Sasol uses a separate catalyst pretreatment reactor in which hydrogen reduction (extent of reduction not specified) is used to activate an iron catalyst prior to its introduction into the slurry reactor. During operation, it is understood that an activated catalyst batch is on "stand-by" so that if a significant upset, such as a slug of sulfur to produce severe catalyst poisoning, causes a significant loss in productivity, the reactor is emptied and a fresh catalyst batch added during a short period of a few hours. On-line catalyst removal and additions are reported to be done without difficulty. Based upon reports of the extent of sulfur poisoning in the fixed-bed ARGE reactors, it should not be surprising if Sasol operators had made several replacements of the catalyst inventory during the seven years of commercial operation.

The authors (51) describe the churning nature of the slurry-base bubble interactions, implying that the Sasol operation operates in the bubbly, rather than slug, flow condition. Because of the isothermal nature of the slurry reactor, the operating temperature can be much higher than in a fixed-bed tubular reactor without fear of hot spots leading to carbon formation and break-up of the catalyst. Hot-spots in the fixed-bed reactor presumably allows for the catalyst in the hot-spot to reach a temperature sufficiently above that of the reactor set-temperature so that carbon formation and rapid catalyst deactivation become possible.

It is reported that for an iron catalyst, the product slate is considerably affected by the age of the catalyst, with wax selectivities decreasing with time. However, "by proper scheduling of catalyst renewal, it is possible to maintain a steady selectivity profile for a single reactor while minimizing the catalyst consumption." It therefore appears that the Sasol operation involves a regular schedule of catalyst addition, presumably to replace catalyst that is intentionally withdrawn as well as that which is lost as catalyst fines due to catalyst attrition.

Foam was found to build up in the reactor under certain conditions but it was reported that this could be prevented by modifying operation procedures. "Separation of gas from the entrained slurry was another development that was easily resolved.", implying that slurry carry-over can be a problem if not handled properly.

Several approaches were tried at Sasol in order to effect wax separation from the catalyst containing slurry. These included close attention to the production of the catalyst and its physical characteristics as well as to the separation processes. The technique currently in use in the commercial operation for wax/slurry separation is considered to be proprietary information. The removal of wax, but not catalyst, is a critical aspect of bubble column reactor operation. While Sasol patents address this, the filter operation is poorly described in most of these.

China

The Chinese have operated a two stage process involving slurry F.-T. synthesis with an iron catalyst and fixed-bed cracking/oligomerization processing using a ZSM-5 catalyst to convert the F.-T. product to gasoline range fuels (88). The F.-T. slurry reactor was 4 cm in diameter and 450 cm in height. The reactor, in a schematic form, is very similar to the one used by Mobil Oil (Figures 30 and 31). They used an unsupported precipitated iron catalyst with a typical composition of Fe:Cu:K₂O = 99.5:0.5:0.29. The sample of catalyst used in the slurry reactor had obviously been calcined [based on CAER work, at temperatures of at least 300°C] since the XRD analysis showed that the main crystal phase was α -Fe₂O₃. The authors indicate that diffusion effects could be neglected for their runs. It appears that they used a slurry that contained 12% catalyst. Most of the published data concerning runs with their pilot plant are for the product following processing with the ZSM-5 catalyst. However, based upon data presumed to be for the F.-T. only operation, the liquid phase is reported to have a composition of approximately 70% C₅₋₁₂, 27 % C₁₃₋₂₂ and 3% C₂₂₊. Thus, based upon the catalyst composition,

the product distribution would be considered to originate from a low-alpha mode of operation, and the composition of the catalyst is consistent with this. Furthermore, the low-alpha mode would probably be preferred for subsequent conversion of the F.-T. products with a ZSM-5 catalyst in the second stage.

The output during the course of a 1,000 hour (40 day) run declined due to loss of catalyst. From the data published for the Chinese F.-T. only operation, it is difficult to reach definitive conclusions on catalyst performance.

Syntroleum

While Syntroleum began work of FTS earlier than 1985, their visibility dates to this period. Much of the early work they reported did not involve liquid-phase synthesis and will not be covered. The first significant public information for liquid-phase synthesis was the construction and operation of a 70 bbl/day integrated pilot plant at ARCO's Cherry Point Refinery near Bellingham, Washington (89). This project was led by ARCO's upstream technology unit. The individual process units were modular in design, were constructed in Tulsa, Oklahoma, and shipped to the site where they were erected (90). The proprietary reactor design for the autothermal reformer was used to generate syngas from natural gas (actually a refinery dry gas stream substitute) and air. The return to the use of air for the generation of the synthesis gas is a unique feature of the Syntroleum process. For the FTS component, they tested their advanced reactor design and a proprietary cobalt microsphere catalyst. The system is described as, "...a moving bed system, where catalyst microspheres are suspended by the gas in circulating liquid." The catalyst is reported to have high activity, attrition resistance, excellent hydrodynamic properties and is readily separated from the hydrocarbon products. The plant is reported to operate in a turbulent mixing regime that is associated with commercial sized moving bed reactors. After several thousand hours of operation under widely varying conditions, there

was no evidence of significant attrition within the unit while catalyst life and activity maintenance met or exceeded expectations.

A recent patent application describes a Syntroleum liquid-phase system that utilizes a fixed catalyst bed (91). To accomplish this, they employ a catalyst that has a voidage ratio greater than approximately 0.45 or 0.6; in another version of this they utilize a catalyst with a voidage ratio greater than 0.4 and a catalyst concentration in the reactor volume of at least 10%. The catalyst is to have a productivity of 200-4000 vol CO/volume catalyst/hour or greater during at least a 600 hour run. In one version, a saturator precedes the reactor to generate a syngas saturated liquid which is used as the feed to the fixed-bed liquid-phase reactor. Another version utilizes a reactor consisting of tubes in a shell that receives the liquid feed that is saturated with syngas. In another version, the reactor may consist of any version from a single vessel with a length/diameter (L/D) greater than 5 to a shell in a tube vessel with a high L/D that receives liquid and syngas feed streams. In another version, the single vessel reactor is filled with a fixed catalyst bed submerged in a liquid and the feed is only syngas. Another reactor resembles the Dortflund type reactor with a series of fixed catalyst beds within a reactor shell, with each reactor bed having the capability of receiving fresh liquid and syngas feed or not, as desired for the operation (Figure 36). In another version the reactor is essentially the same as in a bubble column reactor except that a fixed catalyst bed is utilized.

Rentech

Rentech reports that they have operated during 1982-1983 a commercial-scale gas to liquids facility. This facility utilized a Pueblo, Colorado landfill to produce gas sufficient for a plant with a capacity of about 235 bbl/day of liquid hydrocarbons. This plant has a capacity that is about the same as the reactor for the demonstration plant that Exxon operated at Baton Rouge,

LA. It was soon learned that the landfill was unable to produce sufficient amounts of gas and the operation was discontinued within three months after attainment of full-scale production.

Rentech has at least nine patents to cover their technology. The bodies of most of these patents are either the same or very similar and provides a concise summary of Fischer-Tropsch synthesis that can serve as an excellent introduction for the novice in this area. The claims are more modest in coverage than the body of the patents. Furthermore, it is sometimes difficult to discern when the cited examples are based on theoretical calculations and when they are based upon data obtained by Rentech.

Rentech has operated a 6 inch (0.15 m) diameter, 8 foot (2.54 m) tall slurry reactor with an iron catalyst. They report that they have designed, built and tested two 6-foot (1.83 m) diameter slurry reactors and have produced catalysts batches of more than 7.5 tons (6810 kg) for use in these reactors (92). The wax/slurry separation, as reported in 1992, was accomplished using an external cross-flow filter. Using this technique, separation was still a problem. They apparently utilized later in their pilot plant studies an external separator that involved gravity settling to concentrate a catalyst/wax slurry for return to the bottom of the reactor; this approach was apparently very similar in design to the one Mobil Oil utilized in the work they conducted for their DOE contracts.

U.S. DOE - La Porte

Air Products operated DOE's Alternative Fuels Development Unit, located in LaPorte, Texas. The unit was initially designed to conduct methanol synthesis in the slurry phase and was later expanded to include development work in FTS liquid-phase operations starting in 1992. The methanol synthesis work was very successful and resulted in a commercial operation (reactor 7.5 ft (2.3 m) diameter and 70 ft (21.3 m) tall) at Tennessee Eastman in Kingsport, Tennessee and the initial commercial scale has now been expanded in size.

Four runs for FTS have been described to date (93). The bubble column reactor is 22.5 inch (0.57 m) and 28.3 feet (8.6 m) top to bottom. The actual slurry space is 20 feet (6.2 m) with the remainder serving as a space for vapor disengagement. One inch (2.54 cm) cooling tubes occupy less than 5% of the reactor cross-section (Figure 37). The first two runs utilized iron catalysts: for Run I a high alpha catalyst was used and slurry/wax separation was a problem (94,95) and for Run II a low alpha catalyst was used (96). Apart from the separations problem, Run I was successful. For Run II, the initial activation was attempted with a 44 wt.% catalyst concentration and the run had to be aborted due to slurry thickening due to carbon formation and particle agglomeration . The second portion of Run II utilized 29 wt.% catalyst concentration and both the activation and synthesis periods followed closely the results from work in a CSTR that were conducted at our lab.

Shell runs at LaPorte. Run III utilized Shell's proprietary catalyst and wax to make a slurry that contained 41.2 wt.% cobalt-based catalyst. During the run a number of operating conditions were to be tested: H_2/CO ratio of 1.18 to 2.07, inlet superficial gas velocity from 0.31 to 0.73 ft/sec (9.5 to 22.3 cm/sec), CO conversion of 80 to 90%, temperature from 210 to 250°C, and pressure from 520 to 710 psig (3.6 to 4.9 MPa). Recycle was utilized to obtain the high total CO conversion levels. During run III a productivity of 126 g hydrocarbon/hr-liter slurry was obtained. Poor catalyst integrity caused slurry thickening and mass transfer limitations. Catalyst break-down limited the operational time for Run II. Run IV was a repeat of run III but with a new catalyst formulation and a proprietary filtration system. Run IV was accomplished successfully and covered the period of time scheduled. It appears that the products were lighter than normally expected for a cobalt catalyst; methane was in the range of 20 wt% of the products and the alpha value was in the 0.85-0.89 range. Using the planned operational conditions, we have estimated the productivity for the run. Assuming a slurry density of 2 g/cm³ and the reactor

productivity of 150 g hydrocarbon/L reactor volume/hr, we calculate a productivity of 0.18 g hydrocarbon/g catalyst/hr. The same productivity with a 29 wt.% catalyst slurry would provide a productivity of 0.27 g hydrocarbon/g cat/hr. Assuming that the 29 wt.% slurry has a density of only 1 g/cm³, the productivity would be 0.54 g hydrocarbon/g cat/hr.

Products

Low Temperature vs High Temperature

The product distribution reported by Kölbel was typical of high temperature (low alpha) operation: C₁₋₂:C₃₋₄:gasoline (25-190°C):diesel oil (190-310°C):heavies (>310°C) = 7:17:62:10:3 (97). The olefin content of the C₂₋₄, gasoline and diesel fractions were 72, 74, and 45%, respectively. Kölbel reported in less detail on runs made to produce "medium" and "high" molecular weight products in addition to the ones described above. These products are shown in Table 6. As noted, the production of hydrocarbons per m³ gas increases as the molecular weight of the products increases; however, in no instance does it approach the theoretical yield of 208 g/m³. [The theoretical yield is calculated on the basis that all carbon added as CO is converted to hydrocarbons except for the minimum amount of CO that must be shifted by the water-gas shift reaction to produce sufficient hydrogen to augment that of the feed to satisfy the stoichiometry of the synthesis equation.] On the other hand, Mobil runs consistently produced greater than 200 g/m³. This low hydrocarbon productivity in Kölbel's work is apparently a problem that many investigators have struggled with.

The quality of a diesel fuel can vary considerably. Cetane number is used as one measure of the quality of a diesel fuel much in the same manner as octane number is used for gasoline. However, octane number and cetane may be viewed as opposites. Thus, highly branched paraffins, olefins and aromatics are desirable, and normal paraffins undesirable, components of a fuel if one wants a high octane number; on the other hand, n-paraffins are desirable and highly

branched paraffins, olefins and aromatics are undesirable components for diesel fuel with a high cetane number. In viewing the high molecular weight product slate in Table 6, it is noted that 33% of the product is diesel and 50% is heavier molecular weight material that must ultimately be cracked to produce gasoline and diesel. As produced with an iron catalyst, the diesel fraction of the products (straight-run diesel) contains a significant amount of olefins, and consequently a relatively low cetane number. However, when this fraction is hydrogenated it will contain predominantly (90% or greater) n-paraffins, and this fraction will have a high cetane number (at or greater than 70). Because there is little difference in the ratio of i-/n-paraffin fraction of the hydrogenated straight-run diesel from an iron catalyst and the straight-run diesel from a cobalt catalyst, the straight run diesel produced by either catalyst will be the same, or very similar. Furthermore, it requires the same amount of hydrogen to produce a paraffin irrespective of whether it is produced indirectly by hydrogenating an initially formed olefin produced by iron catalysis or produced directly using a cobalt catalyst. Based upon straight-run diesel, there should therefore be no difference in the quality of the materials produced using either catalyst. Likewise, the >450°C fraction of the iron and cobalt catalyst is composed essentially of n-paraffins, either before or following a hydrogenation step, so that, while the quality of the diesel fuel produced by hydrocracking may depend upon the hydrocracking process utilized, it should not depend upon whether the >450°C fraction is obtained by iron or cobalt catalysis.

It cannot be overemphasized that diesel is not a sufficient specification to use to compare catalysts and/or processes. Straight-run diesel and diesel obtained from hydrocracking will not, in general, have the same properties even when both are composed only of paraffins. The major reason for this is that hydrocracking normally produces a significant fraction of monobranched paraffins; in fact, the classical bifunctional hydrocracking mechanism would produce an i-/n-paraffin ratio of 1 or even greater. Thus, it is important, when discussing cetane number, to

specify whether one refers to what is straight-run diesel, diesel produced by hydrocracking or some blend of these two products. For blending with petroleum-derived diesel to produce a more environmentally friendly transportation fuel, it is desirable that the F.-T. product have the highest possible cetane number. From the point of view of obtaining a superior diesel for blending with petroleum-derived diesel, it appears that straight-run F.-T. diesel would be preferred over hydrocracked diesel when the decision is based on cetane number.

In considering the medium and high molecular weight cases shown above, an equal amount of blended diesel would be produced by combining the straight-run and hydrocracked diesel fraction only if the hydrocracking selectivity was such that it produced only 32 % diesel fraction. The selectivity for hydrocracking is much greater than 32% so that it is obvious that more diesel will be produced from the "high" operation in Table 6. However, for a run at La Porte to generate diesel to make a large-scale test, both straight-run and hydrocracked diesel could be produced using either the medium or high molecular weight mode of operation. For the medium molecular weight case the straight-run fraction would dominate over the hydrocracked diesel whereas the opposite would result from the high molecular weight mode of operation.

Wax/Slurry Separation

In general, there are two approaches to this task: in-reactor separators that retain the slurry while allowing clean wax to pass and external separators where slurry is removed from the reactor and separation is effected in an external separator. Both of these approaches were utilized by Kölbel in his work in the 1950s.

Wax/slurry separation is not needed for fluid bed reactor operation since wax cannot form without causing agglomeration of the catalyst with loss of fluidization. Robust iron catalysts have been formulated for operation in fluid beds and are in commercial operation at Sasol. Presumably supported cobalt catalysts could be operated in this reactor type since fluid

catalytic cracking catalysts have been formulated with the necessary robustness and some form of these materials could be utilized as support for cobalt catalysts (98).

Separation of wax from supported cobalt catalysts is much easier than for an unsupported iron catalyst. A major reason for this is that the support material (alumina, silica, titania, etc) can usually be prepared so that it has the attrition resistance that is required for operation in a fixed or slurry bubble column reactor. While there were problems with one supported cobalt catalyst during operations at the La Porte facility, an improved version of the catalyst could be separated successfully in an external separator that utilized a cross flow filter with slurry circulation using a pump (99). However, operating the same plant with spray dried iron catalyst, the filter became plugged within a few hours or days of operation (100).

Mobil utilized an external system in which slurry is circulated by density differences and the time in the separator is sufficient for the slurry to settle so that solids-rich and a nearly solids free zones are formed; the clean wax is removed from the solids free zone and the solids rich fraction is returned to the bottom of the column. A similar apparatus has been utilized by Rentech, at least in their smaller pilot plant. A number of external filtration systems as, for example, (101) have been patented.

While separation devices have been described in the body of several patents, fewer patents describe filtration devices within the reactor. Most of the patents that describe a reactor mention internal or external separation but usually do not provide details. Statoil patents (102,103) describe a vertical cylindrical filter element in the form of a fine meshed screen, although alternatives could be used, located inside the reactor within the slurry. In the examples, models are used for the separation rather than a working reactor. Sasol has described in some detail their operation in a large pilot plant with a slurry bubble column reactor using a separation

procedure, in one particular case, a spiral wound (candle) filter (104). An improved candle filter has also been described (105).

A process for the separation of a catalyst from FT slurry has been patented by US DOE (106). This process separates the catalyst from the wax product using a dense gas and/or liquid extraction in which the organic compounds in the wax are dissolved and carried away from the insoluble inorganic catalyst particles. This work utilized wax/slurry generated at the LaPorte facility and the separation work was conducted by Kerr-McGee Corp (107). The use of near-critical fluid extraction to remove wax product to provide a solids enriched stream to return to the reactor has also been studied and has shown promise (108). For the latter technique, the extraction would likely be effected at temperatures above the reactor temperature and how this impacts the catalyst remains to be determined.

In summary, the separation of wax from a supported cobalt catalyst slurry will be much easier than from an unsupported iron catalyst. The unsupported iron catalyst rapidly attrits to produce small (1-3 micron) particles (109) that blind the pore openings of the filter. It would therefore be desirable to develop a filter material that can handle the 1-3 micron sized particles without blinding.

In the British work at Greenwich, the catalyst, after "break-in," was 1-3 μm in size. A liquid slip-stream was withdrawn continuously from the reactor and catalyst was recovered in a multiple-stage, gravity-settling apparatus. Because of the relatively rapid catalyst aging rates as well as significant coke formation, reliable data for wax/catalyst separation is not available from this work.

A finely divided powder catalyst was utilized by Kölbel and coworkers (45); the starting material has a particle size $<30\mu\text{m}$ but sizes during or after use are not provided. The liquid level in the reactor was maintained by a float-device. A slip-stream, utilized when excess liquid

was produced, allowed for wax/catalyst separation by pressure filtration. Kölbel operated most of the times under conditions where the liquid inventory of the reactor could be maintained **only by adding** heavier liquid products along with the synthesis gas and wax/catalyst separation was not a problem. As an alternative, wax/catalyst separation could be effected by centrifugation. Capability for replacement of the catalyst was included in the process although catalyst replacement rates are not given. Data are not available to enable one to reach valid conclusions about the effectiveness of the wax/catalyst separation because of the lack of knowledge of catalyst addition rates. Based on the data in Table 6 for the "low" operating conditions, an upper limit of 15% reactor-wax removal can be set, and in practice it should have been much lower.

Supercritical Phase Fischer-Tropsch Synthesis

While supercritical phase synthesis is not strictly a liquid phase synthesis, it approaches liquid phase when operating at higher densities. It is claimed that three main advantages of the supercritical synthesis are: (1) rapid diffusion of reactants, (2) effective removal of reaction heat and (3) effective extraction of wax, α -olefins and water. Thus, the supercritical operation could, if item 3 is accomplished, decrease or eliminate secondary reactions.

Yokota et al. (110) compared the results of the operation of three types of reactors: fixed-bed, liquid and supercritical. In order to make an effective comparison the feed consisted of 22-36 % synthesis gas with the remainder being diluent (nitrogen for the fixed-bed, hexadecane and nitrogen for the liquid, and n-hexane for the supercritical). An iron catalyst was utilized and had the following composition by wt. fraction: Fe, 83.5; Ca, 2.1; Al, 1.5; Si, 0.4; K, 0.5 or Fe, 99; Cu, 0.3; K, 0.3. Thus, both iron catalysts were of the low alpha type utilized by Mobil Oil and La Porte Run II. The total pressure was 5 MPa, 270°C, $H_2/CO = 1$ and $W/F (CO + H_2) = 10$ g-cat h/mol. Each run was conducted for 6 hours. Under no circumstances should it be considered that a steady-state operation was attained.

The authors show the CO conversion, CO₂ yield and chain-growth probabilities for the fixed-bed, supercritical and slurry phase reactors as 33.0, 30.2 and 27.9; 8.65, 7.52 and 9.15; and 0.84, 0.83 and 0.80, respectively. They considered these differences to be significant and attribute the lower CO₂ yield for the supercritical operation as being due to the increased removal of water from the reactor. The reported chain growth probabilities appear high for an iron catalyst that contains such a low level of potassium. These data may be viewed as suggestive.

Fujimoto et al. (111) report that the addition of a small amount of heavy 1-alkene in a supercritical-phase or liquid-phase F.-T. reaction medium greatly enhanced the selectivity of wax products, along with increased CO conversion and suppressed methane selectivity. A cobalt-silica catalyst that contained La was used. The authors reported that the addition of 1-tetradecene or 1-hexadecene significantly decreased the hydrocarbon production for carbon-number products lower than that of the added alkene, and increased significantly the production rate of the carbon-number products with higher carbon numbers than the added alkene (Figure 38). The data shown in Figure 38 are astounding. When alkenes were not added the production rate of the products above carbon number 15 decreased with increasing carbon number; this is expected and observed in normal F.-T. synthesis. However, when the alkene is added, the hydrocarbon production with carbon-numbers above that of the added alkene become essentially constant; i.e., independent of carbon number. It appears that this requires the added alkene to initiate chain growth that differs from that of the F.-T. reaction. If the only impact of the alkene was to initiate additional growing chains, the product distribution above the carbon number of the added alkene should be determined by the Anderson-Schulz-Flory distribution; i.e., the rate of production of all higher carbon-number products may increase but the products should still be produced in the same ratio as they were when no alkene was added. Thus, the amounts of higher carbon-number products may increase but the alpha value should be the same as when the alkene

was not added. The data obtained when 1-heptene, in contrast to 1-tetradecene or 1-hexadecene, was added is in better agreement with the expectation.

Lang et al. (112) utilized a precipitated iron catalyst in a fixed-bed reactor and found that the catalyst activity and lumped hydrocarbon product distribution under the supercritical conditions were similar to those obtained during reaction at the baseline (non-supercritical) conditions. This is in contrast to the views expressed above. Lang et al., (112) reported slightly higher selectivities for the 1-alkenes during supercritical operation (Figure 39). This suggests to them that the F.-T. reaction is not diffusionally limited under their reaction conditions. The higher alkene production during supercritical operation was due to higher diffusivities and desorption rates of the high molecular weight olefins relative to those under normal F.-T. conditions.

Summary

The major attention, both industrial and academic, during the past 10 years, has been given to the slurry bubble column reactor. The slurry phase methanol process has been developed and operated in a commercial setting (113-115). Deckwer has published a major treatise on bubble column reactors (116). Saxena (117) has recently reviewed the use of bubble column reactors in FTS. The reader is referred to these for description of reactor details.

Two major types of slurry bubble column reactors are possible and these are illustrated in Figure 40 (77,118). The reactor containing cooling coils immersed in the slurry is the one that is most frequently encountered (77,78,92,105,118-123). The concept of one type of reactor patented by Exxon has many similarities to the Arge fixed bed reactor except the fixed catalyst bed has been replaced with a slurry catalyst; both utilize the “tube-in-a-shell” reactor concept (77).

As with the three-phase slurry reactor in other applications, the distributor plate is treated as a proprietary topic. Kölbel contends that when the bubble column reactor is operated in the proper gas flow range the bubbles within the reactor will be in dynamic equilibrium with the formation of larger bubbles and their spontaneous break-up.

For modeling, the bubbles within the slurry are usually considered to have a spherical shape, their size distribution taken as some average size, and their breakup and reformation are neglected. The work conducted at Ohio State show that the bubbles are clearly not spherical but are as shown in Figure 41 (124). The influence of elevated pressure and temperature on the shape and rise velocity of a single bubble in a liquid-solid suspension has been investigated in a unique experimental setup (e.g., 125). For very low flows (gas velocity of 0.01 m/s) it is possible to have a reasonably uniform distribution of small (less than 5 mm) bubbles that rise vertically (126) and can be modeled as plug flow. However, to operate in the small bubble, plug flow regime DeSwart et al. (126) calculates that it would require seventeen (17) 11 m diameter reactors to produce the same amount of product as could be produced in four 7.5 m diameter reactors that operate in the churn turbulent slurry regime.

It is found that the bubble rise velocity decreases with increasing pressure and with decreasing temperature. This is mainly due to the changes in the densities of the gas and the liquid velocity. Not only do the bubbles have a shape like a comet with a tail of smaller bubbles, they also do not rise straight to the vertical but exhibit a corkscrew path to the top of the reactor, leaving regions rich in bubbles and regions with a lower concentration (Figure 42) (127). The bubble shape is frequently modeled with variable aspect ratios as cross sections of ellipsoids (128). A representative status of the activities in this research area may be obtained from recent references (124,129-140).

The US DOE has a major effort to understand the many variables affecting the performance of a bubble column reactor. Dudukovic and Toseland (141) outlined the cooperative study by Air Products & Chemicals (APC), Ohio State University (OSU), Sandia National Laboratory (SNL) and Washington University (WU); this program is outlined in Figure 43. The efforts of this group have developed valuable unique experimental techniques for the measurement of gas holdup, velocity and eddy diffusivities in bubble columns. They have obtained data that allows improved insight in churn-turbulent flow and have assessed the impact of various effects (internals, solids concentration, high gas velocity, pressure, etc.). General ideal flow pattern based models do not reflect bubble column reality; to date the models are based on a combination where some parameters are evaluated from first principles and some from the data base.

It has been observed that the time-dependent flow behavior in a cylindrical column is chaotic and not predictable. However, some periodic structures may be detected in the velocity time series in the axial and tangential direction the may lead to some kind of periodicity (142). It has been reported that the transition from the homogeneous to the heterogeneous flow regime in bubble columns can be quantitatively found with high accuracy by analyzing the chaotic characteristics of the pressure fluctuation signal. A distinctive feature of the pressure signal from bubble columns is that it is composed of two different parts: a low frequency part resulting from the motion of the large bubbles and a high frequency part resulting from all other processes (coalescence, collapse, breakup, etc) (143). Delnoij (144) conducted an extensive study and concluded that their computed flow structures resembled the experimentally observed patterns although the time-dependent behavior predicted by the model differed from that observed in their bubble column.

The extensive theoretical and experimental data for bubble column reactors has been applied to situations that are applicable to FTS. Inga and Morsi (86,145) have constructed a 0.3 m diameter, 2.8 m tall slurry bubble column reactor and have operated this in the churn-turbulent regime with catalyst concentrations up to 50 wt.% and pressures to 8 bars. The impact of gas velocity, pressure and catalyst concentration on gas holdup (V_G) has been determined and it was found that under given operating conditions, the gas bubbles can be classified into “small” and “large” bubbles (86,145). The “large” bubbles exhibit plug flow behavior but the “small” bubbles recirculated with the liquid. The gas holdup, (V_G), increases with superficial gas velocity and pressure and decreases with catalyst concentration. At high catalyst loading, coalescence of gas bubbles increased, reducing the number of small bubbles, and the gas interfacial area. The gas/liquid mass transfer coefficient ($k_L a$) values follow the trends of the gas/liquid interfacial area (146).

Van der Laan (147) reported attempts to model FT in a bubble column reactor. His model exhibits well mixed liquid and two gas bubble regimes: small bubbles that are well mixed and large bubbles that exhibit plug flow behavior (Figure 44). Van der Laan also provides a summary of bubble column reactor models that others have utilized (Tables 7 and 8). He concluded that the FT SBCR is reaction controlled due to the low activity of the iron catalyst and the volumetric mass transfer coefficient of the large bubbles due to frequent bubble coalescence and breakup.

Groups are now beginning to apply multicomponent reaction engineering models for FTS in bubble column reactors. Recent examples can be found in the references (147-149). Van der Laan (147) provides the following summary of slurry bubble column reactors:

“A number of patents deal with modifications of Fischer-Tropsch slurry bubble column reactors to reduce the back-mixing of both the liquid and the gas phase

(124,150-152) described the influence of various degrees of back-mixing on the selectivity and productivity based on kinetic data obtained over a Co/TiO₂ catalyst, both in plug flow (fixed bed), bubble column and completely mixed reactors (CSTR). Arcuri (150) claimed that the productivity in a slurry bubble column is equal to or greater than for plug flow, and the same selectivity is obtained for the completely mixed system. Koros (151) reported the invention of a slurry bubble column multi-tubular slurry bubble column reactor with cooling medium around the tubes. The example presented shows a reaction tube of 0.15 m mounted inside a 0.30 m pipe that served as a cooling jacket. According to our opinion, this reactor configuration has several disadvantages: (1) possibility of slug flow conditions, 2) large gas holdup due to the influence of the column diameter on the large gas bubble holdup (152), 3) possibility of maldistribution of the gas, the liquid and the catalyst phases, and 4) low specific cooling area relative to, for example, 1.5 inch cooling tubes. A better option is staging the slurry bubble column horizontally as proposed earlier by Graaf (153) for slurry phase methanol synthesis. Maretto and Piccolo (154) reported the effect of staging a slurry bubble column. The temperature in each stage could be controlled separately. Their model assumed plug flow of the gas phase and complete mixing of the slurry in each stage. Maretto and Piccolo (154) claimed that the liquid phase in the multistage reactor may approach plug flow behavior, resulting in an increase of the synthesis gas conversion with increasing the number of stages. Our model can easily be extended to incorporate the effect of staging of a slurry bubble column. In addition to the study of Maretto and Piccolo (154), extension of the model presented will also predict the effect of staging on

the product selectivity. Maretto and Piccolo (154) did not report on the engineering details of staging bubble columns. One of the possibilities would be the application of horizontal gauzes or perforated plates (155,156). These plates decrease the bubble size of large gas bubbles and slugs which results in a higher gas holdup and improvement of the plug flow characteristics of the gas and liquid phase.”

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Table 1				
Flexibility of Product Composition by Liquid Phase Synthesis (data from ref. 40).				
Synthesis based on molecular size	Low	Low	Medium	High
Hydrocarbon Product - C ₃ + (g/m ³ CO+H ₂)	162	166	175	182
	Wt.%	Wt.%	Wt.%	Wt.%
C ₃ + C ₄	29.6	18.1	6.9	2.2
C ₅ + to 190°C (C ₅ to C ₉)	63.0	68.0	40.0	7.1
190-310°C (C ₉ to C ₁₇)	6.2	10.9	25.7	8.3
320-450°C (C ₁₇ to C ₃₁)	1.2	2.4	18.3	33.0
> 450°C (C ₃₁ +))	-	0.6	9.1	49.4
Alpha values	$\alpha_1, 0.68$	$\alpha_1, 0.68$	$\alpha_1, 0.69$ $\alpha_2, 0.92$	$\alpha_1, 0.40$ $\alpha_2, 0.95$
Fraction of product from α_2	---	---	0.17	0.50
1. Calculated by author from data above. 2. Calculated by author assuming two alpha distribution with α_2 representing the higher carbon number products.				

Table 2		
Operating Data and Results of Liquid-Phase Synthesis for One-Step Operation with a Single Passage of the Gas Over Iron Catalysts (from ref. 45)		
	Demonstration Plant (a)	Laboratory Plant (b)
Effective reaction space (volume suspension including dispersed gas) (L)	10,000	6
Catalyst (kg Fe)	800	0.4
Synthesis gas pressure (bar)	12	11
Synthesis gas (volume ratio, CO:H ₂)	1.5	1.5
Quantity of synthesis gas (Nm ³ /hr)	2,700	1.3
Linear velocity of the compressed gases at operating temperature referred to the free reactor cross section (cm/sec)	9.5	3.5
Total CO + H ₂ used (Nm ³ /hr)	2,300	1.1
Per m ³ of reaction chamber (Nm ³ /hr)	230	183
Per kg of Fe (Nm ³ /hr)	2.6	2.45
Average synthesis temperature, °C	268	266
CO conversion, %	91	90
CO + H ₂ conversion, %	89	88
Synthesis products referred to CO + H ₂ used:		
Hydrocarbons C ₁ ⁺ (g/Nm ³)	178	176
C ₁ ⁺ + C ₃ (g/Nm ³)	12	11
C ₃ ⁺ (g/Nm ³)	166	165
O-containing products in the synthesis water (g/Nm ³)	3	2
Space-time yield of C ₃ ⁺ products including O-products in 24 hr (kg/m ³ of reaction chamber)	930	740

Table 3		
Effect of heating rejuvenation tubes on catalyst activation (from ref. 81).		
Heat addition	no	Yes
Gas rate in tube, scfh	5100	4800
Avg reactor temp, °F	427	427
Avg rejuvenation temp, °F	430	440
CO conv, start to end of run, %	32 to 26 (over 12 hrs)	26 to 36 (over 24 hrs)
Conv, change/day	-12.4	+10.4

Table 4

Improvement in Catalyst/wax Separation in Slurry FT Processes by Removal of Catalyst Fines (from ref. 83)

Classification Solvent	Catalyst/solvent wt/wt	Other	Cycles	Acetone cycles	Filter time	Filter rate	
						(gm/min)	gal/ft ² /min
0.45 μm Millipore filter paper							
Blank	-	-	-	-	95.0	0.5	
Water	15/85	-	6	2	0.9	55.0	
i-C ₃ H ₆ OH/n-C ₇ H ₁₆ (1/9)	10/150	1% Oleic acid added	7	2	1.0	50.0	
i-C ₃ H ₆ OH/n-C ₇ H ₁₆ (1/9)	10/150	1% Aerosol OT-100 added	7	2	1.0	50.0	
0.3 μm glass fiber filter							
FT wax @ 130°C	2/98	Stirred 5 min	none	none	-	-	5.8 @ 14 psig
		Stirred 44 hrs	none	none	-	-	0.05 @ 14 psig
FT wax @ 120°C	2/98	Stirring per cycle 19/48/24	3	none	-	-	14.5 @ 14 psig

Table 5					
Conversion Data for Syngas Conversion Using Fixed-Bed and Slurry Reactors (from ref. 86)					
Test Number	1	2	3	4	5
Reactor Type	fixed-bed	slurry	slurry	slurry	slurry
Temperature, °C	215	225	230	235	240
CO Conversion rate (ccCO/g/h)	215	649	808	992	1210
CO Conversion, %	45.3	8.4	10.4	12.8	15.6
Product Yields, Methane, wt. %	26.6	10.5	11.5	12.5	14.0
C ₅ -C ₂₀ (mg/g/h)	67	325	400	478	560
C ₅ +, wt. %	60.0	79.0	78.0	76.0	73.0

Table 6			
Variations in Product Composition from the Kölbel Reactor (data from ref. 40)			
Molecular Weight Goal	"Low"	"Medium"	"High"
Single-pass C_3^+ product yield (g/m ³ feed) ^a	166	175	182
Distribution of C_3^+ products (%)			
C_{3-4}	18	7	2
Gasoline (C_5 -190°C)	68	40	7
Diesel fuel (190-310°C)	11	26	8
310-450°C	2.5	18	33
> 450°C	0.5	9	50

Table 7							
Comparison of Reaction Engineering Models for the Fischer-Tropsch Synthesis in Slurry Bubble Column Reactors (from ref. 146)							
Reference	Gas Phase	Liquid Phase	Catalyst Distribution	Energy Balance	Components	FT (Table 8)	WGS
Calderbank, et al.	PF	PF	uniform	isothermal	H ₂	1	---
Satterfield, et al.	PF	PM	uniform	isothermal	H ₂	1	---
Deckwer, et al.	PF	PM	uniform	isothermal	H ₂	1	---
Deckwer, et al.	AD	AD	non-uniform	non-isothermal	H ₂	1	---
Bukur	PF	PF,PM	uniform	isothermal	H ₂	1	---
Stern, et al.	PF	PM	uniform	isothermal	H ₂ ,CO,CO ₂ ,H ₂ O	1	---
Kuo	PF	PM,PF,AD	non-uniform	isothermal	C ₅ ,H ₁₀	1	---
Kuo	PF	PF	non-uniform	isothermal	H ₂	2	2
Stenger, et al.	AD	AD	non-uniform	isothermal	H ₂ ,CO,CO ₂ ,H ₂ O,C ₁₋₃	1	1
Prakash, et al.	AD	AD	non-uniform	isothermal	H ₂ ,CO,CO ₂ ,H ₂ O,C ₁₋₃	2	2
Prakash	AD	AD	non-uniform	isothermal		2	2
DeSwart ¹	AD	AD	non-uniform	non-isothermal	H ₂	1	---
DeSwart ²	PF	PM	uniform	isothermal	H ₂	1	---
Mills, et al.	AD	AD	non-uniform	non-isothermal	H ₂	1	---
Inga, et al.	PF	MC	uniform	isothermal	H ₂ ,CO,H ₂ O	1,3	2
Krishna, et al. ²	PF	PM	uniform	isothermal	H ₂ ,CO	3	---
Our Model	PF	PM	uniform	isothermal	H ₂ ,CO,CO ₂ ,H ₂ O,N ₂ ,C ₁₋₁₀₀		
PF: plug flow; PM: perfectly mixed; MC: mixing cells, AD: axial dispersion. 1 Heterogeneous flow regime: large bubbles: PF, small bubbles and liquid: AD. 2 Heterogeneous flow regime: large bubbles: PF, small bubbles and liquid: PM.							

Table 8	
Kinetic Models for Table 7 (from ref. 146)	
FT Kinetic Expressions	WGS Kinetic Expressions
1 $kC_{H_2,L}$	1 $k(C_{CO,L}C_{H_2O,L} - C_{CO_2,L}C_{H_2O,L}/K_p)$
2 $\frac{k_{C_{H_2,L}}C_{CO,L}}{C_{CO,L} + aC_{H_2O}}$	2 $\frac{k(C_{CO,L}C_{H_2O,L} - C_{CO_2,L}C_{H_2O,L}/K_p)}{P_{CO} + aP_{H_2O}}$
3 $\frac{k_{C_{H_2,L}}C_{CO,L}}{(1 + aC_{CO,L})^2}$	

Figure 1. Possible reactors for Fischer-Tropsch synthesis. (a) slurry bubble column reactor, (b) multitubular trickle bed reactor, (c) circulating - and, (d) fluidized-bed reactor.

Figure 2. Slurry phase catalytic reactor for FTS (from ref. 17).

Figure 3. Tubular stirred autoclave with silver cladding (from ref. 18).

Figure 4. Schematic of the FTS reactor unit for the foam process (from ref. 28).

Figure 5. I. G. Farben fixed bed FTS reactor with oil sprayer for cooling (from ref. 35).

Figure 6. Schematic reactor fitted with catalyst trays for the preparation of hydrocarbons from synthesis gas in slurry reactor (from ref. 36).

Figure 7. Schematic of slurry reactor tube subdivided into cells to modify liquid flow patterns (from ref. 30).

Figure 8. Liquid phase synthesis apparatus (from ref. 34).

Figure 9. Schematic of oil recirculation within slurry reactor (Figures 1 and 2 of Figure 9) and the elimination of recirculation by adding shafts (tubes) (Figure 3) (from ref. 43).

Figure 10. Schematic of slurry reactor with shafts (open at top and bottom) to subdivide reactor shell to establish reactor zone with stationary catalyst and liquid condition (from ref. 44).

Figure 11. Reactor wax yield versus methane yield with data from ref. 45 and 49 (redrawn by author).

Figure 12. Reactor fitted with catalyst trays, each containing bubble caps, to effect slurry phase synthesis of hydrocarbons (from ref. 52).

Figure 13. Schematic of bubble caps and gas transport columns for trays in reactor shown in Figure 12 (from ref. 52).

Figure 14. Schematic of slurry reactor with capability of adding preheated liquid as several levels within the reactor (from ref. 31).

Figure 15. Schematic of slurry reactor with recycle of oil to the reactor (from ref. 31).

Figure 16. Synthesis reactor at Bureau of Mines, Louisiana, Missouri plan (from ref. 59).

Figure 17. Method of effecting catalytic reactions (from ref. 64).

Figure 18. Method for synthesizing hydrocarbons and the like (from ref. 66).

Figure 19. Catalytic reactor for liquid-phase synthesis (from ref. 67).

Figure 20. Cross sectional views of reactor in Figure 19 (from ref. 67).

Figure 21. Catalyst concentration versus reactor height for (!) no downcomer and for one 3" downcomer (Q) (from ref. 74).

Figure 22. Schematic of reactor for enhanced gas separation for bubble column draft tubes (from ref. 75).

Figure 23. Relative volumetric productivity represented by activity with days on stream with intervals of hydrogen rejuvenation (12 wt.% Co on titania with 6 wt.% Al_2O_3 as binder (from ref. 81).

Figure 24. Catalyst concentration versus elevation in the reactor with (Q) and without (F) use of draft tubes (from ref. 74).

Figure 25. Conversion using hydrogenation rejuvenation (to day 3 no rejuvenation; rejuvenation after day 3) (from ref. 82).

Figure 26. Schematic of multiple vessels for catalyst rejuvenation (from ref. 83).

Figure 27. Elevation of a shell and tube reactor arrangement showing the gas, liquid, catalyst interconnection both above and below the upper and lower tube sheets (from ref. 77).

Figure 28. Horizontal Section A - A through the elevation of Figure 29 showing a possible arrangement of tubes, that is, reaction zones (from ref. 77).

Figure 29. Detail of a possible distribution zone for one reaction tube/zone (from ref. 77).

Figure 30. Simplified flow diagram of the Mobil Oil two-stage plant for synthesis gas conversion (from ref. 48).

Figure 31. Schematic diagram of the continuous settling system for catalyst/wax separation (from ref. 48).

Figure 32. Schulz-Flory distribution for the first stage Fischer-Tropsch products obtained by Mobil Oil at a reactor wax yield of 46 wt.% (from ref. 49).

Figure 33. Schulz-Flory distribution based on Mobil Oil data at low, intermediate and high alpha synthesis conditions (from ref. 85).

Figure 34. Process schematic for slurry reactor system using cobalt catalyst (from ref. 87).

Figure 35. CO conversion and C₅+ product selectivity for FTS using slurry reactor and cobalt catalyst (data from ref. 87).

27.10 REACTOR

Maximum Pressure 1000 psig
Maximum Temperature 315°C
Typical Catalyst Load 900 lbs
Maximum Inlet Velocity 0.75 ft/sec

Figure 37. Bubble column reactor (27.10) at La Porte (from ref. 93).

Figure 38. Product distribution in the olefin-added supercritical phase FT reaction with a cobalt catalyst: (F) no olefin added; (Δ) 1-tetradecene added; (G) 1-hexadecene added (from ref. 111).

Figure 39. Effect of supercritical FT synthesis on α -olefin (a) and 2-olefin (b) selectivity using an iron catalyst (from ref. 112).

Figure 40. (left) Schematic of Exxon slurry phase reactor (ref. 77); (right) schematic of Sasol slurry bubble column reactor (ref. 118).

Figure 41. Typical particle trajectories within three different flow regions around a rising bubble (ref. 124).

Figure 42. Model of flow scheme in the slurry bubble column (from ref. 127).

Figure 43. SBC phenomena under investigation (ref. 141).

Figure 44. Hydrodynamic model of slurry bubble column reactor in the heterogeneous flow regime (ref. 147).

J. Slurry Bubble Activities

Executive Summary

A Slurry Bubble Column Reactor (SBCR) is a gas-liquid-solid reactor in which the finely divided solid catalyst is suspended in the liquid by rising gas bubbles. The synthesis gas flows in a bubble phase through the catalyst/wax suspension. A gas distributor located in the bottom of the reactor produces the bubbles that rise inside the reactor. The volatile products are removed over together with unconverted gases, and the liquid products are separated from the catalyst suspension through a filter.

A considerable interest has been expressed in using SBCRs to carry out Fischer-Tropsch Synthesis (FTS), particularly for the conversion of stranded natural gas into liquids. Historically, wall effects in small-scale SBCR reactors (diameters less than 30 cm) have presented many challenges with regard to interpretation of kinetic/conversion data for process scale-up. In this paper, we describe a novel 5-cm diameter SBCR system that incorporates a natural slurry recirculation loop that minimizes wall effects and promotes plug-flow behavior in the liquid phase. Conversion performance, catalyst activity decline, and attrition of a precipitated Fe/K FTS catalyst in the improved SBCR is compared to that of a CSTR run using the same catalyst and operating conditions.

Slurry back-mixing in the improved SBCR was significantly reduced by the addition of the down-comer/dip-tube flow path; consequently, the gas and liquid phases likely exhibited more plug-flow behavior. Thus, for a given space velocity, the enhanced SBCR yielded a higher conversion than that of the CSTR. The activity decline measured in the revamped SBCR system was shown to be similar to that of the CSTR experiments. Attrition tests in the SBCR system indicated that the most of the catalyst breakdown occurred between the time period of loading and activation; however, further research will be required to investigate the possibility of particle

size classification/segregation at the sampling points. After activation, the catalyst particle mean diameter decreased in an exponential decay fashion.

Introduction

The Prototype Integrated Process Unit (PIPU) is a pilot plant system built in the early 1980s at the University of Kentucky for studying a multitude of synthetic fuel/chemical processes. Recently, a direct coal liquefaction reactor within the PIPU plant was reconfigured as a SBCR for FTS studies (see Figure 1.). The reactor was originally designed to operate with coarse catalyst pellets ($>500\text{ }\mu\text{m}$). Consequently, the reactor system did not contain a wax separation system sufficient for smaller catalyst particles that are typically used in FTS. Therefore, a slurry accumulator and a batch wax filtration system were installed.

Early attempts to operate the pilot-scale reactor in a F-T mode were successful in that a clear wax product could be obtained. However, the initial activity observed in the bubble column was about 10-15% less than that of comparable CSTR runs. Also, the rate of conversion decline (and apparent catalyst deactivation) in the SBCR was much greater than that observed in the CSTR. It was hypothesized that the apparent increased deactivation rate in the SBCR was caused by the depletion of catalyst inventory due to the nature of the wax/catalyst separation system.

The CAER SBCR plant was overhauled and redesigned to incorporate automatic slurry level control and wax filtration systems. These design changes allowed for a more constant inventory of the catalyst to be maintained in the reactor while reducing slurry hold-up in the catalyst/wax separation system. In addition, the wax filtration system was rearranged to accept a variety of filter elements. These additions were meant to enhance the stability of the reactor operation so that long-term tests can be conducted to study catalyst deactivation and attrition under real-world conditions.

In the following discussion, we will detail the results and operational experiences of a catalyst attrition test with the enhanced SBCR system. Objectives of the study were to: Compare the performance of a precipitated Fe/K Fischer Tropsch Synthesis (FTS) catalyst in the enhanced SBCR and a continuous stirred tank reactor (CSTR); and Determine change of the catalyst distribution within the reactor system due to particle attrition effects.

Experimental

All FTS runs were conducted in either CSTR or SBCR systems. Activation and synthesis conditions for both reactor configurations are listed in Table 1. A precipitated iron catalyst having atomic composition of 100 Fe/4.4 Si/1K was used for this series of experiments.

Table 1. Operating Conditions for SBCR and CSTR Comparison Experiments.

	SBCR	CSTR
H ₂ /CO Ratio	0.7	0.7
Gas Space Velocity (SL/hr-g Fe)	5.0	5.15
Temperature (°C)	270	270
Pressure (Mpa)	1.21	1.21
Gas Superficial Velocity (cm/s)	3	750 RPM

CSTR Apparatus. The one-liter CSTR used in this study has been described in detail in the literature [1-2]. The following is a brief description of the reactor system.

The synthesis gas was delivered to the catalyst slurry via a sparger tube located below an impeller blade turning at 750 rpm. The reactor effluent exited the reactor and passed sequentially through two traps maintained at 333 and 273 K. Accumulated reactor wax was removed daily through a tube fitted with a porous metal filter. A dry flow meter was used to measure the exit gas flow rate.

SBCR Apparatus. A schematic of the SBCR apparatus is shown in Figure 1. In the current configuration, the bubble column has a 5.08 cm diameter and a 2 m height with an effective reactor volume of 3.7 liters. The synthesis gas was passed continuously through the

reactor and distributed by a sparger near the bottom of the reactor vessel. The product gas and slurry exit the top of the reactor and pass through an overhead receiver vessel where the slurry was disengaged from the gas-phase. Vapor products and unreacted syngas exit the overhead vessel, enter a warm trap (333 K) followed by a cold trap (273 K). A dry flow meter downstream of the cold trap was used to measure the exit gas flow rate.

A dip tube was added to the reactor vessel so that the F-T catalyst slurry could be recycled internally via a natural convection loop. The unreacted syngas, F-T products, and slurry exited into a side port near the top of the reactor vessel and entered a riser tube. The driving force for the recirculation flow was essentially the difference in density between the fluid column in the riser (slurry and gas) and that of the dip-tube (slurry only). The dip tube provided a downward flow path for the slurry without interfering with the upward flow of the turbulent syngas slurry mixture. Thus, to some degree, back mixing of the slurry phase and wall effects in the narrow reactor [3] tube were minimized.

Based upon the analysis of the initial SBCR pilot plant runs, several more design changes were carried out to the system to increase the conversion stability. An automatic level controller was added to the overhead slurry/gas separation tank. This insured a constant inventory of catalyst particles was being maintained in the reactor vessel if the superficial gas velocity within the column was constant.

Originally, the overhead separator vessel was designed to enhance settling of the catalyst particles. Thus, slurry to be filtered was extracted near the top of the vessel where the catalyst concentration would be lower than that near the bottom. Unfortunately, this approach required a large hold-up volume of slurry outside the reactor (greater than the reactor volume itself). Hold-up of slurry outside the reactor was lowered by decreasing the volume of the overhead vessel from 18 to 4 liters.

The sintered metal filter tube was moved to the liquid down comer below the overhead separation vessel. Currently, the filter is a flow-through device having a sintered metal tube in a shell. Filtered wax was extracted radially through the tube while slurry flows downward in the axial direction. The shear force of the axial slurry flow prevented excessive caking of the catalyst around the filter media. Filtered wax was metered into a storage tank through a let-down valve operated by the overhead liquid level controller. Pressure drop across the filter media can be varied manually by varying the wax storage tank pressure. The filter assembly was configured such that the filter media could be replaced on-line, without aborting or interrupting the reactor run.

The level or volume of the slurry within the receiver was continuously monitored by measuring the differential pressure across the height of the vessel. Argon was purged through each of the pressure legs to keep the lines free of slurry. Slurry volume within the receiver was controlled to be no more than 1.3 liters by removing wax from the reactor system via the level control valve. The unfiltered slurry flowed back to the reactor via a natural convection loop through a dip-tube exiting near the bottom of a reactor.

Samples of the unfiltered slurry were taken from the bottom of the reactor vessel and the overhead receiver tank on a daily basis. Wax products were Soxhlet extracted according to the method of McCartney [4]. The particle size distributions of the extracted catalyst particles were quantified using a light scattering technique by a Cilas 1064 liquid/particle analyzer.

Results and Discussion

SBCR Conversion Comparisons between CSTR and SBCR runs. One of the objectives of the run was to compare the performance of the enhanced SBCR with that of a CSTR configuration. It was anticipated that the modified SBCR system performance, in terms of catalyst deactivation, would be comparable to that of the CSTR experiments. The run/activation

conditions for the enhanced SBCR system along with the comparison SBCR and CSTR conditions are listed in Table 1.

The CO gas conversions versus time-on-stream for the SBCR and CSTR systems are displayed in Figure 2. The CO conversion for the enhanced SBCR with level control reached a maximum of 78% after 72 hours time-on-stream (TOS). After this catalyst initiation period, the gas conversion started to steadily decline to about 72% after 192 hours TOS.

Slurry back-mixing in the SBCR is significantly reduced by the addition of the down-comer/dip-tube flow path; consequently, the gas and liquid phases likely exhibited more Aplug-flow behavior. Thus, for a given space velocity, the enhanced SBCR should yield a higher conversion than that of a CSTR [5]. Differences in conversion between the enhanced SBCR and CSTR reactor types may also be caused by the dissimilarity of heat and mass transfer phenomena.

SBCR Catalyst Attrition. Heavy wax products must be separated from catalyst particles before being removed from the reactor system. Achieving an efficient wax product separation from the catalyst is one of the most challenging technical problems associated with slurry-phase F-T. The breakdown of the catalyst particles and the production of heavy wax using high alpha catalysts can further exasperate the filtration problem. Thus, designing a physically robust catalyst without compromising activity is an important factor for a stable and economical F-T process. However, small-scale catalyst attrition tests may not be adequate in simulating the environment within a bubble column reactor. In previous studies [6,7] by Jothimurgean and Zhao an air-jet attrition tester as outlined in the ASTM-D-5757-95 test method was used to compare the relative breakdown resistance of catalysts. This method is useful in comparing the relative strength between catalyst candidates; however, it does not yield information as to the rate of attrition during synthesis. Attrition data in CSTR systems are compromised by the

extreme impact and shear forces from the impeller blade on catalyst particles. In contrast, the SBCR unit does not utilize any mechanical pumping devices that could alter the size distribution of the catalyst. Consequently, SBCR particle attrition will depend mainly on chemical changes within particles and perhaps some particle/wall or particle/particle mechanical abrasion.

Figure 3 shows the changing distribution of catalyst concentration with TOS. During the start of activation, only a small fraction of catalyst fines were detected in the reactor effluent stream. However, near the bottom of the reactor the concentration of catalyst particles was greater than 25 wt%. This indicated the liquid recirculation rate was not sufficient to fully entrain the largest (>23 mm) catalyst particles. As the activation process was completed (TOS = 0), the slurry effluent contained about 5 wt% of catalyst fines. Thereafter, the solids concentration of the reactor effluent increased linearly with TOS.

The mean particle size of the reactor bottom and effluent streams are shown in Figure 4. The dotted horizontal line represents the initial mean particle size of the raw catalyst. Physical classification of the catalyst particles was apparent as evidenced by the mean particle size of slurry in the bottom being greater than that of the raw catalyst. As the synthesis progressed, the mean particle size in the reactor dropped below the baseline (23 mm) after only 40 hours TOS. In summary, the data shown in Figures 3 and 4 indicate that a significant portion of the catalyst exited the reactor system due to particle attrition after 40 hours of TOS. Considering the slurry hold-up outside the reactor was maintained at less than 1 liter, the percentage of catalyst lost after 40 hours TOS was less than 20 wt%. Therefore, this lost catalyst must be considered when calculating the space velocity.

Conclusions

Tight control of catalyst distribution within SBCRs should be maintained in order to quantify activity decline, especially for small pilot plant systems. Transient problems with

previous SBCR experiments were caused by a maldistribution of catalyst between the reactor and slurry filtration system. The level indication/control system installed in an enhanced SBCR was robust and effective in maintaining a steady inventory of catalyst slurry in contact with the gas-phase. Measured deactivation rates in the enhanced SBCR system were comparable to that of CSTR experiments under similar conditions.

Attrition tests in the SBCR system indicated that the most of the catalyst breakdown occurred during catalyst activation and the initial synthesis stage; however, further research will be required to investigate the possibility of particle size classification/segregation at the sampling points. After activation, the catalyst particle mean diameter decreased in an exponential decay fashion. Attrition effects must be considered in order to accurately estimate the space velocity in pilot-scale SBCRs.

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Figure 1. Schematic of SBCR pilot plant system.

Figure 2. CO conversion comparison between reactor types.

Figure 3. Catalyst solids distribution (reactor and reactor effluent) versus time-on-stream.

Figure 4. Mean particle size in the catalyst slurry versus time-on-stream (reactor and reactor effluent).

Task 3. Catalyst Characterization

The objective of this task is to obtain characterization data of the prepared catalysts using routine and selected techniques.

A. Impact of Copper on an Alkali Promoted Iron Fischer-Tropsch Catalyst

Introduction

Copper has traditionally been added to precipitated iron Fischer-Tropsch (FT) catalysts to facilitate reduction of Fe_2O_3 to zero valent iron during activation (1) by lowering the reduction temperature when activating with hydrogen, carbon monoxide or syngas (2). This is particularly important when activating with hydrogen because metallic iron which is formed will sinter easily if the temperature is too high; however, it is not as critical when activating with carbon monoxide or syngas because iron carbides are formed and they are not as susceptible to sintering.

The effect of copper on activity and selectivity has not been studied as thoroughly as its effect on catalyst activation. Kölbel reported that copper loadings less than 0.1 % (weight % relative to iron) were sufficient to produce an active catalyst and that increased copper loading had no effect on FT activity (3). It has previously been shown that copper increases the activity of precipitated iron catalysts when operating at low temperature ($<250^\circ\text{C}$) (2). Bukur et al. have reported that copper increases FT activity and water gas shift activity (4). In addition, they reported that copper increased the average molecular weight of the product and increased hydrogenation of alkenes and isomerization of 1-alkenes. Soled et al. have reported that promotion with copper in conjunction with potassium increased FT activity but had little effect on alkene selectivity (5).

Water gas shift activity and FT selectivity have been shown to depend on syngas conversion (6). To determine the true impact of copper on FT selectivity and water gas shift

activity, comparisons should be done at similar conversion. No such study has been reported for the effects of copper. Herein are reported the effects of copper on FT activity and selectivity and water gas shift activity over a wide range of syngas conversions.

Experimental

A base catalyst with atomic composition 100Fe/4.6Si was prepared by precipitation as previously reported (7). The catalyst was impregnated with aqueous K_2CO_3 to give an atomic composition of 100Fe/4.6Si/1.4K. Copper was added by impregnation with aqueous $Cu(NO_3)_2 \cdot 3H_2O$. Catalyst compositions in atomic ratios were:

100Fe/4.6Si/1.4K
100Fe/4.6Si/0.10Cu/1.4K
100Fe/4.6Si/2.0Cu/1.4K

Approximately 5 g of catalyst were mixed with 300 g of Ethylflo 164 decene trimer in a one liter stirred tank reactor. Catalysts were activated with carbon monoxide at 270°C and 1.3 MPa for 24 hours. Following activation, temperature and pressure were maintained and syngas ($H_2/CO=0.67$) was started at a space velocity of 10 l (STP) $h^{-1} g-Fe^{-1}$. The reactor stirring speed was maintained at 750 rpm. Within eight days syngas conversion had stabilized and the space velocity was varied between 5 and 65 l (STP) $h^{-1} g-Fe^{-1}$. Each space velocity was maintained for approximately 24 hours after which liquid samples were taken and a material balance was calculated. The space velocity was returned to 10 l (STP) $h^{-1} g-Fe^{-1}$ after about two weeks on line to check for deactivation.

Results

FT Activity

Syngas conversion for each catalyst as a function of the reciprocal space velocity is shown in Figure 1. Copper increased syngas conversion over the entire range of space velocities studied. Copper also increased hydrocarbon productivity (Figure 2). At the lowest space

velocity the hydrocarbon productivity was about the same for all three catalysts ($\sim 1.1 \text{ g h}^{-1} \text{ g-Fe}^{-1}$). As the space velocity was increased, hydrocarbon productivity increased with increasing copper loading. At the highest space velocity, the hydrocarbon productivity was 5.3, 3.9 and $3.0 \text{ g h}^{-1} \text{ g-Fe}^{-1}$ for the 100Fe/4.6Si/2.0Cu/1.4K, 100Fe/4.6Si/0.10Cu/1.4K and 100Fe/4.6Si/1.4K catalysts, respectively.

Water gas shift Activity

The rate of the water gas shift reaction is defined as the rate of carbon dioxide formation, $\text{mol h}^{-1} \text{ g-Fe}^{-1}$, in this study. In general, the water gas shift rate increased initially with increasing space velocity. The water gas shift rate for the 100Fe/4.6Si/2.0Cu/1.4K catalyst increased over the entire range of space velocities studied; however, it leveled off for the 100Fe/4.6Si/0.10Cu/1.4K catalyst and reached a maximum for the 100Fe/4.6Si/1.4K catalyst (Figure 3). Copper slightly increased the water gas shift rate at the lowest space velocity. As the space velocity increased the impact of copper became more pronounced. At the highest space velocity, the water gas shift rates were 0.21, 0.14 and 0.1 for the 100Fe/4.6Si/2.0Cu/1.4K, 100Fe/4.6Si/0.10Cu/1.4K and 100Fe/4.6Si/1.4K catalysts, respectively. Similarly copper increased the water gas shift rate at all conversion levels studied, although the water gas shift rates were converging at the highest conversion (Figure 4). The approach to equilibrium for the water gas shift can be measured by the reaction quotient:

$$\text{RQ}_{\text{WGS}} = \frac{P_{\text{CO}_2} P_{\text{H}_2}}{P_{\text{CO}} P_{\text{H}_2\text{O}}} \quad (1)$$

The reaction quotient increased with increasing conversion; however, only at syngas conversion greater than 90% did the water gas shift reaction approach equilibrium (Figure 5). Copper had no effect on the water gas shift reaction quotient when compared at similar conversion.

FT Rate Versus Water Gas Shift Rate

The rate of the water gas shift and FT reactions can be defined by equations 2 and 3:

$$r_{\text{wgs}} = r_{\text{CO}_2} \quad (2)$$

$$r_{\text{FT}} = r_{\text{CO}} - r_{\text{CO}_2} \quad (3)$$

where r_{CO_2} is the rate of CO_2 formation and r_{CO} is the rate of CO conversion. The FT rate dominated the water gas shift rate at the highest space velocities (Figure 6). The FT and water gas shift rates decreased as the space velocity decreased and conversion increased. As the space velocity decreased the water gas shift rate approached the FT rate.

Selectivity

Carbon monoxide efficiency was not effected by copper promotion. In general, the selectivity to carbon dioxide decreased with decreasing syngas conversion (Figure 7). Copper had little effect on alkene selectivity (Figure 8) or isomerization of 1-butene (Figure 9) over the entire range of conversions studied. Methane selectivity was fairly constant up to 50-60 % conversion; however, at higher conversions, methane selectivity increased with increasing conversion. In general, the hydrocarbon selectivity shifted to heavier products with decreasing conversion (Figure 11). Copper lowered the methane selectivity at all conversions (Figure 10) and increased C_{12} and heavier products (Figure 11).

Kinetics

Satterfield et al. have proposed the following kinetic expression for the rate of consumption of syngas by the FT synthesis:

$$-r_{\text{CO}+\text{H}_2} = \frac{kP_{\text{CO}}P_{\text{H}_2}^2}{P_{\text{CO}}P_{\text{H}_2} + bP_{\text{H}_2\text{O}}} \quad (4)$$

where k is the intrinsic rate constant, b is the product of the adsorption equilibrium constant of CO and the desorption equilibrium constant of H₂O and the remaining variables are the partial pressures of CO, H₂ and H₂O (8). Equation 4 can be rearranged to give the following linear equation:

$$\frac{P_{H_2}}{-r_{CO+H_2}} = \frac{1}{k} + \frac{b}{k} \frac{P_{H_2O}}{P_{CO}P_{H_2}}. \quad (5)$$

A plot of $P_{H_2}/-r_{CO+H_2}$ versus $P_{H_2O}/(P_{CO}P_{H_2})$ will give a straight line with slope equal to b/k and y-intercept equal to $1/k$ if data fit the model. Data for the three runs are presented in this manner in Figure 12 and results are listed in Table 1. The rate constant, k increased with increasing copper and the adsorption parameter, b decreased with increasing copper.

Discussion

Activity and selectivity data for each catalyst are listed in Tables 2 through 4. Conversion and hydrocarbon productivity increased with increasing copper loading over the range of copper loadings studied and hydrocarbon productivity increased by a factor of 3 to 5 upon increasing the space velocity (decreasing conversion) from 5 to 65 l (STP) h⁻¹ g-Fe⁻¹. The kinetic expression proposed by Satterfield et al. (8) adequately described the data acquired for all three catalysts. Copper increased the intrinsic FT rate constant and also decreased the adsorption parameter, b . Examination of equation 4 reveals that both of these effects result in an increase in the FT rate. The effect of copper on the FT rate is somewhat different than the effect of potassium. Potassium was previously found to decrease the intrinsic rate constant, k and the adsorption parameter, b (9). Since these trends have an opposite effect on FT rate (equation 4),

the effect of potassium depended on the conversion. At high conversion, increasing potassium slightly increased activity, at intermediate conversion (50%) there was an optimum potassium loading and at low conversion increasing potassium decreased FT activity.

Water gas shift

It is conventional wisdom that copper increases carbon dioxide selectivity and the water gas shift reaction quotient (4). In the present study it was found that copper increased the water gas shift rate; however, it did not effect the carbon dioxide selectivity or the water gas shift reaction quotient when comparisons were made at the same syngas conversion. The FT reaction rate was always higher than the water gas shift reaction. This can be seen in Figure 6 where the ratio of the water gas shift rate to the FT rate for all three catalysts increased from about 0.4 at the highest space velocity to greater than 0.8 at the lowest space velocity. The rate of the water gas shift reaction cannot be greater than the rate of the FT reaction because the water gas shift reaction is limited by the rate of water produced by the FT reaction.

It has been reported that copper effects hydrocarbon selectivity in much the same way as potassium, except secondary reactions are slightly enhanced (alkene hydrogenation and 1-alkene isomerization) (4); however, comparisons were not made at similar conversions. In the present study, methane selectivity was constant up to a conversion of approximately 50%, irrespective of copper loading. Above 50% conversion, methane selectivity increased with increasing conversion. Increasing copper did significantly lower methane selectivity and increase the selectivity to heavy products. Alkene selectivity and isomerization of 1-alkenes was not effected by copper when comparisons were made at similar conversion.

Conclusions

Copper is a promoter for the FT synthesis. The FT rate increased with increasing copper loading in the range reported here (0 to 2 atomic ratio per 100 Fe). The effect of copper on FT kinetics has been studied. According to a proposed kinetic expression, the FT reaction rate is dependent on a rate constant, k and an adsorption parameter, b . Copper has been found to increase the rate constant and decrease the adsorption parameter, both of which cause an increase in FT rate.

Copper also increased the water gas shift rate; however, it did not increase CO_2 selectivity when comparisons were made at similar conversion. The water gas shift reaction quotient only approaches the equilibrium constant at high conversion; furthermore, copper did not increase the reaction quotient.

The effect of copper on product selectivity has been determined over a wide range of conversions. Accurate comparisons of catalyst selectivity must be made at similar syngas conversion because selectivity can be greatly affected by the conversion. For example, methane selectivity increased and alkene selectivity decreased with increasing conversion. Copper had a similar effect on product selectivity as potassium. Methane selectivity decreased and products heavier than C_{11} increased with increasing copper loading. Copper did not effect alkene selectivity or the isomerization of 1-alkenes to 2-alkenes.

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Table 1		
Effect of Copper on Kinetic Parameters		
	k (mol h ⁻¹ g-Fe ⁻¹ kPa ⁻¹)	b
100Fe/4.6Si/1.4K	1.75 x 10 ⁻³	3040
100Fe/4.6Si/0.1Cu/1.4K	2.04 x 10 ⁻³	1940
100Fe/4.6Si/2.0Cu/1.4K	2.93 x 10 ⁻³	1590

Table 2									
Activity and Selectivity for 100Fe/4.6Si/1.4K Catalyst									
	Space Velocity (sl h ⁻¹ g-Fe ⁻¹)								
	5.0	6.67	10	15	22	30	40	50	65
CO + H ₂ Conversion %	80	76	71	57	44	36	29	25	20
Hydrocarbon Productivity (g h ⁻¹ g-Fe ⁻¹)	0.89	1.08	1.53	1.91	2.12	2.41	2.73	2.89	3.03
Water-Gas Shift $P_{H_2}P_{CO_2}/(P_{H_2O}P_{CO})$	20	15	9.7	4.0	2.4	1.6	1.2	1.0	0.92
H ₂ /CO usage ratio	0.57	0.58	0.60	0.65	0.72	0.78	0.81	0.90	0.96
Selectivity C basis									
CO ₂	46	47	46	44	42	38	34	32	30
CH ₄	7.1	7.1	4.8	5.3	5.2	5.0	4.8	4.7	4.9
Selectivity (wt.%)									
CH ₄	7.9	7.9	6.5	5.9	5.8	5.6	5.4	5.2	5.5
C ₂ -C ₄	27	27	24	23	24	23	22	22	22
C ₅ -C ₁₁	35	36	34	35	34	32	32	30	30
C ₁₂ ⁺	31	29	36	36	37	39	41	43	43
alkene									
C ₂ -C ₄	60	63	71	77	80	82	83	85	85
C ₅ -C ₁₁	69	73	75	78	82	83	84	85	75

Table 3									
Activity and Selectivity for 100Fe/4.6Si/0.10Cu/1.4K Catalyst									
	Space Velocity (sl h ⁻¹ g-Fe ⁻¹)								
	5.0	6.67	10	15	22	30	40	50	65
CO + H ₂ Conversion %	86	83	76	64	54	44	37	31	25
Hydrocarbon Productivity (g h ⁻¹ g-Fe ⁻¹)	0.87	1.15	1.64	2.15	2.75	3.00	3.50	3.87	3.89
Water-Gas Shift $P_{H_2}P_{CO_2}/(P_{H_2O}P_{CO})$	48	32	12	6.3	3.6	2.4	1.8	1.5	1.3
H ₂ /CO usage ratio	0.57	0.58	0.60	0.60	0.64	0.68	0.72	0.71	0.78
Selectivity C basis									
CO ₂	51	49	46	44	41	41	37	34	34
CH ₄	8.7	7.9	6.0	5.2	4.7	5.1	4.8	4.9	5.3
Selectivity (wt.%)									
CH ₄	9.7	8.9	6.7	5.9	5.3	5.7	5.4	5.4	6.0
C ₂ -C ₄	29	28	23	22	20	22	21	20	22
C ₅ -C ₁₁	42	39	35	34	31	33	33	31	32
C ₁₂ ⁺	19	24	35	38	44	39	40	44	40
alkene									
C ₂ -C ₄	57	58	69	75	79	81	83	83	85
C ₅ -C ₁₁	66	67	73	77	80	82	82	84	84

Table 4									
Activity and Selectivity for 100Fe/4.6Si/2.0Cu/1.4K Catalyst									
	Space Velocity (sl h ⁻¹ g-Fe ⁻¹)								
	5.0	6.67	10	15	22	30	40	50	65
CO + H ₂ Conversion %	89	88	86	77	66	56	48	42	35
Hydrocarbon Productivity (g h ⁻¹ g-Fe ⁻¹)	1.02	1.24	1.92	2.51	3.20	3.74	4.49	4.62	5.30
Water-Gas Shift $P_{H_2}P_{CO_2}/(P_{H_2O}P_{CO})$	42	56	30	14	6.5	4.3	2.6	2.0	1.6
H ₂ /CO usage ratio	0.58	0.60	0.58	0.60	0.63	0.66	0.66	0.75	0.74
Selectivity C basis CO ₂ CH ₄	44	47	45	46	44	43	40	40	37
Selectivity (wt.%)									
CH ₄	7.3	7.9	7.0	6.2	5.5	5.3	4.9	5.4	5.2
C ₂ -C ₄	22	24	21	21	20	20	18	20	19
C ₅ -C ₁₁	32	27	29	33	32	30	27	31	30
C ₁₂ ⁺	39	41	42	40	42	45	49	44	46
alkene									
C ₂ -C ₄	58	57	60	69	75	79	81	82	83
C ₅ -C ₁₁	65	67	67	70	75	79	81	82	83

Figure 1. Syngas conversion as a function of reciprocal space velocity. F, 0 Cu, G, 0.1 Cu, $\diamond$, 2.0 Cu.

Figure 2. Hydrocarbon productivity as a function of reciprocal space velocity. F, 0 Cu, G, 0.1 Cu, $\diamond$, 2.0 Cu.

Figure 3. Water gas shift rate as a function of reciprocal space velocity. F, 0 Cu, G, 0.1 Cu, $\diamond$, 2.0 Cu.

Figure 4. Water gas shift rate as a function of syngas conversion. F, 0 Cu, G, 0.1 Cu, $\diamond$, 2.0 Cu.

Figure 5. Water gas shift reaction quotient as a function of syngas conversion. F, 0 Cu, G, 0.1 Cu, $\diamond$, 2.0 Cu.

Figure 6. Ratio of water gas shift rate to FT rate as a function of syngas conversion. F, 0 Cu, G, 0.1 Cu, ◇, 2.0 Cu.

Figure 7. Carbon dioxide selectivity as a function of syngas conversion. F, 0 Cu, G, 0.1 Cu, $\diamond$, 2.0 Cu.

Figure 8. Alkene selectivity of C₂ (open symbols) and C₄ (closed symbols) as a function of syngas conversion. F and M, 0 Cu, G and O, 0.1 Cu, $\diamond$ and $\blacklozenge$, 2.0 Cu.

Figure 9. 1-butene selectivity as a function of syngas conversion. F, 0 Cu, G, 0.1 Cu, $\diamond$, 2.0 Cu.

Figure 10. Methane selectivity as a function of syngas conversion. F, 0 Cu, G, 0.1 Cu, ◇, 2.0 Cu.

Figure 11. Selectivity of C₁₂ and heavier products as a function of syngas conversion.
F, 0 Cu, G, 0.1 Cu, $\diamond$, 2.0 Cu.

Figure 12. FT rate data fit according to equation 5. F, 0 Cu, G, 0.1 Cu, $\diamond$, 2.0 Cu.

B. Mössbauer Spectroscopy of Iron-Based Fischer-Tropsch Catalysts: Impact of Activation Procedure

Abstract

The impact of activation procedure on the phase composition of precipitated iron Fischer-Tropsch (FT) catalysts has been studied. Catalyst samples taken during activation and FT synthesis have been characterized by Mössbauer spectroscopy. Formation of iron carbide is necessary for high FT activity. Hydrogen activation of precipitated iron catalysts results in reduction to predominantly metallic iron and Fe_3O_4 . Metallic iron is not stable under FT conditions and is rapidly converted to ϵ' - $\text{Fe}_{2.2}\text{C}$. Activation with carbon monoxide or syngas with low hydrogen partial pressure reduces catalysts to χ - Fe_5C_2 and a small amount of superparamagnetic carbide. Exposure to FT conditions partially oxidizes iron carbide to Fe_3O_4 ; however, catalysts promoted with potassium or potassium and copper maintain a constant carbide content and activity after the initial oxidation. An unpromoted iron catalyst which was activated with carbon monoxide to produce 94% χ - Fe_5C_2 , deactivated rapidly as the carbide was oxidized to Fe_3O_4 . No difference in activity, stability or deactivation rate was found for χ - Fe_5C_2 and ϵ' - $\text{Fe}_{2.2}\text{C}$.

Introduction

Iron Fischer-Tropsch (FT) catalysts undergo numerous phase changes which may have profound effects on catalyst activity (1-3), selectivity (4), attrition (5) and deactivation (6). Precipitated and fused iron catalysts are typically oxides before use and need to be activated by reducing to the zero valent state. The activation procedure generally involves reducing with hydrogen to metallic iron or with carbon monoxide or syngas to various iron carbides. Metallic iron, produced by hydrogen activation, is rapidly converted to iron carbides when exposed to syngas under FT conditions (2,3). Additional phase transformations may occur during FT

synthesis. Water is a primary product of the FT synthesis and may reach concentrations high enough to oxidize iron carbides to Fe_3O_4 (7). In addition, carbon dioxide produced by the water-gas shift reaction can reach oxidizing concentrations at high conversion (7). A thermodynamic study of the iron carbide/oxide system under typical FT conditions has shown that both Fe_3O_4 and iron carbide are thermodynamically favored (8).

Several iron carbides have been identified in active iron FT catalysts. Among these are: $\chi\text{-Fe}_5\text{C}_2$, $\epsilon'\text{-Fe}_{2.2}\text{C}$, $\theta\text{-Fe}_3\text{C}$ and Fe_7C_3 . The thermal stability of $\chi\text{-Fe}_5\text{C}_2$, $\epsilon'\text{-Fe}_{2.2}\text{C}$, and $\theta\text{-Fe}_3\text{C}$ carbides with increasing temperature has been reported to be: $\epsilon'\text{-Fe}_{2.2}\text{C} \leq \chi\text{-Fe}_5\text{C}_2 < \theta\text{-Fe}_3\text{C}$ (9, 10). Conducting FT synthesis at moderate to low temperatures ($<270^\circ\text{C}$) generally results in $\chi\text{-Fe}_5\text{C}_2$ and/or $\epsilon'\text{-Fe}_{2.2}\text{C}$ formation (2, 3). The $\theta\text{-Fe}_3\text{C}$ and Fe_7C_3 carbides have been reported at high temperature FT synthesis with fused iron catalysts (7). The role of iron carbides in FT synthesis has been debated since Fischer and Tropsch proposed hydrocarbons were formed by the hydrogenation of bulk iron carbide (11). Emmett demonstrated that hydrocarbons synthesized over a ^{14}C labeled iron carbide catalyst had lower radioactivity than the catalyst thereby demonstrating that bulk iron carbide does not directly participate in hydrocarbon production; however, Emmett did not rule out the possibility that a surface carbide was involved in hydrocarbon production (12). Subsequent studies with ^{13}C tracers have verified that carbon on the surface of carbided catalysts does become incorporated in FT products (13).

In addition to iron carbides, Fe_3O_4 (magnetite) is generally found in used iron FT catalysts. Magnetite has been reported to be both active (14) and inactive for FT synthesis (1). The discrepancy may be due to oxidation of iron carbides by improper passivation prior to analysis (15). Metallic iron has also been proposed to be active for FT synthesis (5). This is unlikely because thermodynamic data predict metallic iron will either be oxidized to Fe_3O_4 or converted to iron carbide(s) depending on the conversion level (8).

Herein, the impact of hydrogen, carbon monoxide and syngas activation on the phase composition of precipitated iron catalysts will be presented. Correlations between phase composition and FT activity and deactivation will be discussed.

Experimental

Catalysts with atomic composition 100Fe/4.6Si/1.0K, 100Fe/4.6Si/2.7Cu/1.0K, 100Fe/3.7Si/0.7K and an unpromoted catalyst were prepared by continuous precipitation and incipient wetness impregnation of promoters as previously described (1). A commercially prepared catalyst with mass composition 100Fe/8.9Cu/1.9K/67kaolin was obtained from United Catalysts Inc. Catalyst and Ethlyflo 164 (Ethyl) C₃₀ oil were charged into a one liter autoclave operated as a continuous stirred tank reactor (cstr). Hydrogen activation was conducted by heating the reactor to 220°C at 120°C/h with hydrogen flow of 120 l h⁻¹ (STP) at ambient pressure; conditions were maintained for 24 hours. Activation with carbon monoxide was conducted at 270°C for 24 hours at 1.3 MPa pressure with a space velocity of 2 l h⁻¹ g-Fe⁻¹ (STP). Syngas activations were conducted at 270°C for 24 hours with H₂/CO=0.7 and space velocity of 3.1 l h⁻¹ g-Fe⁻¹ (STP) at either ambient pressure or 1.3 MPa. Fischer-Tropsch synthesis was conducted at 270°C, H₂/CO=0.7, space velocity=3.1 l h⁻¹ g-Fe⁻¹ (STP) and 1.3 MPa pressure.

Catalyst/slurry samples were removed from the reactor periodically during activation and throughout FT synthesis. Mössbauer spectra were obtained with a conventional constant acceleration spectrometer using 30 mCi ⁵⁷Co in rhodium matrix. Catalyst compositions are given as percent of total iron. For example, 80% Fe₃C₂ refers to 80% of the total iron in the catalyst being in Fe₃C₂.

Results

Hydrogen activation

Mössbauer spectroscopy data of 100Fe/4.6Si/2.7Cu/1.0K catalyst during hydrogen activation are shown in Figure 1. Exposure of the catalyst to hydrogen at 220°C for 2 hours resulted in the catalyst being partially reduced to 20% Fe₃O₄ with the remaining 80% a superparamagnetic species. During the course of the activation, the Fe₃O₄ phase increased at the expense of the superparamagnetic species. Metallic iron (10%) was first detected after 10 hours of activation and after 24 hours of activation the catalyst composition was 65% Fe₃O₄, 24% metallic iron and 11% superparamagnetic species.

Exposure of the hydrogen activated catalyst to syngas at FT conditions caused rapid phase changes. Within 3 hours of starting FT synthesis, the superparamagnetic species had disappeared, the metallic iron decreased to 4% and ϵ' -Fe_{2.2}C (34%) was formed. Following 20 hours of FT synthesis, the Fe₃O₄ had decreased slightly to 59% and the remainder of the catalyst was ϵ' -Fe_{2.2}C. Catalyst composition and syngas conversion as a function of time on stream are shown in Figure 3. The catalyst had high initial syngas conversion (85%) and deactivated slowly at the rate of 0.9% per week. The catalyst was run for over 3500 hours during which the catalyst composition remained constant at approximately 60% Fe₃O₄ and 40% ϵ' -Fe_{2.2}C.

Carbon monoxide activation

Phase changes for a typical iron-based catalyst during carbon monoxide activation are shown in Figure 4 (16). The 100Fe/8.9Cu/1.9K/67kaolin catalyst was initially α -Fe₂O₃ as determined by XRD and Mössbauer spectroscopy. The catalyst was reduced to 100% Fe₃O₄ during the heating from ambient temperature to 270°C (2 hours) under carbon monoxide. Iron carbide phases began to appear after 4.5 hours of activation. The first carbide phase detected was a superparamagnetic carbide; this phase increased to approximately 10% of the iron and

remained constant throughout the activation. χ -Fe₅C₂ (26%) was first detected after 10 hours of activation and continued to increase at the expense of Fe₃O₄. The catalyst composition after 26 hours of activation was 90% χ -Fe₅C₂ and 10% superparamagnetic carbide. Carbon dioxide production as a function of time on stream is also plotted in Figure 4. Carbon dioxide can be produced by the reduction of α -Fe₂O₃ to Fe₃O₄ (equation 1), reduction of Fe₃O₄ to iron carbide (equation 2) and from the Boudouard reaction (equation 3).

Figure 4 shows that enough carbon dioxide was produced after 8 hours to account for 100% carbiding of the catalyst; however, Mössbauer data reveal that the catalyst was approximately 10% iron carbide at this time. By the end of carbon monoxide activation, there was approximately 60% more carbon dioxide produced than was needed to completely carbide the catalyst. This indicates that a large amount of Boudouard carbon was produced.

Figure 5 shows that the iron carbide was partially oxidized to Fe₃O₄ (8%) after 20 hours of FT synthesis. Over the remainder of the run (140 h), the Fe₃O₄ content grew to 16% with the balance a mixture of χ -Fe₅C₂ and superparamagnetic carbide. Catalyst activity remained high during the run with carbon monoxide conversion greater than 65%.

An unpromoted iron catalyst was also activated with carbon monoxide under identical conditions to the catalyst described above. The catalyst was reduced to 94% χ -Fe₅C₂ and 6% Fe₃O₄ after 24 hours of activation; no superparamagnetic carbide was detected. This catalyst initially had high FT activity with syngas conversion of 84%; however, the catalyst was not stable and deactivated at the rate of 3.7% syngas conversion per day. The catalyst composition changed significantly during the deactivation; as the conversion decreased, the amount of χ -

Fe_5C_2 decreased and the amount of Fe_3O_4 increased. The catalyst was 100% Fe_3O_4 after 450 hours of FT synthesis and the syngas conversion had decreased to 18%.

Syngas activation

Catalyst composition and syngas conversion for the 100Fe/3.6Si/0.7K catalyst activated at FT synthesis conditions, syngas ($\text{H}_2/\text{CO}=0.7$) at 270°C and 1.3 MPa, are shown in Figure 6 (16). Initial syngas conversion was 6% and it increased slowly to only 18% after 92 hours on stream; the catalyst was composed of 100% Fe_3O_4 during this time. Since the conversion was low, the catalyst was treated with carbon monoxide for 19 hours at 1.3 MPa and 270°C . The catalyst was partially reduced to 42% $\chi\text{-Fe}_5\text{C}_2$ and superparamagnetic carbide after the carbon monoxide treatment. Fischer-Tropsch synthesis was resumed and the syngas conversion increased rapidly to the same level obtained for another FT run when the catalyst was activated with carbon monoxide (Figure 6). This run was continued for 430 hours during which the syngas conversion remained close to 80% and the catalyst composition was approximately 40% $\chi\text{-Fe}_5\text{C}_2$ and superparamagnetic carbide with the remainder Fe_3O_4 .

Figure 7 shows the composition and syngas conversion for the 100Fe/3.6Si/0.7K catalyst after activation with syngas ($\text{H}_2/\text{CO}=0.7$) at ambient pressure and 270°C for 24 hours (16). In contrast to activation with syngas at 1.3 MPa, activation at ambient pressure resulted in a catalyst with high syngas conversion (82%). The catalyst composition after activation was 68% $\chi\text{-Fe}_5\text{C}_2$ and superparamagnetic carbide and 32% Fe_3O_4 . The total iron carbide content decreased to 53% during the first 24 hours and then slowly decreased to 40% after 400 hours. The remainder of the catalyst was Fe_3O_4 . Syngas conversion decreased slowly to 65% after 400 hours.

Discussion

Activation of the 100Fe/4.6Si/2.7Cu/1.0K catalyst with hydrogen at 220°C for 24 hours partially reduced the catalyst to 24% metallic iron, 11% superparamagnetic species and 65%

Fe_3O_4 . Exposing the activated catalyst to FT conditions caused the conversion of all of the metallic iron and superparamagnetic species and a small amount of Fe_3O_4 to ϵ' - $\text{Fe}_{2.2}\text{C}$. Throughout 3500 hours of FT synthesis, the catalyst composition remained constant at 40% ϵ' - $\text{Fe}_{2.2}\text{C}$ and 60% Fe_3O_4 . The catalyst had high initial activity with syngas conversion greater than 80% and a deactivation rate of only 0.9% syngas conversion per week. In contrast, activation with carbon monoxide resulted in greater than 90% of an unpromoted iron catalyst and a 100Fe/8.9Cu/1.9K/67kaolin catalyst being reduced to χ - Fe_5C_2 and a small amount of superparamagnetic iron carbide. The superparamagnetic carbide was not identified because Mössbauer data were collected at room temperature; however, this may be small particle ϵ' - $\text{Fe}_{2.2}\text{C}$ (9). Activation with hydrogen lean syngas at ambient pressure was very similar to activation with carbon monoxide. The catalyst was composed of 68% χ - Fe_5C_2 and superparamagnetic carbide following activation.

Activation with hydrogen, carbon monoxide or syngas can result in high activity if the appropriate promoters and conditions are applied (Figure 8). Activation with hydrogen requires that the catalyst be promoted with copper to lower the reduction temperature and prevent sintering; catalysts activated with hydrogen that do not contain copper generally have lower activity and require a long induction period (17). In addition, a high space velocity of hydrogen is required to maintain a low water partial pressure in the reactor and thereby prevent sintering of metallic iron (7). In the case of syngas activation, a low hydrogen partial pressure is required to minimize the water concentration in the reactor which if too high prevents Fe_3O_4 from being reduced to χ - Fe_5C_2 (1). If the activation procedure is conducted properly, hydrogen, carbon monoxide or syngas activated catalysts will have similar activity. There does not seem to be a difference in the activity of hydrogen activated catalysts where the carbide phase of the active catalyst is ϵ' - $\text{Fe}_{2.2}\text{C}$ and the activity of carbon monoxide or syngas activated catalysts where the

predominant carbide phase is χ -Fe₅C₂. Likewise the deactivation characteristics of hydrogen, carbon monoxide and syngas activated catalysts are very similar over the span of at least 1000 hours (8). This is surprising because it has been reported that ϵ' -Fe_{2.2}C is not as active as χ -Fe₅C₂ and the transformation of ϵ' -Fe_{2.2}C into χ -Fe₅C₂ has been identified as a cause of deactivation of iron catalysts (6). Although there is no difference in activity of ϵ' -Fe_{2.2}C and χ -Fe₅C₂, a strong correlation between iron carbide content and FT activity has been observed. An unpromoted iron catalyst immediately following carbon monoxide activation was composed of 92% χ -Fe₅C₂ and 8% Fe₃O₄. The catalyst gradually oxidized to Fe₃O₄ during FT synthesis and after 450 hours was 100% Fe₃O₄. Catalyst activity, as measured by syngas conversion, decreased linearly from 84% to 19% as the catalyst was oxidized. Although the syngas conversion was 19% after the catalyst had been oxidized to Fe₃O₄, it is possible that the low activity was due to a small amount of iron carbide not detectable by Mössbauer spectroscopy (<5%) and not Fe₃O₄.

Catalysts which had stable activity were composed of 40% to 85% iron carbide and 60% to 15% Fe₃O₄ throughout FT synthesis. The question of how a catalyst can be partially and not completely oxidize during FT synthesis can be answered by thermodynamic analysis of the C/H/O/Fe system (8). A phase diagram of the C/H/O system is shown in Figure 9. The diagram is a ternary plot on the basis of mole % of C, H and O of the gases in the reactor atmosphere (CO, CO₂, H₂, H₂O and CH_x) at 300°C and 1.5 MPa. Iron carbide and carbon are the stable phases in Region A, iron carbide, Fe₃O₄ and carbon are the stable phases in Region B, Fe₃O₄ and carbon are the stable phases in Region C and Fe₃O₄ is the stable phase in region D. Composition of the reactor atmosphere at syngas conversion ranging from 29% to 84% are shown on the phase diagram for a typical FT catalyst. The gas composition of the reactor atmosphere over this range of conversions lies close to the boundary of iron carbide/carbon and iron carbide/Fe₃O₄/carbon

regions. Another possible explanation for the presence of both iron carbide(s) and Fe_3O_4 is inhomogeneity within catalyst particles. The ultimate particle size of a precipitated iron catalyst is on the order of 200 Å and these particles form agglomerates which can be smaller than 1 µm or as large as 250 µm. Conversion of carbon monoxide and hydrogen to carbon dioxide, water and hydrocarbons in the interior of these agglomerates can cause the water and carbon dioxide concentrations within the particles to be higher than at the surface of the agglomerate which is exposed to the bulk gas phase. This could lead to the formation of particles with a Fe_3O_4 core and an iron carbide surface.

Conclusions

Formation of an iron carbide is necessary for high activity with precipitated iron catalysts. A precipitated iron catalyst (100Fe/4.6Si/2.7Cu/1.0K) which was activated with hydrogen at 220°C and ambient pressure was partially reduced to metallic iron and Fe_3O_4 . Metallic iron was not stable under FT conditions and exposure to syngas ($\text{H}_2/\text{CO}=0.7$) at 270°C and 1.3 MPa converted all of the metallic iron to ϵ' - $\text{Fe}_{2.2}\text{C}$. Catalysts activated with carbon monoxide (unpromoted iron and 100Fe/8.9Cu/1.9K/67kaolin) or syngas with low hydrogen partial pressure (100Fe/3.6Si/0.7K) at 270°C produced predominantly χ - Fe_5C_2 and had high initial syngas conversion. Activation with syngas at 270°C and 1.3 MPa partially reduced the 100Fe/3.6Si/0.7K catalyst to 100% Fe_3O_4 which resulted in low FT activity. Iron carbides produced by carbon monoxide and syngas activation of promoted catalysts were partially oxidized to Fe_3O_4 during the first 24 hours of FT synthesis; however, these catalysts deactivated slowly. There was no difference in the activity, stability or deactivation characteristics of ϵ' - $\text{Fe}_{2.2}\text{C}$ and χ - Fe_5C_2 under the FT conditions employed in this study. Catalysts with stable activity maintained a constant iron carbide level. An unpromoted iron catalyst deactivated more rapidly than iron catalysts promoted with potassium, copper and a nonreducible metal oxide. The

deactivation of the unpromoted iron catalyst was caused by oxidation of active iron carbide to inactive/less active Fe_3O_4 .

The presence of iron carbides and Fe_3O_4 together can be explained by inhomogeneity of gases within individual catalyst particles. Water and carbon dioxide produced by conversion of syngas within catalyst particles can cause the environment inside a particle to be oxidizing while the surface is exposed to reducing conditions of the reactor atmosphere. This would result in the formation of a Fe_3O_4 core and an iron carbide outer layer. Another possibility is that under typical FT conditions the redox potential of the reactor atmosphere lies within the narrow region of the C/H/O/Fe phase diagram where Fe_3O_4 and iron carbides can coexist.

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Figure 1. Phase composition changes of 100Fe/4.6Si/2.7Cu/1.0K catalyst during activation with H_2 at 220°C, 0.1 MPa. (F), superparamagnetic oxide; (G), Fe_3O_4 ; (Δ), Fe^0 .

Figure 2. Phase composition changes of H_2 activated 100Fe/4.6Si/2.7Cu/1.0K catalyst during first 24 hours of FT synthesis (270°C , 1.3 MPa, $\text{H}_2/\text{CO}=0.7$, $\text{whsv}=3.1 \text{ sl h}^{-1} \text{ g-Fe}^{-1}$). (F), superparamagnetic oxide; (G), Fe_3O_4 ; (Δ), Fe^0 ; (M), ϵ' - $\text{Fe}_{2.2}\text{C}$.

Figure 3. Long term phase composition of H_2 activated 100Fe/4.6Si/2.7Cu/1.0K catalyst during FT synthesis (270°C , 1.3 MPa, $\text{H}_2/\text{CO}=0.7$, $\text{whsv}=3.1 \text{ sl h}^{-1} \text{ g-Fe}^{-1}$). (G), Fe_3O_4 ; (M), ϵ' - $\text{Fe}_{2.2}\text{C}$; ($\blacktriangle$), syngas conversion.

Figure 4. Phase composition changes of commercial 100Fe/8.9Cu/1.9K/67kaolin catalyst and moles of CO₂ generated during CO activation. (F), Fe₃O₄; (G), χ-Fe₅C₂; (Δ), superparamagnetic carbide; (M), moles of CO₂. Mössbauer data from reference 16.

Figure 5. Phase composition of CO activated 100Fe/8.9Cu/1.9K/67kaolin catalyst during FT synthesis (270°C, 1.3 MPa, H₂/CO=0.7, whsv=3.1 sl h⁻¹ g-Fe⁻¹). (M), χ -Fe₅C₂ and superparamagnetic carbides; (G), Fe₃O₄; (▲), syngas conversion. Data from reference 16.

Figure 6. Phase composition of 100Fe/3.7Si/0.7K catalyst during syngas activation at 270°C, 1.3 MPa followed by CO treatment at 270°C, 1.3 MPa followed by FT synthesis (270°C, 1.3 MPa, H₂/CO=0.7, whsv=3.1 sl h⁻¹ g-Fe⁻¹). (G), Fe₃O₄ and superparamagnetic oxide; (M) χ -Fe₅C₂ and superparamagnetic carbides; (▲) syngas conversion. Data from reference 16.

Figure 7. Phase composition of syngas activated ($H_2/CO=0.7$, 0.1 MPa, 270°C) 100Fe/3.7Si/0.7K catalyst during FT synthesis (270°C, 1.3 MPa, $H_2/CO=0.7$, $whsv=3.1 \text{ sl h}^{-1} \text{ g-Fe}^{-1}$). (M), χ -Fe₅C₂ and superparamagnetic carbides; (G), Fe₃O₄; (▲) syngas conversion. Data from reference 16.

Figure 8. Comparison of CO conversion for (F), 100Fe/4.6Si/1.0K activated with CO at 270°C, 0.1MPa; (G), 100Fe/4.6Si/1.0K, activated with syngas ($H_2/CO=0.7$) at 270°C, 0.1 MPa; and (Δ) 100Fe/4.6Si/2.0Cu/1.0K activated with H_2 at 220°C, 0.1 MPa. FT conditions: 270°C, 1.3 MPa, $H_2/CO=0.7$, $whsv=3.1 \text{ sl h}^{-1} \text{ g-Fe}^{-1}$).

Figure 9. Ternary phase diagram for solid phase(s) present for graphite/gases (F), Fe/Fe₃O₄/gases (G) and Fe/Fe₃C/gases (Δ) at equilibrium at 300°C and 1.5 MPa. Region A: Fe₃C and C; Region B: Fe₃O₄, Fe₃C and C; Region C: Fe₃O₄ and C; Region D: Fe₃O₄. Gases = H₂O, CO, CO₂, H₂ and CH₄. Gas phase composition during FT synthesis (270°C, 1.3 MPa) at various conversions: CO=86%, H₂=80% (M); CO=78%, H₂=76% (G); CO=68%, H₂=69% (Δ); CO=46%, H₂=54% ($\diamond$); CO=32%, H₂=45% (∇); CO=23%, H₂=37% (F) and syngas composition of H₂/CO=0.67 (M).

C. Mössbauer Study of Precipitated Unpromoted and Potassium Promoted Iron Fischer-Tropsch Synthesis Catalyst

Introduction

As the alternative route to synthesize hydrocarbons other than petroleum industry, Fischer-Tropsch synthesis has been one of the most extensively studied subject in catalysis for several decades. Although most of the recent effort in industry concentrated on cobalt catalyst, iron is still a promising catalyst due to its several advantages, especially for slurry phase reactor. The complexity of phase transformation of iron catalyst during activation and synthesis cause difficulty to accurately elucidate the active phase. Studies to correlate the structure of catalysts with FTS activity were conducted by different authors to define the active phase of iron catalyst. At present the question remains whether magnetite is active for FTS. Early work by Reymond et al (1) and recent work by Kuivila et al. (2) suggest that magnetite is the active phase. Reymond's experiments were performed on both unreduced and reduced iron catalyst. Similar hydrocarbon product distributions were found on these two catalysts, with a maximum activity occurring over a material consisting of approximately equal amounts of magnetite and Hägg carbide. Further carbide formation in the unreduced catalyst coincided with a diminished rate of FT synthesis; therefore, it was concluded that magnetite is an active catalyst. Kuivila studied the reduced and unreduced iron catalyst using the combination of XPS and FTS performance. Their conclusion was based on the fact that they observed only magnetite on the surface of the catalyst after reaction. A similar study was carried out by Dictor and Bell (3) in a slurry-phase reactor using reduced and unreduced Fe_2O_3 powder. However, they concluded that the active phase is Hägg carbide and magnetite is not active.

The work described in this report shows that with appropriate methods to withdraw catalyst samples for characterization, the catalyst situation in the continuous stirred tank reactor

can be revealed during activation and synthesis. Correlation between catalyst composition and FTS activity is made to define the nature of active phase. Comparison with results previously obtained on ultrafine iron catalyst and unpromoted precipitated iron catalyst is made in this report.

Experimental

Catalyst activation and FTS reaction

The catalyst used was prepared by continuous precipitation at a pH of about 9 from aqueous solution of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and concentrated NH_4OH . The precipitate was thoroughly washed with distilled-deionized water and dried at 120°C . A mixture of 64.44g iron catalyst which contains 50.00% Fe, 0.457g of $(\text{CH}_3)_3\text{COK}$ and 290g C_{30} startup oil (Shell decene trimer) was charged into a 1L autoclave operated as a continuous stirred tank reactor (CSTR). The catalyst slurry was heated to 270°C at $2^\circ\text{C}/\text{min}$ under a flow rate of 2.0[NL/hg-(Fe)] CO. CO activation continued at 270°C and 1.20MPa for 24h. Flowing activation, hydrogen flow was started to give a H_2/CO ratio of 0.68 with a flow rate of 3.1NL/hg-(Fe). Catalyst slurry samples (5-10g) were removed from the reactor under the protection of Ar following activation and during different stages of synthesis. Mössbauer samples were prepared in sample holders in a glove bag filled with Ar. Wax products on the catalyst was extracted using THF as the solvent.

Mössbauer analysis

Mössbauer samples were loaded into plexiglass compression holders after extract of wax with THF in a glove bag filled with Ar.

Results

CO conversion versus time on stream was plotted in Fig. 1 for unpromoted iron catalyst and Fig 2 for potassium promoted iron. After 24 hours of activation in CO, both catalysts exhibited high activity (over 80%), and the induction time to attain maximum conversion is very

short. The activity of the catalyst slowly, but continuously, declined with increasing time-on-stream. The deactivation rate for the unpromoted iron is slower than for potassium promoted iron, as observed previously.

Mössbauer analysis results of samples (unpromoted iron) withdrawn from reactor are listed in Table 1. Immediately after CO activation, the catalyst composition was predominantly Hägg carbide (Fe_5C_2), and the Mössbauer spectrum of this sample contains very small magnetite peaks. Fitting results revealed that 93.6% of iron phase is Hägg carbide. No metallic iron was detected. The spectrum of the sample removed after 23h of FT synthesis is more complicated; peaks of magnetite grows larger and overlap with the peaks of iron carbide. As indicated in Table 1, about 83.3% of spectra area was associated with Hägg carbide, and the area ratio of A to B patterns obtained for this phase was 0.76:2; still no metallic iron was found in the spectrum. After exposed to syngas for 168h, peaks of Hägg carbide became relatively lower and the area of magnetite contribute the largest part to the overall spectrum. The data show 58.5% of the iron exists in the form of magnetite and 41.5% Hägg carbide. The A to B site ratio is 0.71:2. The Mössbauer spectrum of sample removed after 453h of Fischer-Tropsch synthesis is simple since the amount of iron carbide is so low that it cannot be observed in the Mössbauer spectrum. The A to B site ratio is 0.95:2.

Discussion

The excellent agreement of catalytic activity with the percentage of iron carbide clearly shows that iron carbide is the active phase while the Fischer-Tropsch synthesis activity of magnetite is negligible.

Mössbauer studies of ultrafine iron catalyst by Huang et al., (4) suggested that after 24h of CO pretreatment, the catalyst was the carbide (ca. 4% iron oxide). With the increase of time on stream, reoxidation of iron carbide took place during the synthesis. After 100h of FT

synthesis, no iron carbide can be observed in Mössbauer spectrum. Consistency of results on precipitated and ultrafine catalyst proved that our results are reliable and repeatable. The work described in this note also supports Huang et al.'s conclusion that CO pretreatment for 24h almost completely transform Fe_2O_3 to Hägg carbide even without the presence of potassium promoter.

Shroff et al (5) emphasized the importance of passivation of iron Fischer-Tropsch catalysts. They claimed that active phase of iron could get oxidized without sufficient attention to passivation. Mössbauer spectroscopy is an ex situ characterization technique. However, our results show that with appropriate methods to withdraw the sample from the reactor, remove wax and load into the sample holder, the iron active phase could be protected without oxidation. The fact that the initial sample withdrawn from the reactor is always found to be nearly all iron carbide eliminates sample contamination after withdrawal determining the sample composition. Furthermore, sample contamination by oxidation by exposure to air should be random, and not to always show a gradual decline. The problem of only observing magnetite as the only detectable phase in the catalyst is most likely due to the sample handling method.

From our results, iron carbide is reoxidized to magnetite with increasing time-on-stream. Water and/or CO_2 are believed to be responsible for such oxidations (6). Rao et al. (7) studied the correlation of catalytic activity of iron catalyst promoted by potassium. They concluded that when a catalyst activation produces both an active catalyst and a high fraction of iron carbide, during the synthesis there will be a conversion of the carbide to the oxide with the attainment of a “pseudo-steady-state” composition. However, our result on precipitated unpromoted iron catalyst shows that oxidation of iron carbide takes place throughout the synthesis procedure. According to Amelse et al (8) and Bianchi et al (9), even at the low conversion rate, there is a strong interaction of water with iron surfaces. Actually, besides accelerating carburization, the

alkali promoter is also believed to stabilize the carbidic phase (3,10). Therefore, the pseudo-steady-state is likely to happen only under the presence of alkali and other promoters which stabilize iron carbide from oxidation.

Magnetite has a unit cell composed of 32 close-packed oxygen atom in which cations occupy 8 tetrahedral (A) and 16 octahedral (B) sites (11). The theoretical value of the A to B ratio for the ideal spinel structure is 1:2. Generally, cation vacancies selectively form on the B-sites; thereby producing a ratio greater than 1:2. A to B site ratios of our sample are 0.77:2 (after activation), 0.76:2 (after 23h FTS), 0.71:2 (after 168h FTS), and 0.95:2 (after 453h FTS). This means that A sites are not occupied by Fe ions. This appears to require that cation vacancies exist or carbon occupies the B-sites. If carbon occupies these sites, the fraction of carbon per “molecule” would be 0.23, 0.24, 0.29 and 0.05, respectively. Therefore, we concluded that magnetite phase contains carbon atoms on the A-sites, especially in the samples with the multiple phases.

The potassium promoted catalyst samples withdrawn from the reactor will be analyzed by Mossbauer spectroscopy and the data will be included in the next report.

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Table 1						
Mössbauer parameters for precipitated iron catalyst after activation and during synthesis						
Sample	Site	HMF(KG)	IS(mm/s)	QS(mm/s)	FW(mm/s)	Fraction
After activation	Fe ₃ O ₄ A	483	0.28	0.04	0.26	1.7
	Fe ₃ O ₄ B	455	0.64	-0.08	0.41	4.4
	Fe ₅ C ₂ I	220	0.26	0.04	0.40	33.6
	Fe ₅ C ₂ II	182	0.20	-0.01	0.42	29.3
	Fe ₅ C ₂ III	101	0.22	0.08	0.50	30.7
FTS run 23h	Fe ₃ O ₄ A	485	0.32	-0.07	0.26	4.6
	Fe ₃ O ₄ B	455	0.67	0.01	0.46	12.1
	Fe ₅ C ₂ I	220	0.26	0.04	0.38	31.1
	Fe ₅ C ₂ II	182	0.24	-0.01	0.36	26.2
	Fe ₅ C ₂ III	100	0.16	-0.1	0.44	26.0
FTS run 168 h	Fe ₃ O ₄ A	487	0.27	0.0	0.28	15.3
	Fe ₃ O ₄ B	458	0.65	-0.01	0.50	43.2
	Fe ₅ C ₂ I	218	0.27	0.04	0.90	23.9
	Fe ₅ C ₂ II	180	0.19	0.09	0.28	5.1
	Fe ₅ C ₂ III	100	0.18	0.11	0.68	12.5
FTS run 453 h	Fe ₃ O ₄ A	488	0.28	0.01	0.25	32.2
	Fe ₃ O ₄ B	459	0.65	0.0	0.32	67.8
	Fe ₅ C ₂ I	----	----	----	----	----
	Fe ₅ C ₂ II	----	----	----	----	----
	Fe ₅ C ₂ III	----	----	----	----	----

Fig. 1 Catalytic activity and iron carbide percentage versus reaction time

Fig 2. CO Conversion as a function of time on stream

D. Characterization of Iron Phase Change During Fischer-Tropsch Synthesis Reaction

Introduction

Iron-based Fischer-Tropsch (FT) catalysts undergo a series of phase transformations during activation and use (1). Activation with carbon monoxide or syngas typically results in the conversion of Fe_2O_3 to Fe_3O_4 and ultimately to one or more carbides (2). During FT synthesis, iron carbides can be oxidized to Fe_3O_4 if the $\text{H}_2\text{O}/\text{H}_2$ or CO_2/CO ratios are high enough (1). There has been considerable debate about the active phase of the FT synthesis. Some studies have indicated an active oxide species (3) while most have supported a carbide species (2,4). Mössbauer spectroscopy has proven to be an effective technique for the analysis of iron-based FT catalysts. *In situ* Mössbauer studies have been reported (5,6); however, these studies have been performed at low pressure and low conversions. Studies performed at industrially relevant conditions have generally involved removing the catalyst from the reactor followed by passivation (7) which, if not performed properly, will oxidize the catalyst (4). Herein are reported the Mössbauer results obtained on an unpromoted precipitated iron catalyst that was activated and reacted in a slurry phase, continuous stirred tank reactor at high conversion and under industrially relevant conditions. Strict measures were observed to prevent oxidation of the catalyst samples. The Fe-Si, Fe-K, Fe-Si-K catalysts were all studied using the same methods.

Experimental

Catalysts were prepared by a previously described procedure (2). A slurry of 64.4 g of catalyst (32.2 g Fe) and 290 g of Ethylflo 164 decene trimer was charged into a one liter autoclave operated as a continuous stirred tank reactor. The catalyst was activated with carbon monoxide ($2 \text{ L h}^{-1} \text{ g-Fe}^{-1}$, STP) at 270°C and 1.3 MPa for 24 hours. Following activation, syngas flow was initiated ($3.1 \text{ L h}^{-1} \text{ g-Fe}^{-1}$, STP) and the temperature and pressure were maintained. Catalyst slurry samples (5-10 g) were removed from the reactor under an argon atmosphere via a

dipleg immediately after activation and at various times during FT synthesis. Light wax was extracted from the cooled slurry samples under an argon atmosphere with deoxygenated tetrahydrofuran. Catalyst samples were loaded into sealed plexiglass holders for analysis by Mössbauer spectroscopy. The spectra were collected by a conventional constant acceleration spectrometer using a 30 mCi ^{57}Co in rhodium matrix.

Results

Syngas conversion versus time on stream for unpromoted iron catalyst is shown in Figure 1. Syngas conversion after 24 hours of FT synthesis was above 84%. Catalyst activity declined steadily throughout the run with an average rate of deactivation of $0.16\% \text{ h}^{-1}$ (absolute syngas conversion).

Catalyst samples for Mössbauer spectroscopy were withdrawn immediately after activation and at 23 h, 168 h and 453 h of FT synthesis. The distribution of iron in the catalyst after activation with carbon monoxide was 94 % $\chi\text{-Fe}_5\text{C}_2$ and 6 % Fe_3O_4 . Exposure to syngas initiated oxidation of the $\chi\text{-Fe}_5\text{C}_2$ to Fe_3O_4 . After 23 hours of FT synthesis, 83 % of the iron was present as $\chi\text{-Fe}_5\text{C}_2$ and the balance was Fe_3O_4 . The amount of iron present as $\chi\text{-Fe}_5\text{C}_2$ had decreased to 18 % after 168 hours of FT synthesis. The only detectable phase after 453 hours of FT synthesis was Fe_3O_4 .

The deactivation rates of Fe-Si, Fe-K, and Fe-K-Si have been determined and the catalyst samples have been withdrawn from the reactor right after activation and at different conversion levels. The Mössbauer spectra of the catalysts are going to be recorded to identify the phase changes.

The Fischer-Tropsch synthesis activity of unpromoted, potassium promoted (100Fe/0.71K), silica promoted (100Fe/4.6Si) and double promoted (100Fe/4.6Si/0.71K)

catalysts were plotted in Figure 2. It can be seen from Figure 2 that Fe and Fe-K catalysts have essentially the same activity during the initial induction period (within 50hrs time on stream) which is higher than Fe-Si and Fe-Si-K catalysts. But the activity of both Fe and Fe-K catalyst decrease steadily with time on stream. For Fe-Si and Fe-Si-K catalysts, they both undergoes an induction period, the activity first goes up until it reaches the maximum and then decrease slowly. After 94 hours of synthesis, the CO conversion of Fe-Si catalyst was 76.1% while the Fe-Si-K catalyst reaches its maximum conversion of 84.04% at 163 hrs time on stream. The average deactivation rate for the catalysts are Fe-K(48%/week), Fe(41%/week), Fe-Si(39%/week) and Fe-Si-K(33%).

Discussion

Based on data generated from several catalysts, a model of the working FT catalyst was developed. In this model, the initial catalyst was essentially comprised of a mixture of iron carbides. As the reaction progressed, the carbide fraction decreased to attain a value of about 30-40%. During this phase change, the conversion did not decrease appreciably. To account for the nearly constant activity while the phase changed a model was proposed. This model had the assumption that the core of each particle was oxidized to form Fe_3O_4 and an out layer remained a carbide form; thus, the surface of the catalyst remained essentially the carbide form while the ratio of oxide/carbide increased as the core consisting of Fe_3O_4 expanded to approach a “steady state at carbide/oxide ratio.

The results with the unpromoted catalyst do not agree with this model. Instead, it appears that the catalyst particle converts from the carbide to the oxide form in parallel with the decline in conversion. Thus, it appears that a steady-state surface carbide phase/core Fe_3O_4 phase is not formed for the unpromoted iron catalyst. One explanation to account for this is that the rate of carbide oxidation is dependent upon the particle size for the unpromoted catalyst.

Work underway with single and doubly promoted catalysts should allow us to define the role of each promoter in determining the composition of the working catalysts.

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Figure 1. Catalytic activity and iron carbide percentage versus reaction time.

Figure 2. CO conversion as a function of time-on-stream.

E. Characterization of promoted Cobalt FTS Catalysts

Introduction

We have studied and are continuing to study the impact on reducibility of cobalt by the use of different supports and by the incorporation of different promoters and additives to supported cobalt catalysts. Although the use of different supports and promoters is well documented, what is less well understood are the reasons for the differences in deactivation rates of these catalysts. Only by rigorous characterization can the properties of the catalysts brought about by differences in preparation, support, and degree and type of promoter be linked to the resulting catalytic properties under reaction. We therefore have spent considerable attention on the characterization of not only the fresh catalysts, but also the spent catalysts sampled after many days on stream in the continuously stirred tank reactor. With this approach, it is our goal to understand what properties are required for high initial activity and, just as importantly, for the maintaining of high stability, and how to achieve them in the catalyst preparation and activation steps. Interestingly, while addition of promoters can markedly improve the reducibility of cobalt FTS catalysts, leading to more available catalytic sites for reaction, these catalysts often display significantly high rates of deactivation. This raises many questions, which should be able to be addressed through careful characterization. For example, is the reducibility of the metal sites changing under reaction conditions and if so, what are the reasons? Is the cobalt and/or promoter cluster size changing under reaction or is there loss in the degree of interaction between the two? Are we forming mobile metal carbonyl species by the addition of CO that leads to loss of metallic sites and changes in the morphology of the clusters with time onstream? To address these questions, we are employing several characterization techniques, including temperature programmed reduction (TPR), hydrogen chemisorption, X-ray diffraction (XRD), transmission electron microscopy (TEM), and in the near future, diffuse

reflectance infrared Fourier transform spectroscopy (DRIFTS) and X-ray absorption spectroscopy methods (XAS) such as extended X-ray absorption fine structure (EXAFS) and X-ray absorption near edge structure (XANES).

Experimental

BET Surface Area Measurements

BET measurements for all catalysts were conducted to determine the loss of BET surface area with loading. These experiments were conducted using a Micromeritics Tri-Star system. Prior to testing, samples were slowly ramped to 160°C and evacuated for 4hrs to approximately 50mTorr.

Hydrogen Chemisorption by the Temperature Programmed Desorption (TPD) Method

Hydrogen chemisorption was measured using a Zeton Altamira AMI-200 unit which incorporates a thermal conductivity detector (TCD). Catalysts were activated using pure hydrogen at the desired reduction temperature (usually 300 or 350°C) for 10hrs and cooled under flowing hydrogen to 100°C. The sample was held at that temperature under flowing argon to remove physisorbed and weakly bound species, prior to increasing the temperature slowly to the activation temperature. At that temperature, the catalyst was held under flowing argon to desorb remaining chemisorbed hydrogen until the TCD signal returned to the baseline. The TPD spectra was integrated and the amount of desorbed hydrogen determined by comparing to the areas of calibrated hydrogen pulses. Table 2 shows the resulting dispersion based on total weight of metal in the sample for a number of cobalt FTS catalysts.

X-ray Diffraction

Diffraction patterns were recorded using a Rigaku X-ray diffractometer utilizing CuK_{Alpha} radiation. Because quantitative information was desired on particle size, we scanned the oxidized samples for the peak corresponding to the (311) planes of Co₃O₄, which appears at a 2θ

value of approximately 37. Scans were taken using a step size of 0.010° . Because of the level of noise for small cobalt clusters, each point was scanned for 10 seconds to improve resolution. Two different software packages were used to fit the results, Jade and Winfit. Peak position and size values for both software packages are included in Table 2.

Transmission Electron Microscopy

Transmission electron microscopy (TEM) imaging was conducted using a JEOL2000FX, which incorporates a 200keV LaB₆ gun. Samples were first reduced in hydrogen at 350°C for 10hrs in a 2:1 Ar:H₂ mixture (as performed prior to catalytic activity testing) and passivated using 1%O₂ in helium passivation gas. Next, they were passed through a 75 micron sieve, and suspended in isopropyl alcohol, prior to loading onto the Lacey carbon on Cu grid, and subsequent drying. Imaging was conducted at various magnifications including 50, 100, 250 and 400K. Negatives and prints were developed, and clusters counted with size to obtain a distribution, where possible. Figures 1 a and b show a TEM micrograph and resulting particle size distribution for a fresh 0.5% Re promoted 15%Co/Al₂O₃ catalyst, while Figures 2 a and b display results for a spent 0.2% Re promoted 15%Co/Al₂O₃ catalyst sampled after reaching a steady state conversion in the CSTR.

Temperature Programmed Reduction

Temperature programmed reduction (TPR) profiles of fresh and spent catalysts were also recorded using the Zeton Altamira AMI-200 unit. Calcined fresh samples were first purged in flowing inert gas to remove traces of water. Spent catalysts were either removed from the reactor via a dip tube during the run, or sampled after completion of a run. In each case, the catalyst sampled reflected the steady state condition of the run. The wax was first extracted using xylenes in a Soxhlet apparatus and the catalyst collected in a 33mm×80mm extraction thimble. The catalyst was dried in an oven at 110°C and then reoxidized under flowing dry air

after ramping to 250°C before TPR was conducted. TPR was performed using a 10% H₂/Ar mixture and referenced to Ar. Resulting profiles were normalized to the height of the main peak so that shifts in the peak positions could be ascertained.

Results and Discussion

BET Surface Area Measurements

Table 1 displays the BET surface area results. The 15%Co catalysts loaded onto Condea Vista B Al₂O₃ had an average BET surface area of 157 m²/g. The Davisil SiO₂ supported catalysts had higher BET surface areas, with the 15% loaded catalysts on Davisil 644 SiO₂ support averaging 208 m²/g and the 15% loaded catalysts on Davisil 952 SiO₂ support averaging 229 m²/g. The 20% loaded catalysts on Davisil 952 SiO₂ support modified by ZrO₂ had a lower average BET area of 197 m²/g. Not surprisingly, the series of catalysts supported on Davisil 952 (ZYQ028 through ZYQ032) exhibited decreasing surface areas with increasing Co loading. Each 5% increase in loading yielded drops in BET surface area in the order 260, 234, 226, 190, and 170 m²/g, respectively. The 15% Co catalysts prepared on Shell 980F had an average BET surface area of 103 m²/g, while the one prepared on Shell 980G was much lower at 52.3 m²/g. The 15% cobalt catalyst on Dagussa P25 TiO₂ had the lowest BET surface area of 41.8 m²/g.

H₂ Chemisorption, XRD and TEM

Dispersion calculations were based on the assumption that the H:Co stoichiometric ratio was 1:1. In general, particle size estimates from H₂ chemisorption measurements are based on the assumption that the metal clusters are completely reduced. One determines the total number of atoms from knowledge of the weight % of loading of the metal and the surface atoms from the desorption of hydrogen. By assuming a particular geometry (e.g., a spherical or cubic structure), one is able to deduce the average cluster size. However, in our case, the assumption of complete reduction may or may not be valid, depending on the support used and type and degree of

promotion. TPR results provide a general indicator for the extent of reduction. In the case where metal oxide clusters remain on the surface during chemisorption (incomplete reduction), the cluster size determination will overestimate the cluster size. This may be particularly important for unpromoted catalysts supported on TiO_2 and Al_2O_3 , where significant metal-support effects occur. For these samples, a considerable fraction of clusters is reduced at very high temperatures in the TPR profiles. For example, assuming complete reduction for 15%Co/ Al_2O_3 leads to a value of 64 nm for the average cluster size. XRD clearly reveals, however, that the cluster is no different in size from the promoted catalysts, however, which are accurately predicted by H_2 chemisorption measurements. Despite the problem with cluster size approximation, the calculated dispersion based on hydrogen uptake should provide an accurate indicator of the number of surface atoms available for reaction, and these can be used appropriately for determining turnover numbers in catalytic testing.

Reaction testing in CSTRs has been conducted primarily on promoted 15%Co/ Al_2O_3 catalysts (ZYQ036, 039, 040, and 041). These catalysts displayed the highest uptakes of H_2 , significantly higher than that of the unpromoted catalyst (ZYQ000). Assuming complete reduction of the Co in the case of the promoted catalysts, the clusters for fresh catalysts were determined to be approximately 12 nm, 14 nm, 12 nm, and 11 nm for 0.5%Pt-15%Co/ Al_2O_3 , 0.2%Re-15%Co/ Al_2O_3 , 0.5%Re-15%Co/ Al_2O_3 , and 1%Re-15%Co/ Al_2O_3 catalysts, respectively. These values are in reasonably good agreement with the values determined by XRD and TEM. For the 0.5%Re-15%Co/ Al_2O_3 catalyst, the metal clusters were found to be primarily approximately 10 nm. For the case of XRD, to convert to the metallic particle size, the multiplier 0.75 should be used. Therefore, it appears that the XRD fitting software Jade fits the results more closely to the actual value, while Winfit apparently underestimates the cluster size.

Characterization of the spent samples was also attempted, and values are reported in parentheses. Further testing is currently being conducted to verify the validity of the results. For example, in hydrogen chemisorption, clusters must be cleaned sufficiently of wax before accurate TPD measurements are obtained. Due to time constraints, in XRD, we only scanned the range where the Co_3O_4 (311) peak occurred at a 2θ of 37. However, further tests are necessary to determine if any other species are present. For example, cobalt rhenium oxide may form after reoxidation for the case of the Re promoted catalysts. Interestingly, a new peak formed at $2\theta = 38.5$ for spent catalysts, and often dominated in intensity over the peak positioned at $2\theta = 37$. We are currently investigating the nature of this new peak, which did not appear in the case of the fresh catalysts.

Temperature Programmed Reduction

Figure 3 shows the TPR profiles for the unpromoted cobalt catalysts. For the two SiO_2 supported catalysts, two peaks emerged, attributed to the reduction of Co_3O_4 to CoO , which decomposes at higher reduction temperatures to metallic Co. As shown in the figure, the addition of surface ZrO_2 to silica did not significantly change the reducibility. In addition to the two peaks observed for the Co/SiO_2 catalysts, the TiO_2 and Al_2O_3 supported cobalt catalysts displayed broad peaks at higher temperatures, due to the metal support interaction, which increases with decreasing cluster size. For the $\text{Co/Al}_2\text{O}_3$ catalyst, an additional low temperature peak is observed, which we assign to the reduction of cobalt nitrate species. Calcining the catalyst at higher temperatures removed this low temperature (200°C) peak.. Therefore, the decomposition of Co precursors was concluded to be more difficult on Al_2O_3 support.

Figure 4 shows a TPR comparison of noble metal promoted catalysts prepared using a variety of supports. The addition of Pt or Ru to the support had a similar effect on each of the

supported catalysts. All the peaks shifted markedly to lower temperatures, presumably due to spillover of H_2 from the reduced promoter to reduce Co oxide species. Of particular importance, peaks attributed to the metal support interaction for Co species on TiO_2 and Al_2O_3 are reduced at much lower temperatures, freeing up the availability of metal atoms for reaction. For the case of Re, the reduction of Re occurs at higher temperatures than Pt or Ru. This is clearly shown in Figure 4. Although the low temperature peaks are not significantly affected, Re still plays a valuable role in reducing the reduction temperature of species for which there is a significant metal-support interaction.

Figures 5 through 12 show the effect of increasing promoter or additive loadings on the reduction temperature for different supported cobalt catalysts. Figure 5 reports the addition of Ru to the 15%Co/ SiO_2 catalysts. With the addition of 0.2% Ru, the greatest shift was found to be that of the low temperature peak which we ascribed to the reduction of Co_3O_4 to CoO. The position of the higher temperature peak assigned to further reduction of CoO to metallic increased slightly. However, further increases in promoter shifted both peaks to lower temperatures. Interestingly, further addition of Ru beyond 1% loading led to only marginal further decrease in temperature.

For the Pt series, the same atomic ratios were used as with Ru, so higher weight percentages of Pt were used. Increasing the Pt loading, in general, led to expected decreases in the reduction temperature, and lower temperatures were achieved on a molar basis with Pt relative to Ru. One exception to the trend was the 0.97% loaded catalyst. Catalysts will be tested in the future by ICP to verify weight percentages.

Figure 7 demonstrates the impact of modifying the surface of SiO_2 with ZrO_2 and incorporating noble metal promoters. As with the SiO_2 catalysts, a large shift was observed for the low temperature peak when Ru or Pt was added, while only a modest shift to lower reduction

temperatures was observed for the higher temperature peak. Interestingly, the Re promoted catalyst behaved much differently, where both peaks shifted slightly to higher temperatures. This suggests that reduction of Re occurs at much higher temperatures than the Pt or Ru catalysts.

Examination of Figure 8 reveals an interesting result when the K concentration is increased for the 15%Co/SiO₂ support. Addition of a small amount (0.5%K) to the catalyst resulted in a remarkable shift to lower temperatures for both peaks (160°C for the low temperature peak and 60°C for the high temperature peak). However, further increases in the K content shifted both peaks back up to higher temperatures, beyond the peak positions of the unpromoted reference catalyst.

Figures 9 through 12 focus on promoting Al₂O₃ support. Unlike the SiO₂ supported cobalt catalysts, there is a strong interaction of the cobalt with the support for a large fraction of the cobalt clusters. Again, evidence for this effect is demonstrated by the broad peak at high temperatures in the TPR profile for the unpromoted catalyst. Therefore, the potential for achieving gains in activity by promoting the support are high.

Figures 9 and 10 show profiles for Re promoted 15%Co/Al₂O₃ catalysts. The difference between the two series of catalysts is in the preparation. The series in Figure 9 references catalysts ZYQ039, 040 and 041, which were prepared by loading the Co three times by successive incipient wetness impregnation steps, where the catalyst was dried between each step. Only one calcination was used after the last step. Figure 10 references catalysts ZYQ051, 052, and 052. These catalysts were prepared in a similar manner, except that the each of the catalysts was calcined after each sequential impregnation and drying step, for a total of three times. Comparing Figure 10 to Figure 9 reveals that no benefit to reducibility was achieved by calcining the catalyst sequentially.

Figure 9 shows that with each increase in loading of Re promoter, the low temperature peak did not change. Again, we ascribe this to the higher reduction temperature of Re in comparison with the Ru and Pt promoters. Interestingly, however, the high temperature peak shifts markedly with each increase in the Re loading. Therefore, we conclude that after reduction temperature of Re is reached, then spillover of H_2 occurs to lower the reduction temperature of Co oxide species for which there is a significant interaction with the support.

As described earlier, both Pt and Ru promoters behave in a similar manner and shift both reduction peaks to lower temperatures for 15%Co/ Al_2O_3 . Figure 11 demonstrates that by increasing the loading of Ru, both reduction peaks shift to lower temperatures, with the effect being more pronounced for the low temperature peak. Remarkably, when a loading of 0.5% Ru is achieved, the broad high temperature peak ascribed to the interaction of the support with the metal has shifted by approximately 100°C. Unfortunately, further increases in loading, and in fact doubling the loading, shows only a marginal improvement in reducibility. Two additional catalysts were prepared incorporating La and Zr to the catalysts. However, no change in the low temperature peak was observed.

Metal-support effects were also seen for the 10%Co/ TiO_2 catalysts. Therefore, the potential benefits for increasing available metal atoms for reaction by promoting the catalyst were high. A number of different promoted catalysts were tested by TPR, and results are depicted in Figure 13. While addition of B to the catalyst had adverse effects on reducibility, the noble metals had an enhancing effect. In a similar manner with Al_2O_3 , both Pt and Ru shifted all peaks in the TPR profiles to lower temperatures, while Re only benefitted the high temperature peaks.

Although promoted catalysts displayed a higher initial activity as expected, due to increased availability of metal atoms for reaction, the deactivation rates differed greatly. In an effort to further understand the differences in deactivation patterns of promoted supported Co catalysts, we have begun to characterize the spent samples, either removed during the run by a dip tube or after the run. In each case, the catalyst was removed after a steady state conversion was achieved. Again, catalysts were sampled, the wax was removed first by extraction with xylenes in a Soxhlet apparatus, and the catalyst was oxidized in flowing dry air at 250°C.

We wished to determine if significant differences in reducibility occurred by comparing TPR profiles for the spent catalysts in reference to the fresh catalyst. We hypothesized that one route to deactivation might be if the promoter-cobalt interaction was decreased due to segregation, agglomeration, or removal by the leaching out of one or both metals as a mobile species (e.g., a metal-carbonyl). If the reducibility changed, then the TPR for the spent would become more like the TPR profile of the unpromoted catalyst. Therefore, in Figures 15 through 18, we have displayed TPR spectra of the fresh, spent, and unpromoted catalysts such that qualitative comparisons could be ascertained.

Before examining the TPR profiles of the promoted catalysts, it is instructive to first review the TPR profiles of the fresh and spent unpromoted catalysts (see Figure 14). Interestingly, both peaks shift to higher reduction temperatures, and the high temperature peak for the spent catalyst is significantly sharpened. This raises questions as to the reducibility of the Co with changes in the cluster size. XRD results indicate a decrease in cluster size for the unpromoted catalyst. One might conclude that a smaller cluster would lead to an increase in the interaction between the support and the cobalt and a shift to higher reduction temperatures in the TPR spectra.

Although Pt promotion gave the largest shifts in reduction temperature for the fresh catalysts, in comparison with other promoted catalysts such as Re and Ru, a 0.53% promoted 14.3%Co catalyst displayed a very high rate of deactivation under FTS reaction. Comparison of the TPR for the spent catalyst in reference to the fresh catalyst showed a strong shift to higher reduction temperatures. There is a strong possibility, therefore, that the metal-promoter surface interface decreases under reaction conditions. Future EXAFS investigations may reveal these changes, as EXAFS is one of the most powerful techniques available for determining local structure surrounding the atom of interest. The TPR spectra for the spent catalyst looks much more like the spectra of the unpromoted catalyst than that of the fresh.

Interesting the comparisons for Re and Ru display a much different result. For these catalysts, the reduction peaks appear near or below the peaks observed for the fresh catalysts, indicating that the metal-promoter interaction remains intact under reaction. Interestingly, these catalysts displayed lower rates of deactivation in comparison with the Pt. The peaks of the Re catalysts also were found to be sharper for the case of the spent catalysts. Again, future EXAFS, XRD, and H₂ chemisorption experiments may reveal the reason for the sharpening.

Conclusions

The activity of cobalt catalysts is generally ascribed to the active sites located on the surface of cobalt metal clusters formed after reduction of the oxidic species formed after calcination. However, the reducibility of cobalt catalysts is strongly influenced by the nature of the support and the degree of promotion by additives, which is the focus of this work. In general, a tradeoff exists as one increases the reduction temperature to activate the cobalt catalyst. Although more sites are reduced, cobalt clusters sinter at higher reduction temperatures. Therefore, TPR and hydrogen chemisorption studies should be conducted prior to catalytic testing, in order to determine the appropriate temperature for catalyst activation. In

general, the number of active sites available after reduction varies with support, promoter type, and degree of promotion. The reason for deactivation of promoted FTS catalysts is a subject requiring further study. TPR studies suggest that there is a difference in the degree of interaction of the promoter with the cobalt after reaction testing for each promoter. However, further experiments, using such techniques as EXAFS, are necessary to determine the extent of these morphological changes. Not only will EXAFS allow the determination of cluster size, but the local structure surrounding Co, including the promoter interaction, may be quantified for the fresh and spent catalysts.

The addition of Pt or Ru to the support had a similar effect on each of the fresh supported catalysts. All the reduction peak positions shifted markedly to lower temperatures, due to spillover of H₂ from the reduced promoter to reduce Co oxide species. Of particular importance, peaks attributed to the metal support interaction for Co species on TiO₂ and Al₂O₃ are reduced at much lower temperatures, freeing up the availability of metal sites for reaction. For the case of Re, the reduction of Re occurs at higher temperatures than Pt or Ru. Although the low temperature peaks are not significantly affected, Re still plays a valuable role in reducing the reduction temperature of species for which there is a significant metal-support interaction.

TPR analysis of spent promoted 15%Co/Al₂O₃ catalysts revealed that while observed peaks for Ru and Re promoted catalysts remained shifted to low temperatures, the peaks had shifted substantially to higher temperatures in the case of the Pt catalyst. This suggests that the Co and Pt interaction is rapidly lost under reaction, and may be the reason for the higher observed deactivation rate.

Table 1

Catalyst Characteristics

Sample ID	Sample Composition	Calcination	BET SA (m ₂ /g)	+/-	Avg. Pore (nm)	Additional Comments
ZYQ000	15%Co/Al ₂ O ₃	400°C, flow, 1X	157.7	0.2	4.2	IWI (3X); Condea Vista B, 100-200 mesh
ZYQ001	15%Co/SiO ₂	400°C, no flow, 1X	217.1	0.7	7.7	IWI (3X); Davisil 644 SiO ₂
ZYQ002	0.2%Ru-15%Co/SiO ₂	400°C, no flow, 1X	222.0	0.6	7.7	IWI (3X); Davisil 644 SiO ₂
ZYQ003	0.5%Ru-15%Co/SiO ₂	400°C, no flow, 1X	233.6	0.5	7.4	IWI (3X); Davisil 644 SiO ₂
ZYQ004	1.0%Ru-15%Co/SiO ₂	400°C, no flow, 1X	205.6	0.6	7.6	IWI (3X); Davisil 644 SiO ₂
ZYQ005	2.0%Ru-15%Co/SiO ₂	400°C, no flow, 1X	208.9	0.5	7.6	IWI (3X); Davisil 644 SiO ₂
ZYQ006	0.39%Pt-15%Co/SiO ₂	400°C, no flow, 1X	200.7	0.6	7.7	IWI (3X); Davisil 644 SiO ₂
ZYQ007	0.97%Pt-15%Co/SiO ₂	400°C, no flow, 1X	224.2	0.7	7.6	IWI (3X); Davisil 644 SiO ₂
ZYQ008	1.93%Pt-15%Co/SiO ₂	400°C, no flow, 1X	169.6	0.5	4.4	IWI (3X); Davisil 644 SiO ₂
ZYQ009	3.86%Pt-15%Co/SiO ₂	400°C, no flow, 1X	217.0	0.6	7.3	IWI (3X); Davisil 644 SiO ₂
ZYQ010	0.5%K-15%Co/SiO ₂	400°C, no flow, 1X	210.9	0.5	7.9	IWI (3X); Davisil 644 SiO ₂
ZYQ011	1.5%K-15%Co/SiO ₂	400°C, no flow, 1X	200.8	0.5	8.1	IWI (3X); Davisil 644 SiO ₂
ZYQ012	3.0%K-15%Co/SiO ₂	400°C, no flow, 1X	168.6	0.4	8.9	IWI (3X); Davisil 644 SiO ₂
ZYQ013	5.0%K-15%Co/SiO ₂	400°C, no flow, 1X	214.0	0.6	7.5	IWI (3X); Davisil 644 SiO ₂
ZYQ014	15%Co/SiO ₂	400°C, flow, 1X	223.9	0.6	7.5	IWI (3X); Davisil 644 SiO ₂
ZYQ015	15%Co/SiO ₂	400°C, flow, 1X	100.0	0.4	15.0	Excess H ₂ O Impreg (2X); Shell SiO ₂ 980F, 500 µm
ZYQ016	15%Co/SiO ₂	400°C, flow, 1X	103.4	0.4	15.2	Excess H ₂ O Impreg (1X); Shell SiO ₂ 980F, 500 µm

Sample ID	Sample Composition	Calcination	BET SA (m ₂ /g)	+/-	Avg. Pore (nm)	Additional Comments
ZYQ017	15%Co/SiO ₂	400°C, no flow, 1X	84.7	0.3	17.3	Excess H ₂ O Impreg (2X); Shell SiO ₂ 980F, 500 µm
ZYQ018	15%Co/SiO ₂	400°C, flow, 1X	112.3	0.3	14.8	Excess H ₂ O Impreg (2X); Shell SiO ₂ 980F, 250 µm
ZYQ019	15%Co/SiO ₂	400°C, flow, 1X	114.2	0.4	15.3	Excess H ₂ O Impreg (2X); Shell SiO ₂ 980F, 150 µm
ZYQ020	15%Co/SiO ₂	400°C, flow, 1X	105.5	0.4	15.8	Excess H ₂ O Impreg (2X); Shell SiO ₂ 980F, 50 µm
ZYQ021	15%Co/SiO ₂	400°C, flow, 1X	52.3	0.2	10.9	IWI (3X); S 980G 2.3, 60-200 mesh
ZYQ022	15%Co/Al ₂ O ₃	400°C, flow, 1X	171.3	0.7	2.0	IWI (3X); Condea Vista B, 100-200 mesh
ZYQ023	15%Co/SiO ₂	400°C, flow, 1X	231.9	0.8	7.2	IWI (3X); Davisil 952 SiO ₂
ZYQ024	15%Co/TiO ₂	400°C, flow, 1X	41.8	0.2	12.3	IWI (3X); Degussa TiO ₂ (P25), 100-200 mesh
ZYQ025	15%Co/SiO ₂	400°C, flow, interval 3X	226.0	0.7	9.1	IWI (3X); Davisil 952 SiO ₂
ZYQ026	15%Co/SiO ₂	400°C, flow, 1X	229.3	0.5	7.3	IWI (3X); Davisil 644 SiO ₂
ZYQ027	15%Co/SiO ₂	400°C, flow, 1X	240.1	0.7	9.3	Excess H ₂ O Impreg (2X); Davisil 952 SiO ₂
ZYQ028	5%Co/SiO ₂	400°C, no flow, 1X	259.7	1.0	10.0	IWI (1X); Davisil 952 SiO ₂ , 60-80 mesh
ZYQ029	10%Co/SiO ₂	400°C, no flow, 1X	234.1	0.9	9.8	IWI (2X); Davisil 952 SiO ₂ , 60-80 mesh
ZYQ030	15%Co/SiO ₂	400°C, no flow, 1X	226.3	0.7	9.6	IWI (3X); Davisil 952 SiO ₂ , 60-80 mesh
ZYQ031	20%Co/SiO ₂	400°C, no flow, 1X	190.0	0.5	9.0	IWI (4X); Davisil 952 SiO ₂ , 60-80 mesh
ZYQ032	25%Co/SiO ₂	400°C, no flow, 1X	170.0	0.6	7.8	IWI (5X); Davisil 952 SiO ₂ , 60-80 mesh
ZYQ036	0.53%Pt-14.3%Co/Al ₂ O ₃	400°C, flow, 1X	161.6	0.2	4.1	IWI (3X); Condea Vista B, 100-200 mesh
ZYQ037	5%La-15%Co/Al ₂ O ₃	400°C, flow, 1X	155.1	0.2	3.9	IWI (3X); Condea Vista B, 100-200 mesh
ZYQ038	15%Zr-15%Co/Al ₂ O ₃	400°C, flow, 1X	160.9	0.1	4.1	IWI (3X); Condea Vista B, 100-200 mesh
ZYQ039	0.2%Re-15%Co/Al ₂ O ₃	400°C, flow, 1X	156.5	0.2	4.2	IWI (3X); Condea Vista B, 100-200 mesh

Sample ID	Sample Composition	Calcination	BET SA (m ₂ /g)	+/-	Avg. Pore (nm)	Additional Comments
ZYQ040	0.5% Re-15% Co/Al ₂ O ₃	400°C, flow, 1X	136.7	0.2	3.8	IWI (3X); Condea Vista B, 100-200 mesh
ZYQ041	1.0% Re-15% Co/Al ₂ O ₃	400°C, flow, 1X	187.7	0.2	4.0	IWI (3X); Condea Vista B, 100-200 mesh
ZYQ042	20% Co/ZrO ₂ -SiO ₂	400°C, flow, 1X	200.0	0.6	8.8	IWI (3X); Davisil 952 SiO ₂ , 60-80 mesh
ZYQ043	0.5% Ru-20% Co/ZrO ₂ -SiO ₂	400°C, flow, 1X	197.0	0.6	8.4	IWI (3X); Davisil 952 SiO ₂ , 60-80 mesh
ZYQ044	0.5% Pt-20% Co/ZrO ₂ -SiO ₂	400°C, flow, 1X	205.5	0.6	9.2	IWI (3X); Davisil 952 SiO ₂ , 60-80 mesh
ZYQ045	0.5% Re-20% Co/ZrO ₂ -SiO ₂	400°C, flow, 1X	191.9	0.6	8.9	IWI (3X); Davisil 952 SiO ₂ , 60-80 mesh
ZYQ050	0.5% Ru-15% Co/Al ₂ O ₃	400°C, flow, interval 3X	161.0	0.2	3.2	IWI (3X); Davisil 952 SiO ₂ , 60-80 mesh
ZYQ051	0.2% Re-15% Co/Al ₂ O ₃	400°C, flow, interval 3X	148.2	0.1	4.0	IWI (3X); Davisil 952 SiO ₂ , 60-80 mesh
ZYQ052	0.5% Re-15% Co/Al ₂ O ₃	400°C, flow, interval 3X	151.8	0.1	4.1	IWI (3X); Davisil 952 SiO ₂ , 60-80 mesh
ZYQ053	2% Re-15% Co/Al ₂ O ₃	400°C, flow, interval 3X	153.3	0.1	3.9	IWI (3X); Davisil 952 SiO ₂ , 60-80 mesh
ZYQ054	0.2% Ru-15% Co/Al ₂ O ₃	400°C, flow, interval 3X	153.8	0.1	4.0	IWI (3X); Davisil 952 SiO ₂ , 60-80 mesh
ZYQ055	1% Ru-15% Co/Al ₂ O ₃	400°C, flow, interval 3X	159.1	0.2	3.1	IWI (3X); Davisil 952 SiO ₂ , 60-80 mesh
LIJ001	10% Co/TiO ₂	300°C, no flow, 1X	---	---	---	IWI: Degussa TiO ₂ P25
LIJ002	10% Co-0.1% B/TiO ₂	300°C, no flow, 1X	---	---	---	IWI: Degussa TiO ₂ P25
LIJ003	10% Co-0.2% Ru/TiO ₂	300°C, no flow, 1X	---	---	---	IWI: Degussa TiO ₂ P25
LIJ004	0.2% Ru-10% Co-0.1% B/TiO ₂	300°C, no flow, 1X	---	---	---	IWI: Degussa TiO ₂ P25
LIJ005	10% Co-0.37% Re/TiO ₂	300°C, no flow, 1X	---	---	---	IWI: Degussa TiO ₂ P25
LIJ006	10% Co-0.39% Pt/TiO ₂	300°C, no flow, 1X	---	---	---	IWI: Degussa TiO ₂ P25

Table 2
Hydrogen Chemisorption and XRD Results

Sample ID	Sample Composition	H ₂ Chemisorption % Dispersion	2θ	XRD Co ₃ O ₄ (311) Jade (nm)	XRD Co ₃ O ₄ (311) Winfit (nm)
ZYQ000	15%Co/Al ₂ O ₃	2.40	37.0 (36.9)	18.3 (9.7)	10.3 (6.3)
ZYQ001	15%CoSiO ₂	0.85	---	---	---
ZYQ007	0.97%Pt-15%Co/SiO ₂	1.24	---	---	---
ZYQ022	15%Co/Al ₂ O ₃	3.03	---	---	---
ZYQ036	0.53%Pt-14.3%Co/Al ₂ O ₃	9.02	37.4 (17.3, 38.6)	13.7 (11.6, 24.5)	9.7 (6.2, 14.4)
ZYQ039	0.2%Re-15%Co/Al ₂ O ₃	7.59 (spent 6.23)	37.0 (36.8, 38.4)	12.5 (6.1, ---)	10.2 (4.9, 20.1)
ZYQ040	0.5%Re-15%Co/Al ₂ O ₃	9.07	---	---	---
ZYQ041	1.0%Re-15%Co/Al ₂ O ₃	9.88 (spent 10.73)	37.1 (37.0, 38.5)	13.0 (8.4)	9.3 (3.3, 32.2)
ZYQ044	0.5%Pt-20%Co/ZrO ₂ -SiO ₂	0.98	---	---	---
ZYQ050	0.5%Ru-15%Co/Al ₂ O ₃	5.00	37.1 (37.1)	---	9.9 (3.0)
ZYQ052	0.5%Re-15%Co/Al ₂ O ₃	5.59	---	---	---
ZYQ053	2%Re-15%Co/Al ₂ O ₃	6.25	---	---	---
ZYQ054	0.2%Ru-15%Co/Al ₂ O ₃	5.58	---	---	---
ZYQ055	1%Ru-15%Co/Al ₂ O ₃	7.11	---	---	---
LIJ001	10%Co/TiO ₂	3.64	---	---	---
LIJ002	10%Co-0.1%B/TiO ₂	3.19	---	---	---
LIJ003	10%Co-0.2Ru/TiO ₂	4.46	---	---	---
LIJ004	0.2%Ru-10%Co-0.1%B/TiO ₂	5.12	---	---	---
LIJ005	10%Co-0.37%Re/TiO ₂	4.78	---	---	---
LIJ006	10%Co-0.39%Pt/TiO ₂	5.11	---	---	---

Figure 1a. TEM micrographs for a 0.5% Re promoted 15%Co/Al₂O₃ fresh catalyst.

Figure 1b. Particle size distribution from analysis of TEM micrographs for a 0.5% Re promoted fresh 15%CoAl₂O₃ catalyst.

Figure 2a. TEM micrographs for a 0.2% Re promoted 15%Co/Al₂O₃ fresh catalyst.

Figure 2b. Particle size distribution from analysis of TEM micrographs for a 0.2% Re promoted 15%Co/Al₂O₃ spent catalyst sampled after reaching a steady-state conversion in the CSTR.

Figure 3. TPR of unpromoted Co catalysts.

Figure 4. TPR of noble metal promoted Co catalysts.

Figure 5. Effect of increasing Ru promoter loading on the reduction temperature of 15%Co/SiO₂.

Figure 6. Effect of increasing Pt promoter loading on the reduction temperature of 15%Co/SiO₂.

Figure 7. Effect of noble metal promoter type on the reduction temperature of 20%Co/ZrO₂-SiO₂.

Figure 8. Effect of increasing K additive loading on the reduction temperature of 15%Co/SiO₂.

Figure 9. Effect of increasing Re promoter loading on the reduction temperature of 15%Co/Al₂O₃ (three interval drying steps and one final calcination step).

Figure 10. Effect of increasing Re promoter loading on the reduction temperature of 15%Co/Al₂O₃ (three interval drying steps and three interval calcination steps).

Figure 11. Effect of increasing Ru promoter loading on the reduction temperature of 15%Co/Al₂O₃.

Figure 12. Effect of La or Zr additive on the reduction temperature of 15%Co/Al₂O₃.

Figure 13. Effect of promoter addition on the reduction temperature of 10%Co/TiO₂.

Figure 14. TPR profiles of fresh and spent unpromoted 15%Co/Al₂O₃ catalysts.

Figure 15. TPR profiles of fresh and spent 14.3%Co/Al₂O₃ catalysts promoted by 0.53% Pt referenced to the unpromoted fresh 15%Co/Al₂O₃ catalyst.

Figure 16. TPR profiles of fresh and spent 15%Co/Al₂O₃ catalysts promoted by 0.2% Re referenced to the unpromoted fresh 15%Co/Al₂O₃ catalyst.

Figure 17. TPR profiles of fresh and spent 15%Co/Al₂O₃ catalysts promoted by 0.2% Re referenced to the unpromoted fresh 15%Co/al₂O₃ catalyst.

Figure 18. TPR profiles of fresh and spent 15%Co/Al₂O₃ catalysts promoted by 0.5% Ru referenced to the unpromoted fresh 15%Co/Al₂O₃ catalyst.

F. Fischer Tropsch Synthesis: Support, Loading, and Promoter Effects on the Reducibility of Cobalt Catalysts

Abstract

Temperature programmed reduction (TPR) and hydrogen chemisorption combined with reoxidation measurements were used to define the reducibility of supported cobalt catalysts. Different supports (e.g., Al_2O_3 , TiO_2 , SiO_2 , and ZrO_2 modified SiO_2 or Al_2O_3) and a variety of promoters, including noble metals and metal cations, were examined. Significant support interactions on the reduction of cobalt oxide species were observed in the order $\text{Al}_2\text{O}_3 > \text{TiO}_2 > \text{SiO}_2$. Addition of Ru and Pt exhibited a similar catalytic effect by decreasing the reduction temperature of cobalt oxide species, and for Co species where a significant surface interaction with the support was present, while Re impacted mainly the reduction of Co species interacting with the support. For catalysts reduced at the same temperature, a slight decrease in cluster size was observed in H_2 chemisorption/pulse reoxidation with noble metal promotion, indicating that the promoter aided in reducing smaller Co species that interacted with the support. On the other hand, addition of non-reducible metal oxides such as B, La, Zr, and K was found to cause the reduction temperature of Co species to shift to higher temperatures, resulting in a decrease in the percentage reduction. For both Al_2O_3 and SiO_2 , modifying the support with Zr was found to enhance the dispersion. Increasing the cobalt loading, and therefore the average Co cluster size, resulted in improvements to the percentage reduction. Finally, a slurry phase impregnation method led to improvements in the reduction profile of $\text{Co}/\text{Al}_2\text{O}_3$.

Keywords: alumina, cobalt, Fischer-Tropsch synthesis, metal-support effects, TPR, TPD, promoters

Introduction

Supported cobalt catalysts are important for the Fischer-Tropsch synthesis of high molecular weight, paraffinic waxes, which can be hydrocracked to produce lubricants and diesel fuels. One important focus in the development of this process is the improvement of the catalyst activity by increasing the number of active Co metal sites that are stable under reaction conditions. Therefore, it is important to understand how the structural parameters of the catalyst influence the activity and stability of catalysts. For example, to improve the number of active sites, the Co is most often present as dispersed clusters on a high surface area support such as SiO_2 , TiO_2 , or Al_2O_3 . In this particular study, it is observed that not only does choice of support largely determine the number of active sites stabilized after reduction, but it also strongly influences the percentage of the cobalt oxide species that can be reduced. Therefore, for a reduction temperature of 623 K, which is a typical standard reduction temperature for Co FTS catalysts, a tradeoff exists between the cobalt dispersion and the percentage of cobalt oxide species reduced. Supports such as SiO_2 , which yield a large cluster size, offer the highest percentage reduction at 623 K, while supports like Al_2O_3 , which stabilize a smaller cluster size, have significant support interactions which impede the reduction. That is, after reduction at 623 K for 10 h, a significant fraction of the Co oxide species interacting with the support remains in a non-reduced state.

In order to gain access to the active sites, noble metal promoters are often employed. These noble metal promoters, such as Pt or Ru, reduce at a lower temperature than the cobalt oxides, and catalyze cobalt reduction, presumably by hydrogen spillover from the promoter surface [1-12]. Thus, addition of small amounts of noble metal shifts the reduction temperature of cobalt oxides and cobalt species interacting with the support to lower temperatures. Due to the added expense of the promoter, it is important to determine the appropriate loading of

promoter to maximize the availability of active cobalt surface sites for participation in the reaction, after catalyst activation. In this work, we have studied the addition of Pt, Ru, and Re to a number of different supported Co catalysts.

Textural promoters, such as catalyst supports and support modifiers, are used typically to increase the dispersion of the clusters, improve attrition resistance, enhance sulfur tolerance, or electronically modify the active metal site. In this work, a number of different metal oxide promoters are incorporated to increase dispersion and/or improve attrition resistance. These modifiers, added by impregnation and calcination, included Zr, La, B, and K. The aim of this part of the study is to determine if addition of textural promoters influence significantly the reducibility of the Co oxide clusters.

Due to its high resistance to attrition in the continuously stirred tank reactor (CSTR) or slurry bubble column reactor (SBCR) and its ability to stabilize a small cluster size, Al_2O_3 is a particularly appealing support for Co based FTS catalysts [13]. However, due to the strong interactions of Co species with the support, more insight is needed in understanding the effect of the loading and size distribution on both the reducibility and the stability of these clusters during FTS. In this work, TPR and H_2 TPD/reoxidation are used to examine a series of $\text{Co}/\text{Al}_2\text{O}_3$ catalysts prepared with different loadings by an incipient wetness impregnation (IWI) method. Finally, a catalyst prepared by IWI with a nominal loading of 25% Co was compared with a catalyst prepared by a slurry impregnation method following a Sasol patent. As is evident from this work, each parameter plays an important role in the accessing of Co metal sites for reaction.

H_2 TPD followed by pulse reoxidation is a useful technique [11], because it quantifies the actual dispersion (cluster size) by taking into account the percentage reduction of cobalt. The desorption of chemisorbed hydrogen yields an active site count, while the uptake of oxygen for

the reduced catalyst at high temperature provides an estimate of the percentage of cobalt metal that was reduced. Combined, the dispersion is determined as follows:

%Dispersion

$$= (\text{\#Co}^0 \text{ atoms on surface} \times 100) / (\text{total \# Co}^0 \text{ atoms})$$

$$= (\text{\#Co}^0 \text{ atoms on surface} \times 100) / (\text{total \# Co atoms in sample})(\text{fraction reduced})$$

Defining the dispersion in this way, an estimate of the actual cluster size can be determined. Without including the percentage of reduction in the calculation, the percentage dispersion is underestimated and, therefore, the resulting cluster size will be overestimated. This correction to the dispersion becomes particularly important in the study of promoted catalysts.

Experimental

Catalyst Preparation

Davisil silica gel 644 (100-200 mesh, surface area 300 m²/g, pore volume 1.15 cm³/g), Degussa P25 titania (120-200 mesh, surface area 45 m²/g, 0.50 cm³/g), Condea Vista Catalox B γ -alumina (100-200 mesh, 200 m²/g, pore volume 0.4 cm³/g) and zirconia modified Davisil 952 silica (60-80 mesh, 309 m²/g, pore volume 1.61 cm³/g) were used as support materials for the preparation of cobalt FTS catalysts. The support was calcined at 673 K. Cobalt loadings of 10, 15, 20 and 25% were used. For example, a three-step incipient wetness impregnation method was used to add a total of 15 wt % cobalt to the supports, with a drying procedure at 353K in a rotary evaporator following each impregnation. Noble metal promoted catalysts were prepared with different loadings of ruthenium, platinum, or rhenium by adding the noble metal solution after cobalt addition and prior to calcination. Additional metal cation promoted catalysts were prepared by incorporating boron, potassium, zirconium, or lanthanum to the support after adding

cobalt and prior to calcination. Following cobalt addition, the promoter was added by incipient wetness impregnation. The precursors utilized for noble metal addition were ruthenium nitrosyl nitrate, tetraammineplatinum (II) nitrate, and rhenium oxide. For the metal cation precursors, boric acid, potassium carbonate, zirconium nitrate, and lanthanum nitrate were employed. After promoter addition, the catalysts were again dried in a rotary evaporator at 353 K. Catalysts were calcined only one time in air at 673 K for 4 hrs following the final impregnation step. One exception was the boron promoted TiO_2 catalyst, where the boric acid precursor was added to the support and calcined prior to cobalt addition.

To understand the influence of loading of Co on the reducibility of clusters, a series of Co/ Al_2O_3 catalysts was prepared by IWI following the procedure outlined above. The catalysts were prepared on 100 m^2/g , 150 m^2/g , and 200 m^2/g Condea Vista Catalox (or Puralox) B γ - Al_2O_3 supports and the Co loading was approximately 15%, 25%, and 33%, respectively. Multiple impregnations of 5% Co were performed with drying steps in a rotary evaporator. Finally one calcination step was employed after the final impregnation.

One Co/ Al_2O_3 catalyst with a loading of 25% was also prepared by a slurry impregnation method. In this method, which follows a Sasol patent [13], the ratio of the volume of loading solution used to the weight of alumina was 1:1, such that approximately 2.5 times the pore volume of solution was used to prepare the catalyst. Two impregnation steps were used to load 12.5% of Co by weight. Between each step the catalyst was dried under vacuum in a rotary evaporator at 333 K and the temperature was slowly increased to 373 K. After the second impregnation/drying step, the catalyst was calcined in the usual manner.

To study the effect of calcination procedure on noble metal promoted catalysts, a series of catalysts with different loadings of Re was prepared where the catalyst was calcined after each sequential impregnation of 5% Co (total of 3 times) after drying and one more time after loading

of the Re promoter. This series of catalysts is labeled “with interval calcination”. The Re promoted catalysts prepared by the standard procedure, where there was only one calcination after loading both Co and promoter, are labeled “without interval calcination procedure.”

Inductively Coupled Plasma

Inductively coupled plasma (ICP) was used to obtain weight percentages of Co metal in the sample. First, the catalyst powder was dissolved in a mixture of aqua regia and HF. A nebulizer was used to introduce the sample to the plasma torch at a diameter of less than 10 microns in Ar carrier. The torch is located in an induction coil, carrying high frequency AC. The electrically conducting ionized gas was thus heated by Joule’s effect to temperatures in the vicinity of 10,000 K. Under these conditions, the particles were atomized and partially ionized. When reverting to lower energy states, photons were emitted and detected for element analysis. A Spectrametrics ICP unit was utilized to verify the Co loadings and for the Zr loadings in the case of the supports modified by ZrO_2 .

BET Surface Area Measurements/BJH Pore Size Distributions

The surface area, pore volume, and average pore radius of the supports and catalysts were measured by BET using a Micromeritics Tri-Star system. Prior to the measurement, the sample was slowly ramped to 433K and evacuated for 4hrs to approximately 6.7 Pa. Results of physisorption measurements are shown in Tables 1 and 2. Pore size distributions (PSD) of a number of supports and catalysts were also quantified by the Barrett, Joyner, Halenda (BJH) desorption model, which provides a relationship where the amount of adsorbate lost during a desorption step gives the average size of the pore emptied during that desorption step. Experimentally, the adsorption branches were employed, and PSDs are shown in Figure 1. Cumulative pore volumes from BJH adsorption/desorption are also given in Tables 1 and 2.

Temperature Programmed Reduction

Temperature programmed reduction (TPR) profiles of catalysts were recorded using a Zeton Altamira AMI-200 unit. Calcined fresh samples were first purged in flowing inert gas to remove traces of water. TPR was performed using a 10% H₂/Ar mixture referenced to Ar at a flowrate of 30 ccm. The sample was heated from 323 K to 1073 K using a heating ramp of 10 K/min.

H₂ Chemisorption by TPD and % Reduction by Reoxidation

The amount of chemisorbed hydrogen was measured using the Zeton Altamira AMI-200 unit, which incorporates a thermal conductivity detector (TCD). The sample weight was always 0.220 g. A typical catalyst was activated using hydrogen at the desired reduction temperature (573 K for TiO₂ and 623 K for other catalysts) for 10 hrs and cooled under flowing hydrogen to 373 K. The sample was held at 373 K under flowing argon to remove physisorbed and/or weakly bound species, prior to increasing the temperature slowly to the reduction temperature. At that temperature, the catalyst was held under flowing argon to desorb the remaining chemisorbed hydrogen until the TCD signal returned to the baseline. The TPD spectrum was integrated and the number of moles of desorbed hydrogen determined by comparing to the areas of calibration pulses of hydrogen in argon. Prior to experiments, the sample loop was calibrated with pulses of N₂ in a helium flow and compared against a calibration line produced from using gas tight syringe injections of N₂ into a helium flow.

After TPD of H₂, the sample was reoxidized [11] at the activation temperature by pulses of pure O₂ in helium carrier referenced to helium gas. After oxidation of the cobalt metal clusters (when the entire O₂ pulse was observed by the TCD), the number of moles of O₂ consumed was determined, and the percentage reduction was calculated assuming that Co⁰ reoxidized to Co₃O₄.

The calculations are summarized below:

$$\text{Calibration Value (L gas/Area Units)} = (\text{Loop Volume} \times \% \text{ Analytical Gas}) / (\text{Mean Calibration Area} \times 100)$$

$$\text{H}_2 \text{ Uptake (moles/g cat)} = (\text{Analytical Area from TPD} \times \text{Calibration Value}) / (\text{Sample Weight} \times 24.5)$$

$$\begin{aligned} \% \text{ Dispersion} &= (\text{H}_2 \text{ uptake} \times \text{Atomic Weight} \times \text{Stoichiometry}) / (\% \text{ Metal}) \\ &= (\text{Number Co}^0 \text{ Atoms on Surface} \times 100) / (\text{Total Number Co}^0 \text{ Atoms}) \end{aligned}$$

$$= (\text{Number Co}^0 \text{ Atoms on Surface} \times 100) / (\text{Total Number Co Atoms in Sample} \times \text{Fraction Reduced})$$

$$\text{O}_2 \text{ Uptake (moles/g cat)} = (\text{Sum of Consumed Pulse Areas} \times \text{Calib Value}) / (\text{Sample Weight} \times 24.5)$$

$$\text{Assuming } \text{Co}^0 + 2/3\text{O}_2 = 1/3\text{Co}_3\text{O}_4,$$

$$\text{Fraction Reduced} = (\text{O}_2 \text{ uptake} \times 2/3 \times \text{atomic weight}) / (\% \text{ metal})$$

$$\text{Diameter of Spherical Crystallite} = 6000 / (\text{density} \times \text{maximum area} \times \text{Dispersion})$$

Results and Discussion

Surface Area Measurements

Results of surface area measurements by adsorption of nitrogen at 77 K (Tables 1 and 2) show that the BET surface areas for the 15% loaded Co catalysts on 200 m²/g γ -Al₂O₃ were all close to 160 m²/g. A weight % loading of 15% metal is equivalent to 20% by weight Co₃O₄. If the Al₂O₃ is the only contributor to the area, then the area of the Co/Al₂O₃ catalysts should be 0.80 × 200 m²/g = 160 m²/g, which matches the measured value. Similarly, with the 15% loaded Co catalysts on 311 m²/g 644 Davisil SiO₂ and the 20% Co loaded catalysts on 295 m²/g 952 Davisil SiO₂, the BET areas should be approximately 0.80 × 311 m²/g = 249 m²/g and 0.73 × 295

$\text{m}^2/\text{g} = 215 \text{ m}^2/\text{g}$, respectively. However, the values are somewhat lower (approximately $210 \text{ m}^2/\text{g}$ and $200 \text{ m}^2/\text{g}$, respectively), which indicates some pore blockage by cobalt oxide clusters. Finally, for the 10% loaded Co catalysts on $45 \text{ m}^2/\text{g}$ Degussa P25 TiO_2 , the BET areas should be approximately $0.87 \times 45 \text{ m}^2/\text{g} = 39 \text{ m}^2/\text{g}$, very close to the measured values. In Table 2, which displays the Co/ Al_2O_3 catalysts with different loadings on three different surface area supports, the increase in average pore size for the highest loading of approximately 33% indicates that some pore blockage of the smaller pores occurred.

Support Effects

Figure 2(a) shows the TPR profiles for the unpromoted cobalt catalysts. For the two SiO_2 supported catalysts, two peaks are apparent and these are attributed to the reduction of Co_3O_4 to CoO, which then reduces at higher temperatures to metallic Co^0 , as observed for reduction of bulk cobalt oxide Co_3O_4 . As shown in the figure, the addition of surface ZrO_2 to silica did not significantly affect the reducibility, although there may have been a slight shift to higher temperatures. The TiO_2 and Al_2O_3 supported cobalt catalysts displayed broad peaks at temperatures that are higher than observed for silica, due to the interaction of the Co surface species with the support.

Figure 2(b) shows the TPR of the 15% Co/ Al_2O_3 catalyst directly after calcination, and another after it was reduced at 623 K for 10 hrs. By taking the difference of the two TPR spectra, it is observed that only a small fraction of the Co surface species responsible for the broad peak is reduced during the standard reduction procedure at 623 K for 10 hours.

In the TPR, the temperature was not ramped high enough to observe the reduction of bulk cobalt aluminate species, which has been shown to occur above 1073 K with up to 30% loading of cobalt [14]. Therefore, the broad peak on the unpromoted catalyst (ca. 700 to 1000 K) is attributed to the reduction of Co surface species that interact with the support, and the different

shoulders are likely due to varying degrees of interaction with the support as a function of cluster size. The smallest Co surface species, with the greatest interaction with the support, are therefore likely represented by the shoulder at 950 K. The precise identity of these species is not clear, although it is surmised that the species are either the result of a strong interaction between very small cobalt oxide clusters and the support (deviating from bulklike cobalt oxides and reducing at higher temperatures than the bulk oxides) or small surface Co species which include support atoms in the structure (reducing at temperatures below that of bulk Co-aluminate). Hereafter, the species responsible for this peak will be referred to loosely as “Co surface support species”.

Al₂O₃ supported Co Catalysts

Influence of Co Loading

As the cobalt loading is increased, important changes in the degree of interaction of the cobalt species with the support are observed. Figure 2(c) shows a reduction profile for the 25% Co/Al₂O₃ catalyst prepared by IWI. In contrast with the 15% loaded catalyst, there is a remarkable decrease in the intensity of the reduction shoulder at 950 K, while there is the appearance of a sharp peak at 600 K. These differences are attributed to the increase in the average cluster size and the resulting loss of interaction with the support. The 25% Co catalyst starts to resemble the two step reduction of bulklike Co₃O₄. Again, a TPR was conducted following the 10 h standard reduction at 623 K, and the catalyst showed a higher percentage reduction, indicated by the smaller peaks remaining after difference in comparison with the 15% loaded Co catalyst (Figure 2(b)).

These changes in reducibility become more apparent when considering several catalysts prepared with different loadings by IWI on three different surface area γ -Al₂O₃ supports, as shown in Figure 3. Moving upward from the 15% loaded catalyst prepared on 200 m²/g to the

150 m²/g support, the low temperature peak of the profile is shifted by 60 K. At a loading of approximately 25% and higher, there is the appearance and sharp growth in a peak at 600 K, which is attributed to the reduction of bulklike CoO species. Also, the maximum in the broad peak shifts stepwise to lower temperature with loss in interaction due to (1) increased loading resulting in increased cluster size or (2) lower support surface area. As expected, the highest loaded catalyst (34.3%) on the lowest surface area support (100 m²/g) showed the greatest resemblance to reduction of bulk Co₃O₄.

In agreement with the results of TPR, H₂ chemisorption/pulse reoxidation results in Table 3 indicate that improvements in the percentage reduction are obtained by increasing the average cluster size by either increasing loading or switching to lower surface area supports with the same loading. The results also stress the importance of including the percentage of reduction measurement in the dispersion calculation, so that the actual number of total Co metal atoms in the sample are used in the denominator, instead of the total Co atoms, as shown below.

$$\% D = \frac{\text{Number Co}^{\circ} \text{ atoms on surface} \times 100}{\text{total number Co}^{\circ} \text{ atoms}} = \frac{\text{Number Co}^{\circ} \text{ atoms on surface} \times 100}{(\text{total number Co atoms})(\text{fraction reduced})}$$

This correction is important in the study of promoters to follow.

Slurry Phase Impregnation

The reduction profile of the 15% Co catalyst prepared by the standard IWI method indicates heterogeneity of oxide cluster size, with each cluster size yielding a different interaction with the support, resulting in a broad reduction peak with a high temperature shoulder. The average cluster size was significantly less than 10 nm, within the size range reported to undergo deactivation by oxidation under FTS conditions in the reactor [15,16].

However, increasing the loading by IWI indicates an even wider range of cluster size, as a sharp shoulder occurs at 600 K corresponding to reduction of bulklike CoO.

Using a slurry phase impregnation method following a recipe in a Sasol patent, an attempt was made to decrease the heterogeneity in cluster size distribution, while maintaining the cluster size above the 10 nm threshold by keeping the loading at 25%. As shown in Figure 4, the sharp peak at 600 K generated by the IWI catalyst is not present in the catalyst prepared by the slurry method. Results of H₂-chemisorption/pulse reoxidation in Tables 3 and 4 indicate that while the average cluster size on the IWI was 13.7 nm, the slurry method catalyst was only slightly lower, at 11.8 nm.

Cluster Resistance to Reduction Treatment

Table 5 shows the results of an experiment where the 15% Co/Al₂O₃ catalyst was ramped by 1 K/min to a desired reduction temperature and then held for 10 h for reduction in hydrogen. The catalyst was then cooled to 373 K and ramped by 10 K/min to the treatment temperature in Ar to desorb the chemisorbed H₂. Each TPD of H₂ was followed by pulse reoxidation. This proceeded in a stepwise manner for reduction temperatures of 473 K, 573 K, 673 K, 773 K and 873 K. Afterwards, a fresh sample was analyzed by ramping directly to 773 K by 1 K/min and reduced for 10 h at 773 K. TPD and pulse reoxidation were conducted in the same manner. Without considering the fraction of cobalt that is reduced, there is a gradual decrease in the average cluster size as the reduction temperature is increased (Table 5). However, the results in Table 5 demonstrate that the corrected average cluster size does not change significantly after reduction at each temperature. Rather, pulse reoxidation reveals that the percentage reduction changes at each step, increasing greatly the number of sites available for reaction. Changing the heating rate (direct heating versus slow ramp and hold) may cause some growth of the cluster, 6.2 nm for direct versus 5.6 nm for ramp and hold. It appears that the smaller particles are being

reduced using the ramp and hold procedure as the temperature is increased since there is a progressive decrease in average particle size: 5.9 nm, 673 K; 5.6 nm, 773 K; and 5.2 nm, 873 K. The only exception is the first value reported after reduction at 573 K. However, comparing this reduction temperature with the TPR spectra indicates that the entire cluster may not be reduced. Therefore, a lower value of the average cluster size at this temperature may be indicative of partial reduction of the cluster.

Promotion by Pt

Figure 5 shows a TPR comparison of Pt promoted Co/Al₂O₃ with the unpromoted catalysts at two different loadings of cobalt – 15% prepared by IWI and 25% prepared by the slurry impregnation method. The addition of Pt caused the peaks to shift markedly to lower temperatures, presumably due to spillover of H₂ from the metallic promoter to reduce the Co oxide and Co surface support species. Of particular importance, peaks attributed to the reduction of Co surface support species [17] are reduced at lower temperatures (ca. 100 K shift), freeing up the availability of metal atoms for catalytic reaction.

Results of H₂ chemisorption by TPD (Table 4) indicate that the number of surface sites increases with addition of the Pt promoter. By performing pulse reoxidation, it is clear that the gain in Co⁰ site density is mainly due to an enhancement in the reducibility of the clusters, and not to improvements in the actual dispersion (cluster size) of the reduced cobalt. However, for both the 15% and 25% cobalt catalysts, addition of Pt appears to cause a slight decrease in the cluster size. This is reasonable, because the comparison was conducted at the same reduction temperature of 623 K, and addition of Pt should cause a fraction of the smaller Co surface species that interact with the support to be reduced in this temperature range, resulting in a slightly smaller average cluster size.

Increasing the Co loading alone caused a lowering of the reduction temperature of both the unpromoted and especially so for the promoted catalysts, as observed previously [14]. With the promoted catalyst, for example, the maximum for the peak attributed to the reduction of Co surface species interacting with the support decreased by 35 K (from 760 K to 725 K), while the lower temperature peak attributed to reduction of cobalt oxides shifted by 70 K (from 500 K to 430 K). Results of H₂ chemisorption by TPD and pulse reoxidation (Table 4) revealed that, for both unpromoted and promoted catalysts, there were significant increases (from 30% to 42% for unpromoted and from 60% to 71% for promoted) in the percentage reduction of the catalyst, with a doubling of the average cluster size. These findings are in agreement with a previous investigation [18].

Promoter Addition and Calcination Pretreatment Effects

The addition of Ru to the catalyst had a similar effect on the TPR as Pt did. Figure 6 shows that addition of 0.2 wt % Ru results in an improvement in the reducibility of the catalyst, but that increasing the promoter loading above 0.5 wt % only resulted in marginal enhancement. As with the case of Pt, H₂ chemisorption (Table 4) indicates that addition of 1% Ru has a greater impact on the cobalt reducibility than the dispersion, resulting in an almost twofold improvement in the number of active sites available for reaction after reduction at 623 K, while maintaining essentially the same average particle size.

The reduction of Re oxide occurs at a higher temperature than Pt oxide or Ru oxide. Figure 6 shows that although there appears to be no improvement in the reduction of the low temperature peak assigned to the reduction of cobalt oxides, Re still plays a role by decreasing the reduction temperature of Co species for which there is a significant surface interaction with the support. The reduction of Co oxides appears as the low temperature shoulder to the sharp peak for reduction of the Co surface support species with the addition of Re. Figure 6 shows that

Re oxide reduces at 620 K, which explains the lack of effect on the low temperature peak responsible for reduction of cobalt oxides. A previous study of promotion of cobalt catalysts by Re [12] found that rhenium oxide on alumina reduced at approximately 698 K, a value that falls between our two TPR peaks for the unpromoted Co/Al₂O₃ catalyst. TPR profiles in Figure 6 show that cobalt oxide crystallites have essentially been reduced before the Re oxide is reduced, so no spillover effect can operate to aid in reducing those species. However, H₂ spillover from the reduced Re metal occurs to facilitate reduction of Co species interacting with the support only after the reduction peak of Re oxide to Re metal is achieved. Again, Table 4 shows by H₂ chemisorption that addition of Re improves the degree of reduction of the catalyst more than the dispersion (cluster size).

Figure 7 shows profiles for two different series of Re promoted 15% Co/Al₂O₃ catalysts. The difference between the two series of catalysts is in the preparation. The dark line spectra correspond to catalysts prepared by loading the Co by three successive incipient wetness impregnation steps followed by loading of the promoter, where the catalyst was dried between each impregnation step. Only one calcination was used after the last step (loading of the promoter). The other series of catalysts was prepared in a similar manner, except that the catalyst was calcined after each sequential impregnation and drying step, for a total of four times (3 times for Co and 1 time for promoter). Clearly, there is a strong advantage with respect to reducibility by decreasing the number of calcination steps used to prepare the catalyst. This suggests that excessive calcination increases the formation of Co surface support species, which are more difficult to reduce.

Figure 8 provides a comparison of different Al₂O₃ supported cobalt catalysts with and without the addition of metal and metal cation promoters. Addition of noble metals aids in promoting the reduction rate, and consequently increases the amount of available Co metal

surface area (see H_2 chemisorption data, Table 4), but their effect on percentage dispersion is minimal. In contrast, as shown in Figure 8 and Table 4, addition of the irreducible ZrO_2 depresses the reduction rate (and hence the H_2 chemisorption) but increases the corrected dispersion. Addition of La_2O_3 had a small negative effect on reduction rate without influencing the dispersion relative to the unpromoted catalyst. As shown in Table 4, increasing the reduction temperature increased the percentage reduction without significantly altering the cluster size. With the ZrO_2 -containing catalyst, the average cobalt clusters were much smaller (Table 4). Therefore, it was expected that the interaction with the support (and perhaps the promoter cation) would be noticeably different in the TPR. Recall that the second peak corresponds to reduction of Co-support interaction species to Co^0 , and that the high temperature shoulder at 950 K in the unpromoted catalyst is attributed to the interaction of smaller clusters with the support. For the ZrO_2 promoted catalyst, the relative intensity of the high temperature shoulder at 950 K is greater than for the unpromoted. Addition of the noble metal promoters (Pt, Ru, or Re), in the amount of 0.5% by weight, to the $\text{Co/ZrO}_2\text{-Al}_2\text{O}_3$, was found to improve the percentage reduction more than the dispersion.

Also, for the ZrO_2 and La_2O_3 promoted samples, there was a noticeable attenuation in the intensity of the peaks corresponding to reduction of Co surface species interacting with the support in comparison to the other samples. In considering the results in Table 4 for percentage reducibility, it is presumed that the rest of the cobalt is present as aluminates, or perhaps some other mixed oxide form including the metal oxide promoter that reduces above 1073 K. In a previous study [14], decreasing the cobalt loading (and presumably, cluster size) changed the ratio of peaks corresponding to oxide and aluminates in favor of aluminates. Another investigation [19], where different atomic contents of Co and Pt were used, yielded results similar to the present study.

SiO₂, ZrO₂ modified SiO₂, and TiO₂ supported Catalysts

TPR shows that, in contrast with the Al₂O₃ supported catalysts, there appeared to be little interaction of the cobalt species with the SiO₂ support (see Figure 2). This is reasonable, since for the SiO₂ supported catalysts, a much larger cobalt cluster size was determined by H₂ chemisorption and pulse reoxidation (Table 6). This suggests that during preparation, cobalt species interact more strongly with Al₂O₃ than SiO₂, resulting in the stabilization of a smaller cluster size for a comparable loading and support surface area. Addition of either Ru or Pt to the support had a similar effect by decreasing the reduction temperature of the cobalt, as shown in the TPR spectra of Figure 9. Both promoters had a more important role in increasing the rate of reduction of the first peak that corresponds to reduction of Co₃O₄ to CoO with a remarkable shift from 570 K to 400 K. On an atom of promoter per atom of Co basis, Figure 9 indicates that Pt was more effective than Ru in enhancing the reduction of Co. In both cases, approximately 4% atomic (with respect to Co) loading of promoter was optimal for a catalyst with a loading of 15% Co. Adding a larger amount of noble metal promoter showed little further improvement in reducibility. H₂ chemisorption and pulse reoxidation results shown in Table 6 for an atomic loading of 8% (corresponding to 3.8 wt % Pt and 2.0 wt % Ru) indicate that the cluster size decreased with percent reducibility with the addition of noble metal promoters. Because the reduction profiles of noble metal promoted SiO₂ catalysts occur over a wider range of temperature than for the unpromoted catalyst, they appear to be less susceptible to sintering. Unlike the Co/Al₂O₃ catalysts, which displayed only a little change in the cluster size with increased percentage reducibility, a notable decrease was found in the series of Co/SiO₂ catalysts. Addition of the cation, K⁺, shifts both reduction peaks to higher temperatures, with a noticeable broadening of the peaks (Figure 10).

Figure 11 in conjunction with Table 6 shows that similar promoter effects were observed between the $\text{ZrO}_2\text{-SiO}_2$ and SiO_2 supported Co catalysts, which displayed a larger average cluster size and less support effects, while the TiO_2 supported Co catalysts showed similar promoter effects as the Al_2O_3 supported catalysts. Data in Tables 4 and 6 indicate that both Al_2O_3 and TiO_2 stabilized a smaller average cluster size than the SiO_2 based catalysts and exhibited greater interactions with the support. Ru and Pt particularly enhanced the rate of reduction of bulk-like cobalt oxides (first peak) for all supports, and for the reduction of Co species where a significant interaction with the support was present (the broad high temperature reduction peak for the Al_2O_3 and TiO_2 catalysts). A moderate enhancement was achieved for Pt and Ru promotion for the $\text{ZrO}_2\text{-SiO}_2$ catalyst for reduction of CoO to Co^0 (second sharp peak), while only a slight shift was observed for the promoted SiO_2 catalysts.

In all cases, Re had a different effect from Pt and Ru. Re played a more important role in catalyzing the reduction of the second peak, attributed to reduction of Co support species to Co^0 , particularly when a strong interaction of the support was present (Al_2O_3 and TiO_2 supported catalysts). The first peak, corresponding to reduction of bulk cobalt oxides, changed very little or not at all for all supported catalysts studied, with Re as the promoter.

Role of Promoters and Cluster Size in Improving Reducibility

If the dispersion is based on the total cobalt that is present, the results indicate that the catalysts prepared in this study are in the range reported by others [20]. However, if the dispersion is considered on the basis of the fraction of cobalt reduced, a different conclusion is reached. As shown in Figure 12 for the silica and titania-based catalysts and Figure 13 for the alumina supported catalysts, the dispersions within a group of similar catalysts are essentially the same. For example, for the 15% $\text{Co}/\text{Al}_2\text{O}_3$ catalyst, the corrected dispersions of all catalysts, noble metal (i.e., Pt, Ru, Re) promoted and unpromoted, are in the 16-20% range; this is true

even though the percentage of cobalt that is reduced varies from 25% to 70%. The incorporation of 5 wt. % La does little to alter the dispersion from that of the unpromoted catalyst.

Interestingly, 10% zirconia promotes the dispersion by about a factor of 2 in comparison with the unpromoted Al_2O_3 catalyst. However, the percentage reducibility drops to a third of the value for the unpromoted catalyst, leading to an overall loss in the availability of surface cobalt atoms.

Increasing the Co loading to 25 wt % causes an increase in the fraction reduced by about 40%, but a decrease in the dispersion of nearly 50%. Thus, the number of surface cobalt atoms is essentially the same for the 15% and 25% catalysts. Figure 14 shows the relationship between percentage reducibility and average cluster size, as determined by H_2 TPD/pulse reoxidation measurements. The sharp decrease in reducibility occurs below approximately 10 nm, the same cluster size below which catalyst deactivation by reoxidation processes has been reported to occur [15,16].

Conclusions

TPR and H_2 chemisorption with pulse reoxidation were carried out on cobalt Fischer Tropsch catalysts prepared using different supports (e.g., Al_2O_3 , TiO_2 , SiO_2 , ZrO_2 modified SiO_2 , ZrO_2 modified Al_2O_3) employing a variety of promoters, including noble metals and metal cations. The different supports did not stabilize a similar cluster size, and TPR screening indicated that the interaction between cobalt surface species and the support increased greatly for supports that stabilized smaller clusters (i.e., Al_2O_3 and TiO_2). Addition of Ru and Pt exhibited a similar catalytic effect on decreasing both the reduction temperatures of cobalt oxides (first peak in TPR) and Co species where a significant interaction with the support was present (broad second peak). Re mainly catalyzed the reduction of the second peak in TPR attributed to reduction of Co species interacting with the support. H_2 chemisorption/pulse reoxidation suggested that, for catalysts prepared with a noble metal promoter and reduced at the same

temperature, the increase in the number of active sites was due mainly to improvements in the percentage reduction rather than the actual dispersion (cluster size). Increasing the cobalt loading, and therefore the average Co cluster size, was found to exhibit improved reducibility by decreasing interactions with the support. Addition of metal oxides (B, La, K, and Zr) was found to decrease the reducibility of the catalyst, thereby lowering the availability of surface Co atoms. In the case of Zr, the cobalt cluster size decreased markedly, and the resulting decrease in reducibility may be caused by greater surface interactions between the smaller Co species and the support.

From an initial catalytic activity standpoint, the number of surface Co metal sites available is directly proportional to the number of micromoles of H_2 desorbed per g of catalyst. Therefore, although Al_2O_3 catalysts are more difficult to reduce, the net result is that the availability of surface sites after reduction at 623 K is still much higher than for the SiO_2 and TiO_2 supported catalysts prepared in this work, due to the stabilization of a smaller cluster size. The trend for initial number of surface Co sites (623 K reduction) available follows $Al_2O_3 > TiO_2 > SiO_2$ in the order 135 > 85 > 35 micromoles per g of catalyst. Further gains in initial number of surface sites can be achieved by noble metal promotion, but the resulting effect on catalyst stability requires further study, as does the stability of the catalyst with Co cluster size. The effect of noble metal promoter addition on initial activity was confirmed by reaction testing in the CSTR, as shown in Table 7. Where a weak interaction of cobalt clusters with the support was present, as in the case of Co/SiO_2 , only small gains in active sites were achieved with noble metal promoter addition, resulting in marginal gains in activity. However, noble metal promoter addition with cobalt on supports like Al_2O_3 and TiO_2 , where significant interactions are present, increased the number of active sites by increasing the percentage reduction, and significant gains

in initial activity were realized. Finally, the slurry phase impregnation method appears to result in a more homogeneous distribution of clusters in comparison to the standard IWI method.

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Table 1 BET Surface Areas						
<i>Support/Catalyst</i>	<i>BET SA* (m²/g)</i>	<i>Pore Volume (Single Point) (cm³/g)</i>	<i>Ave Pore Radius (nm)**</i>	<i>Pore Volume (BJH Adsorp)</i>	<i>Pore Volume (BJH Desorp)</i>	<i>Calcination T (K)</i>
Condea Vista Catalox B γ -Al ₂ O ₃	211	0.500	4.7	0.508	0.507	673
Davisil SiO ₂ gel 644	311	1.135	7.3	1.142	1.141	673
Davisil 952 SiO ₂	295	1.700	11.5	1.710	1.709	673
Degussa P25 TiO ₂	47	0.369	15.5	0.374	0.374	673
15% Co/Al ₂ O ₃	158	0.328	4.2	0.335	0.334	673, flow
15% Co-0.5% Pt/Al ₂ O ₃	162	0.328	4.1	0.335	0.334	673, flow
15% Co-1% Ru/Al ₂ O ₃	159	0.293	3.7	0.300	0.299	673, flow
15% Co-1% Re/Al ₂ O ₃	154	0.288	3.8	0.295	0.294	673, flow
15% Co-5% La/Al ₂ O ₃	155	0.299	3.9	0.306	0.305	673, flow
15% Co-10% Zr/Al ₂ O ₃	161	0.332	4.1	0.339	0.338	673, flow
15% Co/SiO ₂ (Davisil 644)	217	0.840	7.7	0.843	0.846	673, no flow
15% Co-3.8% Pt/SiO ₂	217	0.787	7.3	0.790	0.789	673, no flow
15% Co-2% Ru/SiO ₂	209	0.795	7.6	0.799	0.795	673, no flow
15% Co-0.5% K/SiO ₂	211	0.836	7.9	0.839	0.835	673, no flow
20% Co/ZrO ₂ -SiO ₂ (Davisil 952, 10 wt % Zr)	200	0.883	8.8	0.888	0.887	673, flow
20% Co-0.5% Pt/ZrO ₂ -SiO ₂	206	0.944	9.2	0.948	0.948	673, flow
20% Co-0.5% Ru/ZrO ₂ -SiO ₂	197	0.880	8.9	0.889	0.887	673, flow
20% Co-0.5% Re/ZrO ₂ -SiO ₂	192	0.857	8.9	0.861	0.861	673, flow
10% Co/TiO ₂	38.1 (43.9)	---	n/a (10.9)	0.240	0.244	673, flow
10% Co-0.05% B/TiO ₂	40.8 (48.3)	0.282	13.8 (11.9)	0.288	0.288	673, flow
10% Co-0.20% Ru/TiO ₂	41.0 (47.5)	---	n/a (11.3)	0.269	0.269	673, flow
10% Co-0.20% Ru-0.05% B/TiO ₂	43.4 (49.9)	0.273	12.6 (11.2)	0.279	0.279	673, flow
10% Co-0.34% Re/TiO ₂	44.4 (51.0)	0.266	11.9 (10.7)	0.273	0.272	673, flow
10% Co-0.5% Pt/TiO ₂	40.7 (46.9)	0.264	13.0 (11.5)	0.270	0.269	673, flow
* For TiO₂ supported catalysts, estimates of cumulative surface areas are shown in parenthesis from BJH adsorption. ** For TiO₂ supported catalysts, where pore size was not available from single point adsorption, an estimate is provided from BJH adsorption.						

Table 2						
BET Surface Areas of Co/Al ₂ O ₃ Series Prepared by IWI with Different Loadings, Confirmed by ICP Analysis						
<i>Support/Catalyst</i>	<i>BET SA (m²/g)</i>	<i>Pore Volume (Single Point) (cm³/g)</i>	<i>Ave Pore Radius (nm)</i>	<i>Pore Volume (BJH Adsorp)</i>	<i>Pore Volume (BJH Desorp)</i>	<i>Calcination T (K)</i>
15% Co/Al ₂ O ₃ (200 m ² /g)	161.5	0.335	4.1	0.342	0.341	673K, flow
26% Co/Al ₂ O ₃ (200 m ² /g)	130.1	0.264	4.1	0.272	0.271	673K, flow
33.3% Co/Al ₂ O ₃ (200 m ² /g)	107.3	0.249	4.6	0.260	0.259	673K, flow
15% Co/Al ₂ O ₃ (150 m ² /g)	121.5	0.333	5.5	0.338	0.337	673K, flow
24.4% Co/Al ₂ O ₃ (150 m ² /g)	107.7	0.295	5.5	0.304	0.303	673K, flow
28% Co/Al ₂ O ₃ (150 m ² /g)	87.5	0.243	5.6	0.250	0.250	673K, flow
11% Co/Al ₂ O ₃ (100 m ² /g)	99.7	0.317	6.4	0.322	0.321	673K, flow
27% Co/Al ₂ O ₃ (100 m ² /g)	81.4	0.276	6.8	0.283	0.282	673K, flow
34.3% Co/Al ₂ O ₃ (100 m ² /g)	71.8	0.262	7.3	0.278	0.277	673K, flow
<i>Slurry Phase Impregnation Catalyst</i>						
25% Co/Al ₂ O ₃ (150 m ² /g)	89.0	0.228	4.8	0.233	0.233	673K, flow

Table 3								
H ₂ Chemisorption (TPD) and Pulse Reoxidation Results for Al ₂ O ₃ Supported Catalysts Prepared by the IWI Method, with Changes in Loading and Support Surface Area								
<i>Sample Name</i>	<i>Red. T (K)</i>	<i>μmoles H₂ desorbed per g cat</i>	<i>Uncorr. %D</i>	<i>Uncorr. Avg. diam. (nm)</i>	<i>μmoles O₂ pulsed per g</i>	<i>% Red.</i>	<i>Corr. %D</i>	<i>Corr. Avg. diam. (nm)</i>
15%Co (200 m ² /g)	623	70.5	5.5	18.6	495	29	19.1	5.4
26%Co (200 m ² /g)	623	94.4	4.5	23.2	1476	52	8.6	12.1
33.3%Co (200 m ² /g)	623	72.4	2.6	39.9	2376	64	4.0	25.5
15%Co (150 m ² /g)	623	79.3	6.2	16.6	823	49	13.9	7.4
24.4%Co (150 m ² /g)	623	102.5	4.8	21.4	1814	64	7.6	13.7
11%Co (100 m ² /g)	623	71.5	7.7	13.5	645	52	14.7	7.0
27%Co (100 m ² /g)	623	59.6	2.6	39.7	1947	63	4.1	25.2
33.4%Co (100 m ² /g)	623	45.8	1.6	63.9	2886	67	2.4	42.8

Table 4								
H ₂ Chemisorption (TPD) and Pulse Reoxidation Results For Al ₂ O ₃ (200 m ² /g) Supported Catalysts, With and Without Promoter								
<i>Sample Name</i>	<i>Red. T (K)</i>	<i>μmoles H₂ desorbed per g cat</i>	<i>Uncorr. %D</i>	<i>Uncorr. Avg. diam. (nm)</i>	<i>μmoles O₂ pulsed per g</i>	<i>% Red.</i>	<i>Corr. %D</i>	<i>Corr. Avg. diam. (nm)</i>
15%Co/Al ₂ O ₃	623	66.9	5.3	19.6	509	30	17.5	5.9
15%Co-0.5%Pt/Al ₂ O ₃	623	140.6	11.0	9.3	1024	60	18.4	5.6
15%Co-1%Ru/Al ₂ O ₃	623	115.5	9.7	11.4	823	50	18.2	5.7
15%Co-1%Re/Al ₂ O ₃	623	168.2	13.2	7.8	1187	70	19.4	5.5
15%Co-5%La/Al ₂ O ₃	623	59.8	4.7	22.0	450	27	19.1	5.4
15%Co-10%Zr/Al ₂ O ₃	623	45.5	3.6	28.9	195	11	32.4	3.2
15%Co-10%Zr/Al ₂ O ₃	773	139.7	11.0	9.4	499	29	37.9	2.7
15%Co-10%Zr/Al ₂ O ₃	873	154.6	12.2	8.5	637	38	31.9	3.2
15%Co-10%Zr- 0.5%Pt/Al ₂ O ₃	623	142.4	11.2	9.2	549	32	35.0	3.0
15%Co-10%Zr- 0.5%Ru/Al ₂ O ₃	623	111.6	8.8	11.8	511	30	29.2	3.5
15%Co-10%Zr- 0.5%Re/Al ₂ O ₃	623	122.7	9.6	10.7	549	32	30.1	3.4
25%Co/Al ₂ O ₃ (Sasol method)	623	77.7	3.7	28.2	1174	42	8.7	11.8
25%Co-0.5%Pt/Al ₂ O ₃ (Sasol method)	623	149.0	7.0	14.7	1994	71	9.4	11.0
25%Co0.5%Ru/Al ₂ O ₃ (IWI method)	623	136.2	6.4	16.1	2016	71	9.0	11.4
25%Co-0.5%Re/Al ₂ O ₃ (IWI method)	623	170.5	8.0	12.8	2053	73	11.0	9.4

Table 5								
Resistance of Cluster to Reduction Temperature and Heating Rate. Results of H ₂ Chemisorption by TPD								
<i>Sample Name</i>	<i>Red. T (K)</i>	<i>μmoles H₂ desorbed per g cat</i>	<i>Uncorr. %D</i>	<i>Uncorr. Avg. diam. (nm)</i>	<i>μmoles O₂ pulsed per g</i>	<i>% Red.</i>	<i>Corr. %D</i>	<i>Corr. Avg. diam. (nm)</i>
15%Co/Al ₂ O ₃	473	26.3	2.1	49.9	-	-	-	-
	573	38.6	3.0	34.0	232	14	22.3	4.6
	673	77.6	6.1	16.9	462	27	22.3	5.9
	773	131.8	10.4	10.0	953	56	19.4	5.6
	873	152.8	12.0	8.6	1021	60	19.9	5.2
15%Co/Al ₂ O ₃ *	773	122.1	9.6	10.8	971	57	16.8	6.2
* Direct temperature ramp.								

Table 6								
H ₂ Chemisorption (TPD) and Pulse Reoxidation Results for SiO ₂ and TiO ₂ Supported Catalysts, With and Without Promoter								
<i>Sample Name</i>	<i>Red. T (K)</i>	<i>μmoles H₂ desorbed per g cat</i>	<i>Uncorr. %D</i>	<i>Uncorr. Avg. diam. (nm)</i>	<i>μmoles O₂ pulsed per g</i>	<i>% Red.</i>	<i>Corr. %D</i>	<i>Corr. Avg. diam. (nm)</i>
15% Co/SiO ₂	623	16.9	1.3	77.6	1078	64	2.1	49.7
15% Co-3.8% Pt/SiO ₂	623	25.0	2.0	52.5	1222	72	2.7	37.8
15% Co-2% Ru/SiO ₂	623	37.8	3.0	34.8	1249	74	4.0	25.7
15% Co-0.5% K/SiO ₂	623	17.9	1.4	73.2	994	59	2.0	51.1
20% Co/SiO ₂	623	13.2	1.6	66.3	1652	73	2.1	48.4
20% Co/ZrO ₂ -SiO ₂	623	47.6	2.8	36.8	1149	51	5.5	18.8
20% Co-0.5% Pt/ZrO ₂ -SiO ₂	623	59.0	3.5	29.7	1207	53	6.6	15.7
20% Co-0.5% Ru/ZrO ₂ -SiO ₂	623	61.4	3.6	28.5	1247	55	6.6	15.7
20% Co-0.5% Re/ZrO ₂ -SiO ₂	623	59.0	3.5	29.7	1308	58	6.0	17.2
10% Co/TiO ₂	573	42.8	5.1	20.0	593	52	9.7	10.6
10% Co-0.2% Ru/TiO ₂	573	66.6	7.8	13.3	722	64	12.2	8.5
10% Co-0.34% Re/TiO ₂	573	65.6	7.7	13.4	685	61	12.8	8.1
10% Co-0.05% B/TiO ₂	573	37.4	4.4	23.5	429	38	11.6	8.9
10% Co-0.2% Ru- 0.05% B/TiO ₂	573	63.1	7.4	13.9	692	61	12.2	8.5

Table 7				
Trends in Initial Catalytic Activity ($H_2:CO = 2:1$)				
Catalyst	Space Velocity (SL syngas/ g_{cat}/h)	P (psig)	T (psig)	Conversion (X_{CO})
15%Co/ Al_2O_3	5	275	493	22.7
0.5%Pt-15%Co/ Al_2O_3	5	275	493	40.2
10%Co/ TiO_2	2	350	503	58.4
0.2%Ru-10%Co/ TiO_2	2	350	503	77.9
15%Co/ SiO_2	1	350	493	64.3
1.9%Pt-15%Co/ SiO_2	1	350	493	76.0

Figure 1. Pore size distributions for supports (solid lines) and catalysts (dotted lines) from BJH adsorption measurements of adsorbed N₂. Top left: Davisil 644 SiO₂ and 15%Co/SiO₂; Bottom left: Davisil 952 SiO₂ and 20%Co/ZrO₂-SiO₂; Top right: Degussa P25 TiO₂ and 10%Co/TiO₂; and Bottom right: Condea Vista Catalox B g-Al₂O₃ and 15%Co/Al₂O₃.

Figure 2. (a) TPR of unpromoted Co catalysts. (b) TPR of 15%Co/Al₂O₃ after calcination (bottom); after reduction at 623K for 10 hrs (middle); and the difference showing the degree of reduction of the second peak (top). (c) Same comparison for 25%Co/Al₂O₃ catalyst prepared by IWI.

Figure 3. Influence of loading and support surface area on the Co/Al₂O₃ catalyst reduction profile.

Figure 4. Reduction profiles of 25% catalysts prepared by the standard IWI method (light curve) and by the slurry phase impregnation method (dark curve).

Figure 5. Comparisons of unpromoted (bottom) and 0.5% Pt promoted (top) $\text{Co}/\text{Al}_2\text{O}_3$ FTS catalysts with 15% (light) and 25% (bold) loadings of Co. Note that the intensity of the 15% catalyst was increased by 1.7 to account for differences in loading in order to more easily compare shifts in the peak positions.

Figure 6. (Left) Comparative TPR spectra of unpromoted (bottom) 15%Co/Al₂O₃ catalyst with those promoted with (moving up) 0.2%, 0.5%, and 1.0% Ru. (Right) Comparative TPR spectra of unpromoted (bottom) 15%Co/Al₂O₃ catalyst with those promoted with (moving up) 0.2%, 0.5%, and 1.0% Re. Top spectra is the reduction of Re₂O₇ precursor (unsupported).

Figure 7. Comparative TPR spectra of unpromoted (bottom) 15%Co/Al₂O₃ catalyst with those promoted with (moving up) 0.2%, 0.5%, and 1.0% Re with (light) and without (dark) interval calcination.

Figure 8. TPR comparison of Al_2O_3 supported Co catalysts with and without metal and metal cation promoters.

Figure 9. TPR comparison of unpromoted (bottom) and promoted 15% Co/SiO₂ catalysts with increasing atomic percentages (with respect to Co) of Ru (bold) and Pt (light) in the order (moving up) 0.8%, 2%, 4%, and 8% (corresponding to 3.8 wt % Pt and 2.0 wt % Ru).

Figure 10. TPR comparison of unpromoted (bottom) and K⁺ promoted SiO₂ supported Co catalysts with (moving up) increasing wt. % loading of K⁺ in the order 0.5%, 1.5%, 3.0%, and 5.0%.

Figure 11. TPR comparison of promoted (left) ZrO₂-SiO₂ and (right) TiO₂ catalysts.

Figure 12. Percentage reducibility versus the dispersion for unpromoted (unp) and promoted SiO₂, ZrO₂, and TiO₂ supported cobalt catalysts after reduction at 623 K.

Figure 13. Percentage reducibility versus the dispersion for unpromoted (unp) and promoted Al₂O₃ and ZrO₂-Al₂O₃ catalysts after reduction at 623 K.

Figure 14. Percentage of reduction versus cluster size for unpromoted supported Co catalysts after reduction at 623 K.

G. Characterization of Pt-Re Promoted Co/Al₂O₃ Catalysts

Introduction

We are continuing to study the impact on reducibility of cobalt oxides by the use of different supports and by the incorporation of different promoters and additives to supported cobalt catalysts. The reduction of Co₃O₄, which is present on the catalyst after calcination, is a two step process which passes through an intermediate CoO phase before reduction to the metal. In our previous investigations, we found by temperature programmed reduction that a 15%Co/Al₂O₃ displayed a broad second peak attributed to the reduction of cobalt species interacting with the support. In agreement, hydrogen chemisorption with pulse reoxidation revealed that the unpromoted catalyst displayed poor percentage reduction of only 30% after reduction at 623K, the standard activation temperature of Co FTS catalysts. While promotion of supported Co catalysts with the noble metal promoters Pt and Ru had a similar effect on catalyzing both reduction steps of Co₃O₄ to Co metal, Re only aided in catalyzing the second step when a significant interaction of the Co species with the support was present, such as found on Al₂O₃ supported catalysts. After reduction at 623K, therefore, the number of Co active sites increases remarkably with the addition of noble metal promoter, thereby increasing the initial activity under reaction testing.

We have investigated the possibility of a synergism between Pt and Re on the reducibility of supported Co oxides, and are testing the catalysts in the CSTR to draw conclusions as to the effect of Pt-Re promotion and synergism on the catalyst stability.

Catalyst Preparation

Condea Vista Catalox B γ -alumina (100-200 mesh, 200 m²/g, pore volume 0.4 cm³/g) was used as support material for the preparation of 15% loaded cobalt FTS catalysts. A three-step

incipient wetness impregnation method was used to add 15 wt % cobalt to the supports with a drying procedure at 353K in a rotary evaporator following each impregnation. Noble metal promoted catalysts were prepared with different loadings of platinum and/or rhenium after cobalt addition and prior to calcination. Where both promoters were added, the Pt was loaded first. Catalysts were calcined only one time in air at 673K for 4hrs following the final impregnation step.

Catalyst Characterization

BET Surface Area

BET measurements were conducted using a Micromeritics Tri-Star system for all catalysts to determine the loss of surface area, if any, following loading of the metal. Prior to testing, samples were slowly ramped to 433K and evacuated for 4hrs to approximately 50mTorr.

Temperature Programmed Reduction

Temperature programmed reduction (TPR) profiles of catalysts were recorded using a Zeton Altamira AMI-200 unit. Calcined fresh samples were first purged in flowing inert gas at 623K to remove traces of water. TPR was performed using a 10% H_2 /Ar mixture referenced to Ar at a flowrate of 30 ccm. The sample was heated from 323K to 1073K using a heating ramp of 10K/min and the H_2 consumption measured using a thermal conductivity detector (TCD)..

H_2 Chemisorption by TPD and % Reducibility by Pulse Reoxidation

The amount of chemisorbed hydrogen was measured using the Zeton Altamira AMI-200 unit. The sample weight was always 0.220 g. The catalyst was activated using hydrogen at 623K for 10hrs and cooled under flowing hydrogen to 373K. The sample was held at 373K under flowing argon to prevent adsorption of physisorbed and weakly bound species, prior to increasing the temperature slowly to the activation temperature. At that temperature, the catalyst was held under flowing argon to desorb the remaining chemisorbed hydrogen until the TCD

signal returned to the baseline. The TPD spectrum was integrated and the number of moles of desorbed hydrogen determined by comparing to the areas of calibration pulses of hydrogen in argon. Prior to experiments, the sample loop was calibrated with pulses of N₂ in a helium flow and compared against a calibration line produced from using gas tight syringe injections of N₂ into a helium flow. The volume of the loop was found to be 52 μ L.

After TPD of H₂, the sample was reoxidized at 623K by pulses of pure O₂ in helium carrier referenced to helium gas. After oxidation of the cobalt metal clusters (where the entire O₂ pulse was observed by the TCD), the number of moles of O₂ consumed was determined, and the percent reducibility was calculated assuming that Co⁰ reoxidized to Co₃O₄.

Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) of adsorbed CO

Infrared spectroscopy of adsorbed CO was performed on a Nicolet Nexus 870 FT-IR which is equipped with a DTGS detector. The catalyst was mixed with KBr and placed into a Spectra-Tech High Temperature/High Pressure DRIFTS cell with ZnSe windows that allowed us to perform in situ thermal pretreatments. For each IR spectrum, taken at a resolution of 8 cm⁻¹, 128 scans were added. Samples were pre-reduced ex-situ under H₂:He (2:1) flow of 100 ccm/g catalyst at 623 K and passivated with 1% O₂ in helium at room temperature for 24 hours. Prior to each spectrum, the catalyst was re-reduced in situ in a flow of 33% H₂ in helium for one hour, held in helium for 30 minutes and cooled under helium flow (note: oxygen scrubbers were employed) to room temperature. The background was recorded at this time. Then, the catalyst was exposed to 1% CO in helium for 30 minutes at room temperature, scanned, purged in helium for 30 minutes, and scanned again. The latter step was employed to remove the contributions of gas phase and weakly adsorbed CO.

Results and Discussion

Results of surface area measurements by physisorption of nitrogen are reported in Table 1. Results show that the BET surface area for the 15% loaded Co catalysts on 200 m²/g γ -Al₂O₃ were all close to 160 m²/g. A weight % loading of 15% metal is equivalent to 20% by weight Co₃O₄. If the Al₂O₃ is the main contributor to the area, then the area of the Co/Al₂O₃ catalysts should be 0.80 $\times$ 200 m²/g = 160 m²/g, which matches the measured value. As shown in Table 1, addition of small quantities of noble metal promoters did not measurably impact the BET area.

Figure 1 shows the results of TPR. The unpromoted catalyst exhibits two peaks, and remarkably, the second peak is much broader than observed for similarly loaded TiO₂ and SiO₂ supported Co catalysts. Note that in the TPR, we did not ramp the temperature high enough to observe the reduction of bulk cobalt aluminate species, which has been shown to occur above 1073 K with up to 30% loading of cobalt. Therefore, the broad peak on the unpromoted catalyst (ca. 700 to 1000 K) is attributed to the reduction of Co surface species interacting with the support, and the different shoulders are likely due to varying degrees of interaction with the support as a function of cluster size. The smallest Co surface species, with the greatest interaction with the support, are therefore likely represented by the 950 K shoulder. The precise identity of these species is not clear, although it is surmised that the species are either the result of a strong interaction between very small cobalt oxide clusters and the support (deviating from bulklike cobalt oxides and reducing at higher temperatures than the bulk oxides) or small surface Co species which include support atoms in the structure (reducing at temperatures below that of bulk Co-aluminate). Hereafter, the species responsible for this peak will be referred to loosely as “Co surface support species”. The addition of 0.5%Pt caused the peaks to shift markedly to lower temperatures, presumably due to spillover of H₂ from the metallic promoter to reduce the Co oxide and Co surface support species.

The reduction of Re oxide occurs at higher temperatures than Pt oxide. Figure 1 shows that although there appears to be no improvement in the reduction of the low temperature peak assigned to the reduction of cobalt oxides, Re still plays a valuable role in decreasing the reduction temperature of Co species for which there is a significant surface interaction with the support. Our previous work shows that Re oxide reduces at 620K, which may explain the lack of effect on the low temperature peak responsible for reduction of cobalt oxides. TPR profiles in Figure 1 show that bulk cobalt oxide has essentially been reduced before the Re oxide is reduced, so no spillover effect can operate to aid in reducing those species. However, H₂ spillover from the reduced Re metal occurs to facilitate reduction of Co species interacting with the support only after the reduction peak of Re oxide to Re metal is achieved.

By keeping the same number of moles of noble metal promoter but by varying the ratio of Pt and Re, interesting effects on reduction are observed in TPR. The best molar ratio appears to be 50%Pt and 50%Re. Relative to Pt promoted catalyst, the addition of Re appears to sharpen the peaks somewhat, while relative to Re, both peaks are shifted to lower temperatures. Since our preliminary findings show that Re promotion results in a more stable catalyst than Pt promotion of Co/Al₂O₃, addition of Pt to a Re-promoted catalyst may aid in catalyzing Re reduction.

Results of H₂ chemisorption by TPD (Table 2) after reduction at 623K indicate that the number of surface sites increases with addition of either Pt or Re promoter. By performing pulse reoxidation, it is clear that the remarkable gain in Co⁰ site density is mainly due to an enhancement in the reducibility of the clusters, and not to improvements in the actual dispersion (cluster size) of the reduced cobalt. Addition of Pt or Re causes a fraction of the smaller Co surface species that interact with the support to be reduced in this temperature range. Results of H₂ chemisorption by TPD and pulse reoxidation (Table 2) revealed that, for both unpromoted

and promoted catalysts, there were significant increases (from 30% to approximately 60% with addition of 0.5% noble metal promoter). Maintaining the 50%Pt/50%Re molar ratio but doubling the loading increased the percentage further to 72%. This is in line with the further observed shifts of both peaks in the TPR.

DRIFTS of adsorbed CO is useful for probing the electronic and geometric effects of promoters on supported metal catalysts. Figure 2 shows the resulting spectra after purging the gas phase and weakly bound species with helium at room temperature. The linear stretch vibration of CO adsorbed on Co occurs at approximately 1980 cm^{-1} , while the bridged species are observed at lower wavenumbers. An interesting trend emerges where increasing Re concentration results in a decrease in the linear to bridge-bonded CO ratio (Table 3). Typically, an increase in bridge bonded CO is the result of larger clusters present on the catalyst. The possibility also exists that the increase in linear bonded CO for the Pt promoted catalyst may be the result of a geometric alloying effect, whereby Pt might break up the geometry to Co sites. Clearly, adsorption of CO also occurs on the promoter. For CO on Pt, the band occurs at approximately 2080 cm^{-1} . However, one cannot rule out the possibility of an electronic effect.

To test for the possibility of alloy formation, we are continuing to study these catalysts by High Resolution Transmission Electron Microscopy. With this technique, we may be able to determine if there are changes in the lattice spacing due to alloy formation. At this time, important differences were observed for Pt and Re promoted catalysts in terms of reducibility and catalyst stability. Future catalytic testing results combined with characterization should provide insight into the nature of these differences.

Table 1			
BET surface areas			
Support/Catalyst	BET SA (m ² /g)	Ave Pore Size (nm)	Calcination T (K)
Condea Vista Catalox B γ -Al ₂ O ₃	200	-	-
Unpromoted 15%Co/ γ -Al ₂ O ₃	161.5	4.14	623, flow
0.5%Pt/15%Co/Al ₂ O ₃	156.1	3.97	623, flow
0.477%Re/15%Co/Al ₂ O ₃	160.2	3.94	623, flow
0.239%Re/0.25%Pt/15%Co/Al ₂ O ₃	157.7	4.01	623, flow
0.477%Re/0.5%Pt/15%Co/Al ₂ O ₃	160.5	3.92	623, flow
0.358%Re/0.125%Pt/15%Co/Al ₂ O ₃	166.5	3.92	623, flow
0.120%Re/0.375%Pt/15%Co/Al ₂ O ₃	161.5	3.96	623, flow

Table 2

H₂ Chemisorption by TPD and Percentage Reduction by Pulse Reoxidation

Sample Description	Red T(K)	Micromoles H ₂ -Desorbed/g	Uncorr. Disp.	Uncorr. Diam. (nm)	% Reduced	Corr. Diam. (nm)	Corr. Dispersion
Unpromoted 15% Co/Al ₂ O ₃	623	70.5	5.5%	18.6	29%	5.4	19.1%
with 0.5% Pt	623	151	11.9%	8.7	64%	5.6	18.6%
with 0.120% Re/0.375% Pt	623	148.6	11.7%	7.7	61%	5.4	19.2%
with 0.239% Re/0.25% Pt	623	157.7	12.4%	7.3	63%	5.2	19.7%
with 0.358% Re/0.125% Pt	623	139.7	11.0%	9.5	61%	5.7	18.0%
with 0.477% Re	623	136.7	10.7%	9.6	65%	6.2	16.5%
with 0.477% Re/0.5% Pt	623	175.5	13.8%	7.5	72%	5.4	19.2%

Table 3

Linear to Bridged Ratio for Adsorbed CO as Measured by DRIFTS

Catalyst	L/B
15% Co/Al ₂ O ₃	0.296
0.5% Pt-15% Co/Al ₂ O ₃	0.258
0.375% Pt-0.20% Re-15% Co/Al ₂ O ₃	0.308
0.235% Re-0.25% Pt-15% Co/Al ₂ O ₃	0.269
0.477% Re-0.5% Pt-15% Co/Al ₂ O ₃	0.242
0.36% Re-0.125% Pt-15% Co/Al ₂ O ₃	0.207
0.477% Re-15% Co/Al ₂ O ₃	0.195

Figure 1. TPR profiles of Pt and/or Re promoted 15% Co/Al₂O₃ catalysts.

Figure 2. DRIFTS of adsorbed CO profiles of Pt and/or Re promoted 15% Co/ Al_2O_3 catalysts.

H. EXAFS Characterization of Used 0.2% Re - 15% Co/Al₂O₃ Catalysts

ABSTRACT

The deactivation of a promoted 0.2%Re-15%Co/Al₂O₃ catalyst during Fischer-Tropsch synthesis in a CSTR was investigated. A novel method was utilized to isolate samples of catalyst from the reactor during the course of the reactor run, so that the catalyst was cooled in the solid wax for XAFS investigation. Results showed, as suggested in an earlier study of spent noble metal promoted catalysts, that the deactivation involves two processes. EXAFS strongly indicates significant cluster growth with time on-stream by a sintering process as a major component to the deactivation. However, in line with our previous investigation, XANES of the most heavily deactivated samples indicates that a fraction of Co species underwent a phase transformation to a phase resembling that of CoAl₂O₄. Addition of metal promoters to achieve reduction of Co species in interaction with the support results in higher initial activity by the formation of additional active sites. However, these additional Co metal clusters are unstable and are likely the cause of the higher initial deactivation rates of these catalysts during Fischer-Tropsch synthesis.

INTRODUCTION

Extended X-ray absorption fine structure (EXAFS) spectroscopy is a powerful tool in that it provides information on the local structure surrounding the type of atom under investigation. For example, the average coordination information can be obtained [1,2], which is very useful for obtaining information regarding the dispersion of fresh catalysts, as well as the changes in the cluster size of supported metal catalysts during the course of a reaction. In some cases, information regarding cluster morphology can also be predicted [1,2]. It is important to note that, although EXAFS provides information regarding the local structure surrounding an atom, including atom type, degree of coordination, radial distances, and disorder parameters, the

method represents an average over all the clusters present on the catalyst. XANES, on the other hand, can provide qualitative information on the oxidation states of species present on supported metal catalysts [3].

Re addition was found to catalyze the reduction of the very well dispersed Co species in interaction with the support, thereby increasing the number of Co active metal sites for reaction. The reduction of these additional species showed a slight lowering of the average cluster size in H₂ chemisorption/pulse reoxidation measurements in reference to the unpromoted catalyst, demonstrating that they were more highly dispersed. However, while the initial catalytic activity by addition of Re promoter was increased relative to the unpromoted catalyst, the deactivation rate was higher. Therefore, one focus of this paper was to use XAFS techniques to provide information on the nature of the deactivation of these small cobalt metal clusters, which were reduced in the presence of the Re, during the course of Fischer Tropsch synthesis. In order to carry out these experiments, we developed a method of isolating catalyst samples in the solid wax directly from the CSTR during the course of reaction testing.

EXPERIMENTAL

Catalyst Preparation

Condea Vista Catalox (high purity γ -alumina, 100-200 mesh, 200 m²/g) was the support for the cobalt FTS catalysts. To obtain a cobalt loading of 15%, a three step incipient wetness impregnation (IWI) was used with intermediate drying steps at 353 K in a rotary evaporator following each impregnation. The promoter was added after the third drying step by IWI of an aqueous solution of rhenium oxide salt. The catalyst was dried and then calcined under air flow at 673 K for 4 hrs following promoter addition. The cobalt loading was verified by ICP analysis.

Temperature Programmed Reduction

Temperature programmed reduction (TPR) profiles of catalysts were recorded using a Zeton Altamira AMI-200 unit. Calcined fresh samples were first purged in flowing inert gas to remove traces of water. TPR was performed using a 10% H₂/Ar mixture referenced to Ar at a flowrate of 30 ccm. The sample was heated from 323 K to 1073 K using a heating ramp of 10 K/min. Results are shown in Figure 1.

H₂ Chemisorption by TPD and % Reducibility by Reoxidation

The amount of chemisorbed hydrogen was measured using the Zeton Altamira AMI-200 unit, which incorporates a thermal conductivity detector (TCD). The sample weight was always 0.220 g. The catalyst was activated using hydrogen at 623K for 10 hrs and cooled under flowing hydrogen to 373 K. The sample was held at 373 K under flowing argon to prevent adsorption of physisorbed and weakly bound species, prior to increasing the temperature slowly to the reduction temperature. At that temperature, the catalyst was held under flowing argon to desorb the remaining chemisorbed hydrogen until the TCD signal returned to the baseline. The TPD spectrum was integrated and the number of moles of desorbed hydrogen determined by comparing to the areas of calibration pulses of hydrogen in argon. Prior to experiments, the sample loop was calibrated with pulses of N₂ in a helium flow and compared against a calibration line produced from using gas tight syringe injections of N₂ into a helium flow.

After TPD of H₂, the sample was reoxidized [4] at the activation temperature by pulses of pure O₂ in helium carrier referenced to helium gas. After oxidation of the cobalt metal clusters (where the entire O₂ pulse was observed by the TCD), the number of moles of O₂ consumed was determined, and the percentage reduction was calculated assuming that Co⁰ reoxidized to Co₃O₄.

In order to estimate the average cluster size, the percentage reduction was included in the dispersion calculation as follows, assuming a H:Co stoichiometric ratio of 1:1, as reported previously [5].

$$\%D = (\text{number of surface Co}^0 \text{ atoms})/(\text{number of total Co}^0 \text{ atoms})$$

$$\%D = (\text{number of surface Co}^0 \text{ atoms})/[(\text{number of total Co atoms})(\text{percentage reduction})]$$

In Table 1, the dispersions and cluster sizes are first reported as uncorrected, which assumes that all of the cobalt is reduced. Then, the percentage reduction is included in the calculation and the corrected dispersion and cobalt cluster size is reported. This demonstrates the importance of considering the fraction of cobalt species reduced in any estimate of dispersion based on chemisorption measurements.

XAFS

Used catalyst samples were obtained from the continuously stirred tank reactor (CSTR) at different points of catalyst deactivation with time onstream. The catalyst particles, well-mixed with the reactor wax, were removed by a pressure letdown valve to a collection trap under inert gas. The wax was allowed to cool, sealing the catalyst in the solid wax matrix for EXAFS analysis.

XAFS spectra at the Co *K* edge were obtained at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory (BNL) in Upton, New York at beamline X18b. The X-rays were tuned by a Si(111) double crystal monochromator, which was detuned slightly to prevent glitches from harmonics. The used catalyst in the wax was pressed into a disk and loaded into a XAFS cell, which was cooled to liquid nitrogen temperatures prior to scanning under flowing helium. XAFS spectra of the Co foil, Co₃O₄, CoO, and CoAl₂O₄ were also measured. Several scans of the catalyst samples were obtained and the spectra averaged to improve the signal to noise ratio.

XANES and EXAFS spectra were first background corrected and normalized by dividing by the height of the edge jump to account for the concentration of Co atoms in the sample. For EXAFS spectra, appropriate splines were used to remove the background based on the Nyquist criteria [6]. The Chi function in energy space was extracted and converted to k space and weighted with either k^0 or k^3 weighting for examination of the changes in coordination number of the different Z scatterers. To obtain information on Co-Co coordination and therefore, changes in the cluster size, the k^3 -weighted spectrum was transformed from k space to r space to obtain the radial distribution function. The EXAFS spectrum for the first Co-Co coordination shell was isolated and the inverse Fourier Transform was conducted. Fitting of the spectra in k space was carried out using FEFFIT [4]. Theoretical EXAFS were generated using FEFF [7] using model Co metal crystal parameters generated by Atoms [8]. In order to use coordination number as a fitting parameter, S_0^2 was first obtained from analysis of the Co foil assuming a fixed coordination number N_1 of 12 for the first shell. The other fitting parameters utilized by FEFFIT included the overall E_0 shift e_0 applied to each path, Δr to account for lattice expansion, and σ^2 , which is based on a correlated Debye model used to approximate the mean square disorder in the path length of each path [8].

RESULTS AND DISCUSSION

Figure 2 shows the points during the initial deactivation period of the catalyst where the catalyst was removed. Figure 3 shows the k^0 and k^3 -weighted radial distribution functions for the used catalyst withdrawn from the reactor at 1800 hours onstream and a comparison against those of the standards. The aim of this part of the investigation was to determine whether the small Co metal clusters showed signs of reoxidation, as had been suggested in earlier reports [9,10], or whether the main cause of the deactivation was by growth of the Co metal cluster by a sintering mechanism, leading to a loss of surface sites.

Figure 3 displays the normalized XANES spectra of the catalyst samples removed at 1800 and 2135 hours onstream with a comparison against those of the reference compounds, including the Co metal foil and CoO, Co₃O₄, and CoAl₂O₄ standards. Interestingly, as noted previously in other spent catalysts [11], the XANES reveals two contributions, a strong contribution of the reduced Co metal and three small peaks which match very well the positions of the CoAl₂O₄ standard. The positions are more pronounced when one considers the derivative spectra. These suggest the possibility that a small fraction of the clusters may have undergone a phase transformation to an oxidized state. In comparison with our earlier study [11], the extent of formation of this oxidized phase is less pronounced than the unpromoted catalyst, indicating that Re promoter may play a role in suppressing its formation.

Both the k^0 and k^3 -weighted radial distribution functions displayed in Figure 4 for the used catalyst withdrawn from the reactor at 1800 hours onstream strongly resemble the corresponding spectra of the Co foil. Surprisingly, even in the k^0 -weighted spectra, there is not a peak present at low R between 1 and 2 Angstroms that suggests an increase in the Co-O coordination, in comparison with the references where the Co is in an oxidized state. Also, a comparison in k^3 of the CoO, Co₃O₄, and CoAl₂O₄ standards show the Co-Co distances are shifted to higher R, as expected, in comparison with the Co foil. However, there is no indication of a contribution from Co-Co distance at these higher R in the used catalyst sample, rather only the Co-Co distance which matched closely that found in the Co metal foil. Therefore, this suggests that if there is deactivation due to reoxidation, it is either likely limited to the surface of the catalyst or a surface phase, unable to be viewed by EXAFS, or the reoxidation is part of a dynamic oxidation/reduction cycle. That is, the EXAFS results suggest that the small Co metal clusters do not sustain a bulk reoxidized CoO or Co₃O₄ phase under the normal partial pressures of H₂O encountered in the Fischer Tropsch reactor in the presence of the reducing syngas.

Figure 5 shows the EXAFS data $\chi(k)*k^3$ v. k , the Fourier transform magnitude in r -space, and the first shell inverse transforms for Co metal and catalysts. The inverse transform is the solid line, while the plotted points indicate the fitting obtained from FEFFIT. It is clear by the augmentation of the intensity of the envelope in k -space and by the growth in the Fourier transform peak for Co-Co coordination, that the average metal cluster size has experienced an increase in size with time onstream in the CSTR. Table 2 shows the direct parameters obtained from FEFFIT analysis with their corresponding uncertainties.

Clearly, a substantial increase in Co-Co coordination as cobalt metallic phase is evident during the initial stages of the deactivation period, with a leveling off achieved at approximately 1800 hours of time onstream. This time also correlates very well with the greatest degree of deactivation in the CO conversion, as shown in Figure 2. Therefore, one cannot rule out a sintering mechanism as the main reason for the catalyst deactivation. Certainly, there is an additional fraction of Co metal reduced by addition of Re promoter as shown by the shift in reduction peaks to lower temperature, as demonstrated in Figure 1. This leads to a higher fraction of very small Co metal clusters at the onset of reaction testing. These may be the result of the reduction of a surface phase of Co containing atoms of the support in their structure, or the reduction of very tiny Co oxide clusters which interact with the support and deviate from bulklike Co metal behavior. In either case, their resulting reduction results in a fraction of very small cobalt metal clusters, which causes a lowering of the average cluster size, as demonstrated by H₂ chemisorption/pulse reoxidation measurements in Table 1, in reference to the unpromoted catalyst.

These clusters, therefore, will have a higher surface free energy than the clusters reduced at the same temperature on the unpromoted catalyst. Such unstable clusters, with a greater number of dangling bonds, may therefore be more susceptible to cluster growth, although the

actual kinetics of the process is not yet well understood. On the basis of XPS evidence which indicated surface oxidation of small Co clusters under H_2O /syngas mixtures, it is possible that the sintering may be the result of a dynamic reoxidation/reduction cycle. Such cycles have been shown previously to result in metal cluster growth.

One should also consider the possibility that a fraction of the small metal clusters underwent a phase transformation to an oxidized state during reaction. XANES suggest the formation of a CoAl_2O_4 -like phase, which may not be seen directly by EXAFS. Loss of small metal clusters to an oxidized phase would also result in an increase in the average Co metal cluster size, which would show increased Co-Co coordination in the metallic phase. However, if the oxidation was sustained, then one would also expect to see the appearance and growth of a Co-O peak as well as a contribution from a Co-Co coordination at higher R for an oxidized Co phase, especially after the extent of deactivation observed in Figure 2. The EXAFS results presented here as a function of time onstream suggest an increase in the Co cluster size only, most likely the result of a slow loss of surface sites by a sintering process. Finally, addition of Re promoter does aid in reducing the Co species, thereby generating a greater number of initial active sites, improving the initial activity. However, the resulting catalyst also showed a higher initial rate of deactivation than the unpromoted catalyst, indicating that promoter addition alone does not guarantee a better catalyst from the standpoint of long-term stability.

CONCLUSIONS

The deactivation of a promoted 0.2%Re-15%Co/ Al_2O_3 catalyst in a CSTR was investigated. A novel method of isolating samples of catalyst directly from the reactor during the course of reaction testing in solid wax for XAFS investigation was demonstrated. Results showed, as suggested in an earlier study of spent noble metal promoted catalysts, that the deactivation likely involves two processes. First, EXAFS of samples with time onstream

strongly indicates significant cluster growth by a sintering process as a major component to the deactivation. However, in line with our previous investigation, XANES of the most heavily deactivated samples indicates that a fraction of Co species underwent a phase transformation to a phase resembling that of CoAl_2O_4 . Addition of metal promoters to achieve reduction of Co species in interaction with the support results in unstable Co metal clusters, which are likely the cause of the higher initial deactivation rates of these catalysts during Fischer-Tropsch synthesis.

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Table 1							
H ₂ chemisorption (TPD) and pulse reoxidation results for Al ₂ O ₃ (200 m ² /g) Supported catalysts, with and without Re promoter							
<i>Catalyst</i>	<i>μmol H₂ desorbed per g cat</i>	<i>Uncorr %D</i>	<i>Uncorr diam. (nm)</i>	<i>μmol O₂ pulsed per g cat</i>	<i>% Red</i>	<i>Corr %D</i>	<i>Corr diam. (nm)</i>
15%Co/Al ₂ O ₃	67	5.3	19.6	509	30	17.6	5.9
0.2%Re-15%Co/Al ₂ O ₃	142	11.2	9.2	939	55	20.4	5.1
0.5%Re-15%Co/Al ₂ O ₃	143	11.3	9.2	993	59	19.1	5.4
1.0%Re-15%Co/Al ₂ O ₃	168	13.2	7.8	1187	70	18.9	5.5

Table 2									
Best-fit values for average coordination number (N_1) for the first Co-Co shell, shift in E_0 , Debye-Waller factor (σ^2), lattice expansion ($delr$), and fractional misfit (r). Relative uncertainties are also displayed.									
Sample	N_1	ΔN_1	e_0	Δe_0	σ^2	$\Delta \sigma^2$	$delr$	$\Delta delr$	r - factor
355 hours	2.68	0.43	2.56	1.94	0.00359	0.00133	-0.0258	0.0120	0.115
665 hours	3.47	0.37	3.10	1.27	0.00422	0.00093	-0.0216	0.00808	0.045
980 hours	5.61	0.28	5.49	0.59	0.00389	0.00043	-0.0166	0.00375	0.018
1340 hours	6.50	0.32	7.21	0.57	0.00399	0.00043	-0.00673	0.00368	0.017
1800 hours	7.56	0.27	7.74	0.41	0.00455	0.00032	-0.00407	0.00268	0.0088
2135 hours	7.65	0.34	7.70	0.50	0.00500	0.00041	-0.00303	0.00339	0.013

Figure 1. Comparative TPR spectra of unpromoted (bottom) 15%Co/Al₂O₃ catalyst with those promoted with (moving up) 0.2%, 0.5%, and 1.0% Re. Top spectra is the reduction of Re₂O₇ precursor (unsupported).

Figure 2. Deactivation profile of the 0.2%Re-15%Co/Al₂O₃ catalyst. Reaction testing conditions were as follows: 493K, 275 psig, 34 SL CO/g cat hr. Arrows indicate points where wax-containing catalyst samples were removed from the reactor for EXAFS analysis.

Figure 3. Normalized Co *K*-edge XANES spectra (left) and XANES derivative spectra (right) of the used catalyst after deactivation time of 1800 hours and 2135 hours in the Fischer-Tropsch Synthesis CSTR reactor versus those of comparative standards, including Co metal foil, Co_3O_4 , CoO , and CoAl_2O_4 .

Figure 4. k^3 and k^0 -weighted Fourier transform magnitudes of Co K -edge EXAFS spectra of the used catalyst after deactivation time of 1800 hours in the Fischer-Tropsch Synthesis CSTR reactor versus those of comparative standards, including Co metal foil, Co_3O_4 , CoO , and CoAl_2O_4 .

Figure 5. EXAFS results $\chi(k) \cdot k^3$ vs k , the Fourier transform magnitude, and first shell inverse transforms for used 0.2%Re-15%Co/ γ - Al_2O_3 catalysts sampled during deactivation at 355, 980, and 1800 hours onstream, respectively. The solid lines represent the inverse transform, while the plotted points indicate the fit by FEFFIT.

Task 4. Wax/Catalyst Separation

The objective of this task is to develop techniques for the separation of catalysts from FT reactor slurries.

A. A Summary of the CAER Experience with Catalyst/Wax Filtration

For the use of an iron Fischer-Tropsch synthesis catalyst in a continuous bubble column slurry reactor, a serious problem is the continuous separation of the heavy wax product from the catalyst slurry. Various approaches have been utilized to separate wax from the catalyst slurry. These include gravity settling with removal of the clean wax, centrifugation, and either external or internal filtration.

While the separation of wax from the catalyst slurry is a problem at the commercial scale, it usually becomes even more difficult as one reduces the scale to one that is practical at the laboratory level. In the following we describe some results obtained at the laboratory scale.

The surface area of our precipitated iron catalysts is of the order of 300 m²/g. TEM examinations show that the individual particles have nearly spherical shape. Both TEM and surface area measurements indicate that the individual particles are about 3.0 nm (30 Å) in diameter. These small particles agglomerate into clusters that are in the 1-3 micron size range. Spray drying of the slurry allows the individual agglomerates to be formed into spherically shaped particles which have an average diameter that depends upon the variables utilized during spray drying. The SEM pictures at four magnifications of a typical product from the spray drying of the precipitated iron catalyst are shown in Figure 1. At the lower magnification, one can readily see that very uniform spheres are produced by spray drying and that they have the appearance of a good catalyst as defined by Sasol (1). At the highest magnification of one of these spheres, it is evident that the spheres consist of 1-3 micron particles.

Using the 2"x6' bubble column reactor, four activations were performed with a spray dried iron catalyst batch that was prepared by United Catalyst Inc. The activation consisted of treating in flowing carbon monoxide for twenty-four hours, ramping the temperature to 200°C in nitrogen and then to 280°C during three hours. At the end of the twenty-four hour activation period, the shape and size of the catalyst particles were identical to the initial catalyst spheres (2). A sample of the activated catalyst was placed in an oil and tumbled at room temperature for increasing periods of time. It was found that, under these conditions, the iron spherical particles attrited by a gradual removal of the outer layers of the sphere rather than by fracturing the product into two or more fragments (schematically illustrated in Figure 2).

There are two properties of the iron/carbon system that contribute to the problem. The first is the change in volume as the iron oxide is converted to the iron carbide form that is needed to have an active catalyst. As the iron oxide is converted to the carbide, there is merely 100% decrease in the density as determined from X-ray diffraction. Likewise, if the iron carbide is oxidized during usage, there will be a nearly 100% expansion in size. This expansion/contraction exerts severe strain on the particle and leads to loss of the integrity of the catalyst particle that was formed by spray drying. There are two extreme views of the impact of the contraction/expansion: in one instance the spherical catalyst particle would remain the same size and any volume change would be restricted to the smaller particles that make up the primary catalyst sphere and in the other instance the entire catalyst sphere would undergo shrinkage to nearly one-half in size as the carbide was formed (schematically shown in Figure 3). The limited data obtained in the 2" diameter slurry bubble column reactor show that the catalyst sphere remains the same size after carbiding as it had in the oxide form. This means that the size of the individual particles making up the catalyst sphere undergoes a volume contraction during carbide formation and that this will significantly increase the void space between the individual

particles and, at the same time, greatly reduce the contact area between individual particles that serve to hold the sphere together.

A second factor is the hardness of the iron oxide. An empirical relationship has been established between strength, hardness and melting-point of inorganic solids with respect to the ability to form pellets. As illustrated in Figure 4, the properties of iron oxide cause it to fall in a region where it would be unpelletable. Thus, the forces that develop during drying that are caused by the presence of water at the points of contact are not sufficiently strong to overcome the hardness of the iron oxide particle. The result of this is that the agglomerate that forms during spray drying is held together by very weak forces, and is therefore easily broken down to the 1-3 micron sized individual particles. To alleviate this problem, some component needs to be present that will assist in making a stronger bond between the individual particles as the spherical particle is formed during the spray drying operation.

Summary of Filtration with Different Catalysts

We have utilized a variety of catalysts for Fischer-Tropsch synthesis in the CSTR using internal filters. Our experience with many runs with each type of catalyst is summarized in Table 1.

Our filtration experience with alumina and silica supported cobalt catalysts, with a few instances when the alumina support did not possess attrition resistance, have been successful. We have run for periods of three months without encountering problems with filtration. This has been the case even when the catalyst loading was so large that the amount of wax produced required us to filter two times per day.

Our limited experience with iron supported catalysts (silica, alumina, magnesium silicate and magnesium aluminate) has, in general, not been reproducible. All four supports show attrition resistance during the CSTR runs. Thus, it appears that the filtration problems, when

encountered, are due to the iron particles being removed from the support and interfering with the filtration and/or separation by gravity settling. More work needs to be done to confirm this.

Problems are not encountered in removing the small amount of reactor wax from the reactor when using the low-alpha precipitated, unsupported iron catalyst. With intermediate iron catalysts, filtration problems are encountered in some runs but not in others. These runs may be of 1,000 hours duration or longer. For the high alpha, precipitated, unsupported iron catalyst we almost always encounter filtration problems at some point in the run; however, the point at which this occurs is very variable.

Estimation of Filtration Rate at Sasol

One approach to evaluate the needed filtration rate is to try to estimate one that is realized in a commercial operation. In the following we utilize the published data for the size of the Sasol slurry reactor (5m x 22m) and the productivity of the reactor (2,500 bbl/day). Assuming that the reactor is only 2/3rds filled with slurry and that the hydrocarbon has a density of one, one can calculate that the productivity is 57.8 kg/hr/m³ reactor volume. It is further assumed that the filter has a cylindrical shape and occupies 1% of the reactor volume; that is, the reactor volume would be reduced by 1% by the filter. It is assumed that 75% of the total product is removed from the reactor through the filter and the remainder goes overhead. One m³ of reactor volume will contain 1.36 m² of filter area. With these assumptions, the filtration rate is 0.53 kg/min/m² of filter area. It is realized that there may be significant errors introduced in the assumptions leading to this calculated value; however, attempts have been made to make assumptions on the conservative side so that the value should be viewed as a conservative estimate.

In operating the CAER CSTRs we have made estimates of the rate of filtration through Mott sintered metal filters. In making this estimate, it has been assumed that the filter is

completely immersed in the slurry and that the total filter area is utilized. In actual practice, it is likely that during part of the filtration time the filter is only partially immersed, and this will make the measured rate be lower than the actual filtration rate. Likewise, it is assumed that the removal of wax occurs during the entire draining period. In actual practice, the wax removal will occur during the earlier portion of the time the valve is open, and this will also make the measured value be lower than the actual value under optimum operation. During one of the runs the measured rate was 2.4 kg/min./m² filter area. Thus, the sintered metal filter will easily provide the filtration rate, and much higher, than is estimated for the Sasol commercial operation. If this is the case, then the filtration problems are associated with technique, and not with the initial capacity of the sintered metal filter.

CAER Filtration Procedure

A schematic of the CSTR system is shown in Figure 5. Two paths are available for the reactor products to exit, depending on the configuration/arrangement of the valves associated with the sample traps. The components of interest are the hot (or rewax) letdown valve and trap, the warm (or wax) letdown valve and trap, and the equalizing valve between the hot/rewax and warm/wax traps).

The primary path for products to exit the reactor is via a line that connects a port on the upper, inner surface of the reactor head to the warm/wax trap. Ideally, these products are in the vapor phase. After exiting the reactor head, they pass through a 7 μ m sintered stainless steel filter and then through the warm/wax trap letdown valve to pass through the warm/wax product trap (typically set for a temperature of 100°C). The reactor effluent then flows to the oil trap to condense the oil fraction (usually set for 0°C). The remaining product gas passes through the back pressure regulator, where the pressure is reduced to a value slightly above atmospheric, and then to either an on-line gc or to the vent line.

An alternate path for the products to exit the reactor is via the rewax filter. This filter has been positioned at several levels below the inner top surface of the reactor head, ranging from the liquid-gas interface to being immersed in liquid near the bottom of the reactor. The porosity of the rewax filters have ranged from 0.5 to 2 μ m. The material exiting the rewax filter then passes through the hot trap letdown valve and then on into the hot/rewax product trap (normally set to 200°C). The products then pass through an "equalizing" valve located between the rewax and wax traps and then passes in turn through the wax and oil traps and finally through the back pressure regulator to either the gc or the vent line. Note that in this configuration the wax trap letdown valve is closed, thus eliminating a short circuited path for the reactor effluent. This ensures that the reactor effluent flows through the series arrangement of first the rewax trap, then the wax trap, and finally the oil trap.

Ideally, the system should be operated to have a continuous gas plus liquid products exit the reactor. To accomplish this the reactor product should continuously exit the reactor through the rewax filter and pass through the series arrangement of the rewax, wax, and oil traps. In this mode of product removal the wax trap letdown valve would be closed so that no product could be shunted around the rewax trap. In theory, utilizing this mode of operation for product letdown would allow for an accumulation of reactor contents to a fixed level, which would be determined by the positioning of the rewax filter. Once the slurry level had increased to the level of the rewax filter, both gas and liquid product would be continuously at the slurry-gas interface from the reactor through the rewax filter (thereby achieving a volumetric steady state condition). If the slurry level did rise to completely submerge the rewax filter, the reactor inlet gas pressure would temporarily rise and this should be sufficient enough to force the excess liquid product out through the filter, allowing the pressure to return to the desired setting once gas breakthrough occurred. This mode of operation is appealing in theory, in that a fixed volumetric inventory

could be maintained. Unfortunately, the accumulation and build up of product/catalyst with time on the rewash filter causes a pressure drop across the rewash filter to increase; this results in an increase in the reactor pressure. In fact, in the past, the increased pressure drop across the rewash filter has resulted in the reactor pressure attaining a value equal to the inlet pressure of the mass flow controllers, resulting in no flow into the reactor.

Due to the inability to operate in the continuous mode mentioned above, a different technique for the letdown of reactor products was developed. The continuous method was modified by allowing the rewash trap to be bypassed for the majority of the sample period. Sample periods are typically one day in duration, with the exception of those following weekends and holidays when longer periods are encountered. The valving arrangement for this modified technique has the rewash trap letdown valve in the closed position and with both the wax trap letdown and the wax/rewash trap equalizing valve in the open position, for the majority of the time. In this configuration, the slurry in the reactor can increase to levels above that of the rewash filter, resulting in an unsteady state volumetric condition. Usually, several hours prior to the daily collection of trap products, the rewash letdown valve would be opened and the wax trap letdown valve would be closed, while the wax/rewash trap equalizing valve would remain in the open position. This permitted the reactor product (gas and/or liquid) to exit exclusively through the rewash filter (either 0.5 or 2 μm filter) as opposed to essentially an open port in the top of the reactor head (which does have the 7 wax filter). In this configuration, it was expected and realized that the reactor pressure would increase, particularly if the level of the reactor's contents was sufficient to completely immerse the rewash filter. To insure that the reactor pressure did not increase to values much higher than that of the specified pressure for FTS or to pressures that would stall out the mass flow controllers, required continual monitoring of the reactor pressure. If and when the reactor pressure increased to an unacceptable level, the wax letdown valve

would be opened slightly to allow venting down of the pressure build up in the reactor, and then the wax letdown valve would be closed to continue the reactor liquid product letdown procedure.

Not only did this procedure result in pressure swings during the liquid letdown period, but at best, the reactor inventory would oscillate about some level, neither of which to be considered steady state. In fact, there was no guarantee that the amount of liquid reactor product withdrawn was equivalent to that which was being produced in the reactor for a given sample period. Later, a technique was adopted that utilized a computerized mass balance method designed to predict the day-to-day reactor accumulation of product.

Another valving modification and letdown technique that was tried was to have all the valves associated with the sample traps (i.e., the letdown valve for the rewax trap, the wax trap, and the equalizing valve between the rewax and wax traps) in the open position at all times. It was thought that the two parallel paths for the reactor products to exit the reactor, which recombine at the inlet to the wax trap, would allow for the continuous removal of both the gaseous and liquid products to exit without variations in the reactor pressure. The reactor pressure did in fact remain constant as there was always a path for the overhead condensable gaseous products to exit the reactor via the wax discharge line (through the 7 μ -wax filter and then through the letdown valve leading to the wax trap). The second of the two parallel paths for products to exit, which is for the removal of the accumulated liquid reactor product, incorporates the 0.5 or 2 μ m rewax filter, which is internal to the reactor, and the letdown valve leading to the rewax trap. As mentioned, the discharge line from the rewax trap feeds through a "wax/rewax trap equalizing" valve into the inlet of the wax trap. The pressure difference across the path for removal of the accumulated liquid product is at least equal to, or slightly greater than, that of the pressure difference that exists across the discharge path for the condensable gas products. It was thought that the force that was generated as a result of this pressure difference, although small in

value, would be sufficient to provide the necessary driving force to aid in the removal of the accumulated liquid reactor product. In practice, this was not the case and liquid would accumulate in the reactor more rapidly than it was removed through the rewax filter.

Experimental Data-Process Operations

The initial runs effected separation of reactor product from catalyst slurry using a 0.5 μ Mott Metallurgical Corporation sintered stainless steel filter (0.5 " O.D. and 1" in length for a surface area of 0.0109 ft²). This filter was positioned so that the bottom surface is about 3 inches from the upper internal surface of the head of the one-liter CSTR, which has an internal diameter of 3" and an internal height of 10 $\frac{1}{4}$ " with a hemispherical bottom and a cylindrical shaped top. Since using the Polywax PWR3000 high molecular weight wax (average molecular weight of 3,000) as a reactor solvent, problems have persisted in that the filter was increasingly being blinded off, resulting in an increasing inability to remove the reactor product (i.e., the heavy liquid product at reactor temperature and pressure we refer to as 'rewax'), allowing the reactor to ultimately fill up, resulting in aborting the runs. Potential solutions to this problem have been suggested and/or implemented.

The first attempt, which has been incorporated, was to lower the filter to insure that it is completely immersed in the catalyst slurry. This allows the filter to be continually washed by the slurry and eliminate or at least minimize the blinding off of the filter. To accomplish, the filter is lowered at an elevation so that its bottom surface is about seven inches below the upper surface of the reactor; that is, the bottom of the filter is positioned about $\frac{1}{4}$ inch above the upper surface of the gaspersator blades.

The first run using this lowered filter configuration was LGX263 using a low-alpha catalyst (100Fe:4.60Si/2.72Cu/0.00K). As shown in Figure 6 (i.e., Rewax Flux Density vs Sample Day for Run LGX263), problems were encountered in attempting to remove the rewax

for the first 12 days of operation. This was due to the fact that the line from the reactor head to the rewax trap was heated at a too low of a temperature, specifically lower than the melting point of the Polywax PWR3000 (130°C). When additional heat tracing was applied to the line, rewax removal was then permitted as can be seen for sample days 13-17. The rewax collected during this run showed no visible traces of iron. The filtration rate was about 0.06 gallon/min/ft² filter area/min., a value that compares favorably with that estimated for the Sasol commercial plant.

Another run that also incorporated the lowered filter utilized a high alpha iron catalyst (LGX266; (100Fe:4.60Si/2.72Cu/7.52K). Figure 7 shows the performance of the filter, as measured by flux density (gpm/ft²), decreased with time. The implication is that blinding of the filter increases with subsequent rewax letdown periods. As in run LGX263, the rewax product showed no visible evidence of iron catalyst content. Two rewax samples, LGX266-005 and LGX266-007, were analyzed for iron content and showed 0.03wt% Fe and 0.01wt% Fe, respectively. Also, note that on this figure there is reference to the Regimesh Filter that has a flux density of 0.13-0.20 gpm/ft, surface area of 0.175 ft², and a porosity of 18μ (corresponding to about 16 times the area and an increase of 36 times the porosity of the Mott SS-filter that we were using). With the maximum pressure drop across the Mott SS-filter at 75 psi and the pressure drop across the Regimesh filter unknown, a comparison of the performance of the filters is not possible. From the liquid flow characteristic graphs supplied with the Mott product catalog, by changing the μ-grade from 0.5 to 20μ (while holding the viscosity and pressure drop constant) the flux density should increase about 100-fold. However, if the pressure difference is varied and the μ-grade and viscosity held constant, the relationship between the flux density and pressure drop is linear.

After the completion of run LGX266, an attempt was made to test a 2μ Mott SS-filter. This was accomplished by opening up the reactor after it had cooled to 130°C and replacing the

0.5 μ -filter with a 2 μ -grade filter. Comparing the liquid flow media charts in the Mott catalog for the 0.5 μ and 2 μ filters, at equal pressure differences and viscosities, the average flux density should increase by a factor of seven. Once the reactor was back to normal operating conditions, the rewax valve was opened for a rewax letdown period of one hour. About 300g of reactor contents were removed. The collected product contained catalyst but it was not possible to decide if:

- 1) the wax/catalyst leaked through an improperly tightened filter fitting,
- 2) had it passed straight through the 2 μ filter,
- 3) was due to the fact that the level had dropped so much that the filter was exposed to the gas/froth space that may contain finely ebullated catalyst particles, or
- 4) possibly a combination of the above.

Since the results of the 2 μ filter at the end of Run LGX266 were inconclusive, another 2 μ filtration test was attempted after Run LGX268 was completed (LGX268 used the 100Fe:4.60Al/2.72Cu/3.66K as well as a 0.5 μ filter). The results from this series of rewax letdowns was more promising since the rewax product collected appeared catalyst free. Thus, a run was made with the installation of a 2 μ filter prior to the start of a run (LGX271; (100Fe:4.60Al/2.72Cu/15.87K). During a 240 hour run, with CO conversion at about 30%, rewax could be removed that did not contain catalyst. The run was terminated because of the low catalytic activity.

The second of the potential solutions to address the problem of rewax removal and reactor overfilling was to develop a mass balance for the system to allow for the prediction of the amount of rewax to be removed so that a constant reactor inventory could be maintained. Simply stated,

$$\text{Reactor Accumulation(g)} = \text{Gas in(g)} - \text{Gas out(g)} - \text{Trap Products out(g)}.$$

Two versions of this mass balance were developed. The first just accounts for the mass of the gas out based on the Carle Series 400 AGC chromatographic data and is referred to as the simplified mass balance. The second, and certainly more sophisticated, utilizes chromatographic data from the HP-5790 as well as the AGC data. By adding either reactor accumulation terms to the starting weight of the wax/catalyst slurry, a predicted reactor inventory is determined. Runs LGX's 267, 269, and 270 have had either one or both of these mass balances applied to them, with mixed results. Figure 8 shows run LGX267 (100Fe:4.60Al/2.72Cu/0.00K) using the second mass balance which predicted that there was about 127g remaining in the reactor, while in fact the reactor contents were measured at 92g after the completion of the run. Note that the dashed line across the graph indicates the starting weight of the of the reactor slurry, which was 318.68g. Figure 9 is for run LGX269 (100Fe:4.60Al/2.72Cu/7.52K), which also had a starting weight of 318.68g. Both mass balances are presented and up until run hour 144, agree rather well with one another. After run hour 144 there is a divergence of predicted reactor contents in which there is an approximate 50g difference in values. At the end of the run the disagreement was at about 40g, but the actual measured amount of wax/catalyst in the reactor for this run was at 598g, 55% more than the second mass balance predicts and 73% more than the first, i.e., the simplified mass balance prediction. These discrepancies have yet to be resolved. A final application of the mass balances, to date, was used for run LGX270 (100Fe:4.60Al/2.72Cu/11.58K) shown in Figure 10. For this run the predicted reactor contents agree to within about 20 g of one another, 384.8g for the simplified and 363.2g for the second method (within 6% of each other), as well as both prediction models compared to the final measured wax/catalyst weight of 310g (24% high for the simplified method and 17% high for the second method). Although there is some disagreement with either method and the final actual weight of the reactor contents, this is potentially a very useful technique for maintaining and

predicting reactor inventory, as well as predicting the amount of rewax to be removed from the reactor on a daily basis.

The third of the solutions for addressing the problem of reactor rewax removal and that of avoiding reactor overfilling involves the installation of a liquid back flush bomb for the rewax filter. Presently, the rewax bomb itself can be used as a gas charging vessel by closing the rewax letdown valve and the equalizing valve between the rewax and wax traps. An inert gas can then be introduced into the rewax bomb at a pressure higher than that of the reactor, the rewax valve opened and the gas pressure can force the hydraulic column of rewax (contained in the rewax line and the rewax filter) to back flush the filter. Although this capability does exist and has been used, there is probably not enough rewax present in the line and filter to perform an adequate backflush. In addition, the rewax letdown valve is a flow control/throttling type of valve and does not allow for an instantaneous surge of higher pressure gas to force the rewax material as, for example, a ball valve would allow. With a bomb installed on the branch of a tee (with a ball valve separating the bomb and the branch of the tee) and the run of the tee plumbed between the reactor head rewax discharge port and the existing rewax valve, liquids such as C-30 oil could be used to facilitate this back flush. Such an apparatus will be constructed and tested.

The most recent method/technique used in assisting the removal of reactor liquid product involves isolating and charging the hot/wax trap (see Figure 5) to a pressure about 75 psi lower than that of the reactor. Once the trap is at the desired pressure, the hot trap letdown valve can be opened to allow the pressure difference to force out the reactor liquid product. A variation of this technique uses the gas law to predict the pre-letdown pressure for a desired volume of reactor liquid removal.

The importance of cleaning the filter cannot be understated, and can be demonstrated by returning to Figure 7. It is seen that as time progresses, the flux density decreases, requiring

longer periods of letdown time to remove the desired amounts of rewax, which are determined by using either of the reactor mass balance techniques. This was experienced for FTS runs LGXs 267, 269, and 270. The situation was such, that to remove the necessary amount of rewax, the letdown periods were approaching six to seven hours in duration.

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Table 1			
Summary of Filtration with Iron and Cobalt Catalysts			
Alpha	Iron, Unsupported	Iron, Supported	Cobalt, Supported
Low ($< \approx 0.7$)	No Problem	No Problem	---
Intermediate (0.7 to 0.85)	Problems in some runs	-----	No Problem
High (> 0.85)	Problems	Problems	No Problem

Figure 1. Scanning electron microscope pictures of spray-dried, precipitated, iron catalyst at four increasing magnifications (x100, 200, 500, 1,000; size scale indicated in picture).

Figure 2. Schematic of attrition of spray-dried precipitated iron catalyst by a gradual decrease in size of the primary particle.

Particle Contraction / Expansion

Figure 3. Schematics of size changes in activation of an iron catalyst and then reoxidation for: (top) whole particle changes size and (bottom) whole particle remains same size and individual units of particle changes size.

Figure 4. Relationship of physical properties and pelletability of compound classes.

Figure 5. Schematic of CAER reactor system (top) and CSTR (bottom).

Figure 6. Rewax flux density vs. sample day for run LGX263_{R7}
(100Fe:4.60Al/2.72Cu/0.00K).

Figure 7. Rewax withdrawal weight and rate vs. sample day for run LGX266_{R7} (3.0wt.% Cu, 5.0 wt.% K, $T_{\text{syn}} = 230^{\circ}\text{C}$).

Figure 8. Predicted reactor inventory vs. time-on-stream for run LGX267_{R1}.

Figure 9. Predicted reactor inventory vs. time-on-stream for run LGX270_{R4}.

B. Filtration with High Alpha Unsupported Fe Catalysts

The filtration problems need to be addressed from two viewpoints: the ability to operate the CSTRs and the ability to filter at the pilot or commercial plant scale.

To date we have been able to filter the products from the operation of CSTRs when we operate with cobalt catalysts. In these operations we utilize 10 wt.% catalyst (total catalyst, not cobalt) and have operated for nearly 4,000 hours on occasion. Only on very rare occasions have we encountered problems with filtration. Thus, in 95+% of the runs, the pressure generated when we open the internal filter to remove reactor wax is less than 40 psig and the wax (up to 75 grams) can be removed in less than three hours, and usually in a shorter time period. Thus, from the viewpoint of operating a CSTR with alumina or silica supported cobalt catalysts, we have been able to remove wax and operate the CSTR for extended run periods. We have less experience with a titania supported catalysts but during about 10 runs we have been able to remove the reactor wax. In general, these cobalt catalysts are what we define as intermediate alpha (0.75-0.90) catalysts. Thus, while the wax is highly hydrogenated it does not have the very high molecular weight of a high alpha catalyst (alpha greater than 0.90).

We continue to have problems removing reactor wax from the CSTR when using the unsupported high-alpha iron catalysts. When we operate with a 0.5- or 2.0 micron Mott sintered metal filter, we find that the reactor wax that is withdrawn has a low iron content (30 ppm or less). Thus, the filter functions to retain the precipitated iron catalyst with particles in the 1 to 3 micron size range in the reactor. However, with time the ability to remove wax decreases.

The following data demonstrate the difficulty in quantifying the filtration ability during a run with a high-alpha precipitated iron catalyst. The particular catalyst used for run BAO-029 produced a soft wax that is representative of an intermediate alpha catalyst (alpha approaching 0.90). The filtration rate was obtained from the amount of reactor wax withdrawn and the time

that the internal, submerged filter was open to the collection vessel. The removal line is fitted with a pressure gauge that permits us to reduce the pressure in the collection vessel by an amount that is known and is below that of the reactor in order to provide a driving force for the removal of wax. At present, we do not have the ability to adjust the pressure in the collector to maintain a constant head pressure to provide a constant driving force. Thus, as gas passes through the filter along with the reactor wax, the pressure in the collector increases and this results in a decrease in the driving force together with a decrease in the filtration rate.

Early in the run, the amount of wax removed was low, presumably because the small amount of startup solvent and the rate of production of wax did not keep the filter submerged in the liquid during the entire time that the filter was open to the collector (Figure 1). Thus, for about 50 hours of operation the filtration rate was increasing to attain a value of about 6,000 g/hr-ft² (100 g/min-ft²), a much higher value than reported in the last quarterly report (0.1 g/min-ft² or lower). During about 100 hours, the filtration rate remained at about 6,000 g/hr-ft², then appeared to gradually decline to about 1,000 g/hr-ft² (16 g/min-ft²) and then remain essentially constant during 200 hours of operation. The run was terminated because of scheduled laboratory shut-down, and not due to filtration problems.

Attempts have been made to operate the reactor by calculating, based upon the experimental values of other samples collected and the gas flows, the amount of reactor wax that should be withdrawn and then withdrawing that amount of wax. This has had variable success. The cumulative grams of hydrocarbon products produced during the nearly 400 hour run are shown in Figure 2 together with the cumulative calculated grams of wax produced and the cumulative grams of wax withdrawn. According to the data shown in Figure 2 we should have accumulated about 754 grams of reactor wax but when we opened the reactor the amount was only about 500 grams. This amounts to less than 4% error in the mass balance during the entire

run. Since some sample is lost due to flashing during the collection of the products from each of the three traps for each collection period, the mass balance is considered to be excellent.

The filtration rate shown in Figure 1 is not a reliable estimate of the actual filtration rate and is therefore impacted upon the sample removal technique. There was concern that too much wax was accumulating in the reactor so that at 216 hours, a large amount of wax was withdrawn during a 7-hour period. The average filtration rate during this 7-hour period was greater than 5,000 g/hr-ft² (shown as □ in Figure 1), near the maximum rate obtained earlier in the run. Thus, the low rate shown before and after 216 hours must be due to the sampling technique and this must be defined so that a more quantitative filtration rate can be obtained.

Figure 1. Filtrate rate as a function of time-on-stream.

Figure 2. Cumulative hydrocarbon and wax produced and wax withdrawn as a function of time-on-stream.

C. Initial Filtering Studies with Pall Corporation Filters

Summary of Separation Work

Wax separation from a catalyst slurry for slurry bubble column reactor operation can be viewed from two perspectives:

1. Separation of wax from large (50-100 micron) sized catalyst particles formed by spray drying and made attrition resistant.
2. Separation from small catalyst particles (1-3 micron) and eliminate the need for attrition resistant large particles.

The immediate separation problem to be solved by CAER work is to be able to operate a laboratory reactor to define activity, selectivity and aging characteristics of high alpha iron catalysts. A longer term solution is to develop procedure for the operation of the LaPorte facility and potential commercial operation.

The CAER efforts apply for two catalyst systems: cobalt and iron.

Cobalt Catalysts

CAER personnel have prepared supported cobalt catalysts based on alumina, silica and titania support material. The supports have sufficient attrition resistance to retain their physical shape and size during weeks of operation in a CSTR.

CAER personnel have successfully removed wax from the reactor during operations of up to five months using supported cobalt catalysts. The only wax separation problem with cobalt catalysts was when testing for a company (work outside DOE contract) due to attrition of a poor support.

Conclusion

Wax separations from catalyst slurry is not a problem using a fine (2 to 5 micron) porous metal filter. Operations of laboratory reactions with wax production of 100g/day or higher can

be accomplished. Wax removal is therefore not a problem with supported cobalt catalysts in the laboratory setting. For Run 4 at LaPorte, it has been reported that filtration was not a problem but was a problem for Run 3 with a similar catalyst.

Iron Catalysts

All spray dried iron catalysts that have been tested at CAER have attrited to 1-3 micron sized particles during the activation period. Supported iron catalysts can be utilized without attrition of the support.

Using a porous metal filter with the small (1-3 micron) sized iron catalyst, operates with a 10 wt.% slurry of a high-alpha unsupported iron catalyst had to be terminated after 200-400 hours due to filter plugging, resulting in the reactor filling with wax. With the supported high-alpha iron catalysts, the support did not attrite but the filter plugged; it is assumed that this was due to the small iron particles being released from the support.

Wax removal has now been accomplished when the small (1-3 micron) high-alpha (0.92) iron catalysts are used in a laboratory reactor containing 10 wt.% slurry. A Rigimesh filter permitted operation for 1450 hours (2 months) without having the filter plug. When the run was voluntarily terminated, the filtration rate had not declined. The run was terminated in order to make a run that contained a higher wt.% catalyst slurry. Using the same catalyst with finer pore openings resulted in filter plugging after 100 hours (very fine filter) and 1000 hours (medium porosity filter). Using the Rigimesh filter, the catalyst loss with the withdrawn wax was about 1%/week; the catalyst activity also declined at about 1%/week.

Conclusion

The Rigimesh filter can be utilized to permit the operation of the laboratory reactor to define the long-term activity and selectivity of intermediate and high-alpha iron catalysts. The wax removal flux is lower than desired for commercial operation; however, the rate obtained

during the CAER initial work should be viewed as the minimum. Should this initial success continue, we will be able to operate laboratory reactors without the need to develop attrition resistant iron catalysts.

Detailed Description of Filtration Study with Pall Filter

Two filters manufactured by Pall Corporation were installed in 1000 mL continuous stirred tank reactors. The filters had the same geometrical external surface area as the Mott Metallurgical sintered filters used previously. Two types of filtering media were used. One filter used a material called Rigimesh (filter A). Rigimesh is a sintered woven wire mesh which Pall Corp. reports as having the greatest permeability for comparable removal efficiency. Sintering increases the strength of the mesh by bonding the wire at each point of contact which prevents shifting of the wires and maintains a constant pore size. The filter used in this study was a multilayer composite of different mesh sizes. The other filter tested is composed of PMM medium (filter B). PMM medium is a thin sintered matrix of stainless steel powder within the pores of sintered stainless steel mesh. The sintered powder allows for filtration down to μm and the stainless steel mesh provides strength.

Each filter was tested with the same high alpha catalyst. The catalyst was prepared by standard continuous precipitation techniques and impregnated with KNO_3 and $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ to give an atomic composition of 100Fe/4.6Si/2.0Cu/5.0K. The reactor was loaded with 32.2 g of catalyst and 310 g of decene trimer. The catalyst was activated with CO at 270°C , 175 psig for 24 hours. Following activation, syngas ($\text{H}_2/\text{CO} = 0.67$) was started at a space velocity of $3.1 \text{ sl h}^{-1} \text{ g-Fe}^{-1}$. The temperature and pressure were maintained at 230°C and 175 psig, respectively.

A schematic of the reactor, traps and filtering system is shown in Figure 1. Reactor effluent (vapor phase) exited through valve 1 which was open at all times, unless the filters were being purged. Valve 2 was normally closed. Wax removal was accomplished by venting the

wax trap to 125 psig (50 psi less than reactor pressure) with valve 3 closed (wax trap isolated from reactor and 60°C trap) followed by slowly opening valve 3. Wax removal was considered to be finished when the pressure of the wax trap was equal to the reactor pressure. Accumulated reactor wax was removed approximately every 24 hours. The first wax samples appeared black due to catalyst penetrating the filters. After a few days the wax samples appeared clean, presumably due to the formation of a filter cake on the filter. The amount of wax removed during the first 5 minutes that valve 3 was open was determined on most days to calculate the rate of filtration and determine if the filters were plugging. The initial filtration rates for the two types of filters are shown in Figure 2. The filtration rate of the PMM filter was higher than the Rigimesh filter for the first 380 hours. It is emphasized that these are minimum filtration rates.

The reactor plumbing was arranged such that the filter could be periodically purged with Ar in order to clean the filtering medium and prolong filter life. To purge the filter, valves 1, 2 and 3 were closed. Valve 4 was opened to pressurize the wax trap with Ar up to 250 to 400 psig. Valve 3 was opened slowly to allow Ar to flow back into the reactor through the filter. The first time the filter back purge was done was at approximately 390 hours of the run with the Rigimesh filter. The filter was purged with 300 psig Ar and showed no signs of plugging because the reactor pressure rose immediately and within seconds the wax trap and reactor pressures were identical. A wax sample was taken 30 minutes after purging the filter and it appeared black due to catalyst penetrating the filter (just like the wax samples at the beginning of the run). Twenty-four hours after purging the filter the wax withdrawn through the filter appeared clean. Once again, the clean wax was probably due to better filtration from the build-up of a cake on the filter. The PMM filter was also purged after approximately 510 hours on stream. This filter seemed to be partially plugged because it needed to be purged 6 times with Ar pressure ranging from 250 to 400 psig; however, it was successfully cleaned by the back purges. The cumulative

wax yield for each run is shown in Figures 3-5. The cumulative wax yield was the same for each run and after 700 hours, and about 1.4 kg of wax had been removed from each reactor (Figure 3).

Syngas conversion as a function of time on stream is shown in Figure 6 for both runs. The conversion was nearly superimposable for the two runs, indicating excellent reproducibility of catalyst activation and activity measurements. There was an induction period of about 3-5 days in which the conversion increased from about 17% to 49%. After the conversion peaked, the catalysts deactivated at the rate of 3.4% syngas conversion (absolute, not relative) per week. Methane selectivity for the two runs decreased to below 2% after 100 hours (Figure 7) on stream which is indicative of high alpha catalysts (alpha-2 was 0.92 for both catalysts).

These runs represent the first time that a high loading of precipitated iron catalyst was run at the CAER under high alpha conditions with 10 wt.% slurry for an extended time (> 800 h). Typically with the Mott Metallurgical filters, high alpha runs were terminated after approximately one week due to filter plugging and subsequent filling of the reactor with wax.

The cumulative iron in the products from run BAO 36 (using the filter A) and BAO 35 (using filter B) are shown in Figures 8 and 9, respectively. During the period up to about 150 hours very little reactor wax was removed as the reactor filled to the filter level. For the period of about 150 to 200 hours the first significant reactor wax was removed from the reactor (Figure 4). During this same period a significant amount of iron (about 1 g) was removed using filter A (Figure 8). This is a clear demonstration of iron leakage through the filter during the initial wax withdrawal period. From the period of about 200 to 390 hours on stream, the removal of iron was slower and at a nearly constant rate of about 0.22 g Fe/week. At run hour 390 the filter was backflushed using argon. After the backflushing, there was a period of rapid iron removal (about 0.4 g Fe in one day). This conclusively shows that the backflush was effective in partially, or completely, cleaning the “cake” of iron deposited on the filter. Following this backflush, the

filter was operated without backflushing. From 400 to 1,000 hours on stream the iron and reactor wax was removed at a constant rate. During this 600 hour period, the slope of the line in Figure 8 indicates that iron was removed at a rate of 0.18 g Fe/week. The values of 0.22 and 0.18 g Fe/week for the two periods of constant iron removal are in excellent agreement considering the length of time for the run. Since the reactor was loaded with 20 g of iron, the filter permitted the passage of about one percent per week of the iron. The run was terminated after almost 1500 hours (2 months) of continuous operation. The filter was operating as well at the end of the run as it was during the course of the run. The termination with this filter was voluntary, and not due to filter plugging. **Thus, we consider this to be a demonstration of our ability to operate the CSTR so that we can now define the activity, selectivity and catalyst deactivation characteristics for both the intermediate and high alpha catalyst.**

The run (BAO 35) using filter B was less effective than for filter A. The run had to be terminated after about 1,000 hours on stream due to the filter plugging. This allowed the reactor to fill with reactor wax. This filter has been sent to be cleaned by a commercial organization recommended by Pall to learn whether it can be reused after cleansing or whether the plugging is so severe that the filter must be discarded. Filter B has a component that has finer openings than filter A; thus, it is assumed that the plugging is due to the finer average pore opening.

The alkali content of the high-alpha, low-temperature catalyst has a significant impact upon the conversion that is attained. The alkali content of the catalyst utilized in these two runs was about 5 wt%, and this is below the level that should give the maximum conversion. Even so, the conversion is in the range of 30-45% and the hydrocarbon productivity rate is 0.22-0.35 g hydrocarbon/g Fe/hr. This productivity rate compares favorably with those reported for the productivity of cobalt catalysts when the cobalt productivity is based on g hydrocarbon/g

catalyst/hr). Early indications are that the catalyst formulation with 7.5 wt.% potassium has about twice the productivity of the catalyst containing 5 wt% potassium.

There is a reasonably long induction period in which the activity increases, then attains a maximum which is followed by a period where the activity gradually declines to a nearly constant activity after about 500 hours on stream. During the period between 800 and 1463 hours, the activity declines at a rate of 0.8% CO conversion/week. During this period the iron catalyst in the reactor is declining at a rate of about 1%/week. **Thus, the activity decline is at approximately at the same rate as the loss of catalyst, and the catalyst activity decline is clearly lower than the DOE target of 1% CO conversion/week.**

The catalyst with 5 wt% potassium is a high-alpha catalyst with the second alpha being about 0.92. The methane make is consistent with a high alpha catalyst and is about 1.5 wt% of the total hydrocarbon fraction (Figure 7). The fraction of the C₂ fraction (Figure 10) that is represented by ethylene (about 85%) is representative of a high-alpha catalyst, as is the C₃ (Figure 11) and C₄ (Figure 12) olefin fractions. The fraction of CO converted by the water-gas-shift reaction is about 0.35; thus, about 65% of the CO that is converted is to hydrocarbons.

Figure 1. Schematic of the reactor, traps and filtering system.

Figure 2. Cumulative wax yield rates for two types of filters.

Figure 3. Filtration rate (first 5 min.) For two types of filters.

Figure 4. Accumulation of rewax vs. time on stream for filter A.

Figure 5. Accumulation of re wax vs. time on stream.

Figure 6. Syngas conversion as a function of time-on-stream.

Figure 7. Methane selectivity as a function of time-on-stream.

Figure 8. Accumulation of iron vs. time on stream.

Figure 9. Accumulation of iron vs. time on stream.

Figure 10. C₂ ratio vs. time on stream.

Figure 11. C₃ ratio vs. time on stream.

Figure 12. C₄ ratio vs. time on stream.

D. Hi-alpha Catalyst and Special Filter

Today, the marketplace place a premium on FTS diesel but not gasoline; thus, the current view is that the most attractive option is to produce high molecular weight FTS products and then to hydrocrack them to produce high quality diesel fuel. High molecular weight FTS products are not volatile at the usual reaction temperatures and pressure. This requires that liquid products be separated from the catalyst.

The inability to operate the fixed-bed reactor isothermally makes it attractive to use a slurry bubble column reactor. With the slurry reactor, a wax-catalyst separation must be accomplished, either within or external to the reactor.

This report presents the preparation of three of high alpha iron catalysts that can produce large quantities of high molecular weight FTS products and four filters to be used for wax-catalyst separation within the slurry reactor.

100Fe/4.6Si (Atomic ratio) is prepared by dissolving $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (18907.29 g) and tetraethyl orthosilicate (448.76 g) in distilled water, then precipitated with concentrated ammonium hydroxide. The pH of the slurry was >9 . The slurry was filtered. The filter cake was dried at 110°C . The base catalyst was crushed to approximately $60\mu\text{m}$ and calcined in air at 350°C for 4hr.

The 100Fe/4.6Si base catalyst was impregnated with the appropriate amount of K_2CO_3 and $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ to give an atomic composition of 100 Fe/4.6Si/2.0Cu/5K, 100Fe/4.6Si/2.0Cu/7.5K and 100Fe/4.6Si/2.0Cu/10K. The amount of K_2CO_3 and $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ added will depend on the iron content of base catalyst. Typically the base catalyst is about 68 wt% Fe. For an atomic composition of 100/Fe/4.6Si//2.0Cu/7.5K, 80.05g of 100 Fe/4.6Si was impregnated with 26.4 ml of an aqueous $\text{Cu}(\text{NO}_3)_2 \cdot 9\text{H}_2\text{O}$ (17.8289 g $\text{Cu}(\text{NO}_3)_2 \cdot 9\text{H}_2\text{O}$ Per 100ml solution). Following the impregnation the catalyst was dried at 110°C with

good mixing. The same procedure was used to add K. It was impregnated with 26.4ml of a K_2CO_3 solution (5.0484 g K_2CO_3 per 50ml solution). The catalyst was dried at 110°C with good mixing.

Approximately 32.22g of catalyst (100Fe/4.6Si/2.0Cu/5K, 100Fe/4.6Si/2.0Cu/7.5K or 100Fe/4.6Si/2.0Cu/10K), respectively, and 310g Ethylflo 164 oil (C_{30}) were loaded into a 1-liter stirred autoclave reactor. The slurry was treated with carbon monoxide at 40 Lh⁻¹ at 1.31MPa pressure; the temperature was then increased to 270°C at 120°C h⁻¹ and held at this temperature for 24h. The temperature was reduced to 230°C. CO flow was decreased and hydrogen flow gradually increased until the total flow was 3 SL/gFe/hr. The ratio of H₂ and CO is 0.7.

These catalysts (100Fe/4.6Si/2.0Cu/5K, 100Fe/4.6Si/2.0Cu/7.5K and 100Fe/4.6Si/2.0Cu/10K) have very low methane production and high alpha value (see Table 1). That means these catalyst produce a large amount of high molecular weight FTS products (reactor wax).

The main purpose for running these catalysts was to test whether these four filters possess sufficient ability to remove reactor wax from reactor, and whether these filter have enough ability to separate reactor wax from iron catalyst. Running conditions and filter specification are given in Table 2.

Carbon monoxide conversion for each high-alpha catalyst is shown in Figure 1. The 100Fe/4.6Si/2.0Cu/7.5K catalyst had the highest conversion. The catalysts went through an induction period in which the conversion increased from about 10 to 43 %. These high-alpha catalysts have sufficient activity at 230°C for FTS.

The alkene selectivities, as a function of carbon number, are similar for the three high-alpha catalysts (Figures 2-4). These three high-alpha catalysts produce more alkene than the lower atomic K% catalysts.

During 1000 hrs. of run time, the amounts of reactor wax removed from the reactor are 1800g, 2000g, 1500g and 1200g for 100Fe/4.6Si/2.0Cu/5K, 100Fe/4.6Si/2.0Cu/7.5K, and 100Fe/4.6Si/2.0Cu/10K catalysts, respectively (Figures 5-8). The reactor wax removed from the reactor depend on potassium content of the catalyst, and during this time does not depend on the filter surface area and pore size. These filters, compared with the 2 micro sinter metal filters (used from 1991 until now for removing reactor wax) posses ability to remove reactor wax for high-alpha catalysts. For example, during a 100 hr run, using 100Fe/4.6Si/2.0Cu/10K high-alpha catalyst, we were able to remove only 5g of reactor wax form the CSTR but with these special filters we can remove about 120g.of reactor wax from CSTR each day. Filtration data for these filters are shown in Table 3.

For special filter, 1.8-2.1 g of iron (about 8–9.6 % of iron) is lost after 1000 hr running (Figures 9 and 10). Much of this iron (20-30%) is lost during the period of cake build-up and can be eliminated by engineering design.

In summary, these catalysts have sufficient activity to merit consideration for producing high molecular weight FTS products and the preliminary data using the filters suggest that they may have sufficient ability to remove reactor wax form CSTR.

Table 1			
CH ₄ Selectivity and Alpha Value			
Run No.	Average CH ₄ Selectivity	α_1	α_2
Bao035	1.60	0.68997	0.91438
Bao036	1.50	0.73293	0.91468
Bao041	1.50	0.71138	0.92363
Bao043	1.70	0.76618	0.90876

Table 2							
General Information							
Run No.	Catalyst	Reactor Temp, °C	Reactor Pressure (psig)	Filter Length (inch)	Filter Diameter (inch)	Filter Surface Area (inch) ²	Pore Size
Bao035	100Fe/4.61Si/ /2.0Cu/5K	230	175	0.5	1	1.57	2μ
Bao036	100Fe/4.6Si/ 2.0Cu/5K	230	175	0.5	1	1.57	18μ
Bao041	100Fe/4.6Si/ 2.0Cu/7.5K	230	175	1.0	1	3.14	18μ
Bao043	100Fe/4.6Si/ 2.0Cu/10K	230	175	1.5	1	4.71	18μ

Table 3

Filtration of Bao041 (Filter L = 1"; reactor pressure = 175 psig; pressure of rewax trap set = 125 psig)

Number	Time Sample Taken (min.)	Amount of Wax Removed (g/5 min)
1	5	2.5
2	5	4.32
3	5	2.99
4	5	5.35
5	5	2.77
6	5	1.69
7	5	2.70
8	5	2.25
9	5	3.60
10	5	1.64

Figure 1. CO conversion Vs TOS at 230 °C

**Figure 2. olefin/(olefin+paraffin) Vs. carbon number
for the catalyst containg 5%K(Bao035**

**Figure 3. olefin/(olefin+paraffin) Vs. carbon number
for the catalyst containing 7.5%K (Bao041)**

**Figure 4. olefin/(olefin+paraffin) Vs. carbon number
for catalyst containing 10%K (Bao043)**

**Figure 5 Cumulation Rewax Removal Vs. Time on stream
for 100Fe/4.6Si/2.0Cu/5K Catalyst**

**Figure 6 Cumulation Rewax Removal Vs. Time on stream
for 100Fe/4.6Si/2.0Cu/5k Catalyst**

**Figure 7. Cumulation Rewax Removal Vs.Time on stream
for 100Fe/4.6Si/2.0Cu/7.5K**

**Figure 8. Cumulation Rewax Removal Vs.time on stream
for 100Fe/4.6Si/2.0Cu/10K**

**Figure 9 Cumulatiol of iron Vs. time on stream
for 100Fe/4.6Si/2.0Cu/5K Catalyst**

**Figure 10 Cumulation of Iron Removal vs. time on stream
for 100Fe/4.6Si/2.0Cu/5K Catalyst**

Task 5. Oxygenates

The objective of this task is to obtain a better understanding of the factors that affects catalyst selectivity toward oxygenates for iron-based Fischer-Tropsch catalysts.

OVERVIEW OF FISCHER-TROPSCH SYNTHESIS WITH COBALT CATALYSTS

SUMMARY

This review of the use of cobalt catalysts for the Fischer-Tropsch synthesis emphasizes results of the past thirty years. It is primarily intended to define catalyst formulations, both available to the public and of limited use because of patent coverage, that can be utilized in studies to define relationships between catalyst composition and process variables. To accomplish this literature review, two approaches have been utilized. In the first, a summary is provided by research topics: catalyst preparation, catalyst activation, catalytic activity and productivity, and catalyst aging and rejuvenation. Because of the likelihood that these catalysts will eventually be utilized in bubble column reactors, a brief survey of these reactors is presented. The proposed work will involve both fixed-bed and continuous stirred tank reactors (CSTR) and, at this time, the results from these two types of reactors cannot be directly related to large-scale bubble column reactor operations.

FIRST THIRTY YEARS (1925-1955)

The early work on the conversion of synthesis gas to hydrocarbons using cobalt catalysts has been extensively reviewed [1-3]. The Bureau of Mines review [3] of the literature contains 3771 abstracts and the second part covering patents contains 4017 abstracts; each section has an extensive index. The cobalt catalyst compositions center on those that eventually became the "standard" catalyst for the German Synthine process: Kieselguhr supported cobalt and thorium oxide together with other activating materials. This catalyst defined the use of a support and a nonreducible promoter for cobalt catalyst for the Fischer-Tropsch synthesis. It was demonstrated that the presence of copper, up to about 2 wt.%, significantly decreased the temperature

required to reduce the cobalt to the metallic state [4]. This work defined the use of an easily reduced metal oxide as a promoter for reducing cobalt catalysts at lower temperatures than would occur in their absence. However, it was also reported that while the copper allowed reductions to be effected at lower temperatures, the resulting catalyst declined in activity more rapidly [5]. Magnesia has been in use in cobalt catalyst formulation since 1938. The magnesia extends the catalyst life to eight months at normal pressure conditions [6]. The magnesia was added to increase the hardness of the catalyst; it also depressed the methane production and carbon formation.

During this period, the Fischer-Tropsch synthesis was carried out at the commercial scale by the Germans and the Japanese in processes that employed supported cobalt catalysts in fixed-bed reactors [1]. During this period, Kölbel and coworkers completed laboratory and pilot plant operations with a bubble column reactor to directly produce products emphasizing gasoline and diesel range materials using what would be considered today to be low-alpha iron catalysts [7].

MORE RECENT REPORTS OF COBALT CATALYST FORMULATIONS

A representative listing of promoters and supports reported in patents that are covered in **Chemical Abstracts** since 1962 are compiled in Attachments I and II.

For the purpose of the proposed study under this contract, the catalyst preparation and compositions of a patent issued in 1978, and now expired, are of interest [4]. This patent describes a process for the conversion of synthesis gas to hydrocarbons having only a minor amount of methane. The process utilizes a catalyst consisting of a major amount of cobalt and a minor amount of ruthenium as the active catalytic components. A sub-claim indicates that the catalyst formulation can contain an inert support. The standard cobalt catalyst used in this work was prepared following a

recipe that is, or is similar to, the standard German cobalt catalyst and consists of Co, Mg and Th on a kieselguhr support. Cobalt can comprise from 1 to 50 wt.% of the finished catalyst for the improved catalyst formulation. The molar ratio of cobalt to ruthenium in the finished catalyst can be from 5:1 to about 200:1. The active catalytic materials are "distended" on a suitable support material. Those metal oxides typically used as support materials can be employed to prepare the Co-Ru catalyst. Examples of suitable supports include oxides of the metals of Groups II, III, IV, V and VIB of the Periodic Chart [Group VIB is obviously intended to be IVB as described in a following sentence]. The oxides of Group II, IIIA, and IVB are preferred, e.g., alumina, boria, zinc oxide, magnesia, calcium oxide, strontium oxide, barium oxide, titania, zirconia and vanadia. It is further stated that a combination of these metal oxides, e.g., silica-alumina, can be used. The support can be natural occurring or synthetic, and examples include: kieselguhr, carbon, attapulgite clays, diatomaceous earth, activated carbon, coke, charcoal, and molecular sieves (both X and Y type). The method employed to deposit the catalytic metals onto the support is not critical, and any technique well known to those having ordinary skills in the art to distend the catalytic metals in an uniform thin layer on the catalyst support is suitable. The catalyst is normally dried, calcined and reduced in a gas such as flowing hydrogen. An interpretation of a phrase from a subclaim, "...with a catalyst consisting essentially of a major amount of cobalt and a minor amount of ruthenium distended in a uniform, thin layer on a catalyst support..." is a demanding task. One could conclude that this patent includes a catalyst with a nonuniform deposition of cobalt within the support particle. The patent covers operating temperatures from 60 to 450°C and pressures from atmospheric to 300 psig. In the body of the patent it is written that, "...using the catalysts of this invention can

occur in a fixed, fluid or moving bed type of operation, and the type of operation would not appear to be critical." A catalyst falling within this description was used in a bubble column reactor that was reported in a 1985 South African patent application [9].

Another report of interest for the proposed work describes the use of Pt and Pd as promoter for Co-alumina catalysts in which the alumina support does not exhibit an XRD pattern [10]. This disclosure permits the use of these noble metals to compare with catalysts containing Ru as disclosed in the Gulf Res. & Dev. Co. patent described above.

The patents described above utilize a range of metal salts, including cobalt carbonyl, to prepare supported cobalt catalysts that contain a variety of promoters - both easily reducible metal oxides including Ru, Pt, Pd and Cu as well as nonreducible metal oxides including zirconia, titania, alumina and silica.

Air Products utilized impregnation techniques to prepare catalysts during their work under DOE contracts in the 1980s. Catalyst precursors and supports were purchased from commercial sources [11]. The supports (γ - Al_2O_3 (Catapal SB, 217 m^2/g , 45 μm), silica (Davison 952, 339 m^2/g , 70 μm), $\text{MgO} \cdot 3.6\text{SiO}_2$ (Florisil, 298 m^2/g , 75 μm) and titania (Degussa P-25, 50 m^2/g , 2 μm) were calcined at 500°C for 3 hours in air prior to catalyst preparation. The catalysts and precursors were protected from air and moisture using the Schlenk technique and/or dry box. All solvents were distilled from sodium benzophenone detyl in a nitrogen atmosphere. Prior to use, the supports were further dried at 110°C under vacuum for 1-2 hours. Catalysts were prepared using the incipient wetness technique with separate solutions containing the promoter and metal carbonyl applied to the support in sequential steps. Their patents concerning the preparation of Fischer-Tropsch catalysts contain the following: "The invention was

made under DOE Contract No.----- and is subject to government rights arising therefrom."

CATALYST ACTIVATION

Benson et al. [12] indicate that, "Cobalt required carefully conducted prereduction with hydrogen, followed by an equally rigid schedule of induction with synthesis gas." Induction, as utilized in the reports of work at the Bureau of Mines, refers to the protocol followed during the early stages of exposure of the catalyst to hydrogen, or hydrogen and carbon monoxide, after adding the catalyst to the slurry oil/wax, or vice versa, in the reactor.

The majority of laboratory studies utilized hydrogen reduction followed by transfer of the reduced catalyst to the reactor. The transfer could be conducted by transferring the reduced catalyst to an outgassed start-up solvent in the absence of oxygen sources or by first passivating the catalyst with oxygen/air at low temperatures and then re-reducing the catalyst in the reactor [11].

A process that was claimed to provide a catalyst with superior activity involved the reduction of the dried (or calcined) catalyst in hydrogen, reoxidation, and then re-reduction in hydrogen (the ROR method) [13]. When the ROR method is utilized in a fixed-bed reactor, there are no problems in interpreting the approach since the catalyst can be contacted with synthesis gas in the reactor immediately following the re-reduction, and without exposure to oxygen. The ROR method was employed for testing using a bubble column reactor; however, the method used to transfer the catalyst to the reactor, if indeed it was transferred rather than activated in the bubble column reactor, was not defined in detail [9].

Mitchell [14] claimed a method for activating an essentially fresh, reduced cobalt containing FT catalyst which comprises treating the catalyst with hydrogen or a hydrogen containing gas in the presence of hydrocarbon liquids for a period sufficient to increase substantially the initial catalyst productivity. The induction utilized by the Bureau of Mines workers was to significantly increase the productivity of the catalyst during the early period of catalyst usage.

While there are a number of patents that cover activation of catalysts in hydrogen, none appear to provide specifics as to the mode of operation with respect to catalyst composition.

In a different approach, Nay et al. [15] claimed an activation that involved the oxidation of a cobalt catalyst followed by a reduction using carbon monoxide. This approach was claimed to produce a catalyst which produced less methane and more C_5+ products than when the same catalyst was activated using hydrogen.

Air Products conducted extensive work with cobalt catalysts during the 1980s, and the results are covered in reports and in patents [16-18]. In these studies they utilized both fixed-bed and CSTRs. The catalyst was loaded into the fixed-bed reactor; this was accomplished in a glove-box with air sensitive catalyst precursors. The reactor was then placed in line after the rest of the system had been flushed with nitrogen for at least 10 minutes. After leak testing, the catalyst was activated following two procedures. In the first, the catalyst was activated using $CO/H_2 = 1.0$. To accomplish this the catalyst precursor was heated to $180^\circ C$ in a nitrogen flow at atmospheric pressure. At $180^\circ C$, the flow was switched to the synthesis gas ($CO/H_2 = 1$) and then heated to the reaction temperature. At the reaction temperature, the pressure was increased to the one used for the synthesis. Later in their work, they compared the

impact of activation in pure H₂ or syngas (CO/H₂ = 1). For a 4%Co-zirconia promoted alumina catalyst, they found that the sample activated in hydrogen had a significantly higher activity and higher yield of liquid fuels. For the slurry phase tests, catalysts were activated in a separate, 150 cc fixed bed tubular unit using either pure H₂ or 20% syngas in nitrogen. The activated catalyst was then slurried in a deoxygenated paraffin oil in a dry box and transferred to the slurry autoclave under a blanket of nitrogen.

CATALYST ACTIVITY - PRODUCTIVITY

With an iron catalyst the productivity per gram of iron is not independent of CO conversion. Thus, the hydrocarbon productivity is highest at low conversion levels and then declines to about 0.5 g. hydrocarbons/g. Fe/h at the 90%+ CO conversion level (figure 1) [19]. Similar productivity rates are obtained for H₂/CO ratios typical of synthesis gas derived from coal (0.7) or from natural gas (1.7). Based on kinetics, it is anticipated that the productivity of a cobalt catalyst should also be dependent on the CO conversion level, although perhaps not to extent that it is for the iron-based catalyst.

The impact of particle size upon supported catalysts operated in a fixed-bed reactor was demonstrated by work carried out at Gulf Oil (Attachment VIII). As the particle size of the catalyst was decreased in the range from 1.6 to 0.2 mm, the methane production decreased (figure 2) and the C₅+ hydrocarbon fraction increased (figure 3). Likewise, the temperature dependence of synthesis at 185 and 195°C clearly demonstrated that the reaction suffered diffusion limitations in the larger catalyst particle sizes (figure 4). More recent quantitative descriptions of the effect of the catalyst particle size on product selectivity and on activity has been presented (figure 5) [references 20,21].

The results from synthesis in a bubble column slurry reactor showed that the methane production increased and the C₅+ hydrocarbons decreased as the temperature was increased in the 220-240°C range (figure 6) [9].

It is very difficult to obtain reactor productivity for pilot plant or commercial operations from either the open or patent literature. It is almost always necessary to make one or more assumptions about the operation and this introduces uncertainties in the estimate of productivity. The results summarized in Attachment V suggest that one should be able to obtain productivities in the range of 0.5 g. hydrocarbon/g catalyst/h for either unsupported iron or supported cobalt catalysts.

DECLINE IN CATALYTIC ACTIVITY

Data to define the decline in catalytic activity are not readily available. For a Co-Zr-silica catalyst that is operated with a H₂/CO = 1 at 260°C, the rate of activity decline is about 1% CO conversion per week (figure 7) [22]. On the other hand, a Co-silica catalyst exhibited an activity decline of about 35% CO conversion per week; however, for the same catalyst operated at a higher flow rate so that the CO conversion is only about 10% the activity decline was less than 1% CO conversion per week [23]. This result implies that the activity loss may be conversion dependent, presumably influenced by the partial pressure of water. A recent report indicates that there is a rapid activity decline during the first five days of operation after which the decline becomes much slower (figure 8) [24]. A definition of a series of aging-rejuvenation cycles has been reported (figure 9) [25]. There appears to be a reasonable relationship between the rate of activity decline and the time of the total decline as well as the rate of activity recovery and the time of the total decline. It should be realized that this patent

claims to demonstrate a catalyst rejuvenation technique and that accelerated aging conditions may have been employed during the study.

As important as the initial decline in activity is the regeneration (or rejuvenation) of the catalyst. The early work by the Germans and the U.S. Bureau of mines show that the initial activity of a cobalt catalyst can be attained again, or closely approached, by a brief treatment of the aged catalyst with hydrogen.

KINETICS

Several kinetic equations for synthesis gas conversion have been advanced for both iron and cobalt catalysts. For CO conversion levels to about 50%, both catalysts exhibit little dependence on CO partial pressure and a direct dependence on H₂ partial pressure. Thus, at low conversion the data have been fitted with the equation:

$$\text{rate} = k P_{\text{H}_2}.$$

Several variations of the inhibition effect of the reactants and products, especially H₂O, on the kinetics at higher conversion levels have been proposed. Unfortunately, the scatter in the experimental data at these high conversion levels makes it impossible to settle on a single kinetic expression.

There are several reports of the activation energy for both iron and cobalt catalysts and these are in the 20-25 kcal/mole range.

SLURRY REACTORS

It was recognized soon after the discovery of the Fischer-Tropsch synthesis that a reactor employing the catalyst in direct contact with a cooling oil was an attractive approach to maintain temperature control of the exothermic reaction. U.S. patents were obtained by I. G. Farbenindustrie A.-G., Standard Oil Development Company and Standard Catalytic Company. The Standard Catalytic Company was established by six

U.S. petroleum companies to develop processes for the production of synthetic fuels, and included an agreement with I. G. Farbenindustrie A.-G. Some of these patents are summarized in Attachment VI. Included in Attachments VII and VIII are the claims of several recent patents covering the use of bubble column reactors for the Fischer-Tropsch synthesis.

Recently, Inga [26] has studied the factors involved in relating data obtained in small-scale laboratory reactors to larger ones that would be utilized in industry. In brief, Inga concludes that the data from small reactors can be related **directly** to large commercial reactors only if the mixing in the small reactor will be the same as encountered in the large bubble column reactor. Thus, the usual results from the small-scale reactor is adequate for a definition of the scientific and engineering principles for bubble column operation but is not appropriate for direct application to any commercial scale bubble column reactor.

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7. H. Kölbel and M. Ralek, Catal. Rev.-Sci. Eng., 21, 225 (1980).
8. T. P. Kobylinski, U.S. 4,088,671, 05/09/1978 (assigned to Gulf Res. & Dev. Co.).
9. H. Beuther, T. P. Kobylinski, C. E. Kibby and R. B. Pannell; "Conversion of synthesis gas to diesel fuel in controlled particle size fluid system," South Africa Patent 855317, 7/15/85; ZA 8505317, issued 02/26/86.
10. R. S. Sapienza, M. Sansone and W. A. R. Slegier, U.S. Patent Application 482372, 06/22/84, (United States), available from NTIS.

11. H. P. Withers, Jr, K. F. Eliezer and J. W. Mitchell, Novel Fischer-Tropsch Slurry Catalysts and Process Concepts for Selective Transportation Fuel Production; DOE/PC/70030-T9, Final Report, December 1987.
12. H. E. Benson, J. H. Field, D. Bienstock, R. R. Nagel, L. W. Brunn, C. O. Hawk, J. H. Crowell and H. H. Storch, "Development of the Fischer-Tropsch oil-recycle process," Bureau of Mines Bulletin 568, 1957.
13. T. P. Kobylinski, C. L. Kibby, R. B. Pannell and E. L. Eddy, U. S. Patent 4,605,679, August 12, 1986.
14. W. N. Mitchell, "Activation of hydrocarbon synthesis catalyst;" U.S. Patent 5,292,705 (Mar. 1994).
15. B. Nay, M. R. Smith and C. D. Telford, "Catalyst treatment;" U.S. Patent 5,585,316, December 17, 1996.
16. P. N. Dyer, R. Pierantozzi and H. P. Withers, Supported Fischer-Tropsch catalyst and method of making the catalyst, US 4,681,867, July 21, 1987.
17. P. N. Dyer and R. Pierantozzi, Catalyst for selective conversion of synthesis gas and method of making the catalyst, US 4,619,910, Oct 28, 1986.
18. P. N. Dyer, R. Pierantozzi and H. P. Withers, Fischer-Tropsch process, US 4,670,472, June 2, 1987.
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20. E. Iglesia, Appl. Catal. A: General, 161, 59 (1997).
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22. H. P. Withers, Jr., K. F. Eliezer and J. W. Mitchel, Ind. Eng. Chem. Res., 29, 1807, (1990).
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24. P. J. van Berge and R. C. Everson, "Cobalt as an alternative Fischer-Tropsch catalyst to iron for production of middle distillates,; Natural Gas Conversion IV (M. de Pontes et al., Eds.), Studies Surf. Sci. Catal., 107, 207 (1997).
25. W. N. Mitchell, "Rejuvenation of hydrocarbon synthesis catalyst," U.S. Patent 5,283,216, February 1, 1994.
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ATTACHMENTS

- I. FT Catalyst Promoter - Patents
- II. FT Supports - Patents
- III. The Preparation of Cobalt Fischer-Tropsch Catalysts - Literature From 1962
- IV. Fischer Tropsch - Examples of Activation
- V. Productivity - Slurry Phase
- VI. Early Slurry Reactors
- VII. Tube-in-Shell Fischer-Tropsch Reactor
- VIII. Cooling Coils in or outside the Fischer-Tropsch Reactor Shell
- IX. Review of Air Products Fischer-Tropsch Synthesis Work
- X. Review of Exxon Patents
- XI. Listing of Open Literature Description of Exxon FT Work
- XII. Review of Fischer-Tropsch Work by Gulf Oil
- XIII. Review of Fischer-Tropsch Work by Statoil
- XIV. Review of Fischer-Tropsch Work by Rentech

Figure 1. Reaction rate for Fischer-Tropsch synthesis (□, ") and water-gas shift (▲) with an iron catalyst.

Figure 2. Methane production for synthesis in fixed-bed reactor with different particle size catalysts (from XII.17).

Figure 3. C₅+ product selectivity for three particle size catalysts in fixed-bed reactor (! , 185°C, H₂/CO = 2; ▲, 195°C, H₂/CO = 2; G, 195°C, H₂/CO = 1.5) (from XII.17).

Figure 4. Reaction rate for CO conversion in fixed-bed reactor for three particle size catalysts (! , 185°C, H₂/CO = 2; ▲, 195°C, H₂/CO = 2; G, 195°C, H₂/CO = 1.5) (from XII.17).

Figure 5. The effect of structural parameters (X) on FTS selectivity. Diffusion-enhanced readsorption (---) and diffusion-inhibited chain growth (....) simulations and experimental data (○, dispersion/support effects; ▲, pellet size variations; □, eggshell thickness variations). Top) C_5+ selectivity; bottom) CH_4 selectivity [473 K, 2000 kPa, $H_2/CO = 2.1$, 55-65% CO conversion] (X values from eq. 2 with r_p and R_o in m and θ_{Co} in surface Co atoms m^{-2}) (from E. Iglesia in "Natural Gas Conversion IV," (M. De Pontes, R. L. Espinoza, c. Pl. Nicolalides, J. H. Schulz and M. S. Scurrrell, eds.), Elsevier, Amsterdam, 1997, pp 153-162).

Figure 6. CO conversion and C_5+ product selectivity for FTS using slurry reactor and cobalt catalyst (data from XII.17).

Figure 7. Bulk activity maintenance for extended slurry reactor test of catalyst at baseline conditions (260°C, 2.07 Mpa, CO/H₂ = 1.0, and SV = 2.0 nL/h per g of catalyst).

Figure 8. Stability run with a cobalt catalyst (period A, conditioning phase; B irreversible, slow deactivation) (from P. J. van Berge and R. C. Everson, Natural Gas Conversion IV, 107, 207 (1997)).

Figure 9. Relative volumetric productivity represented by activity with days on stream with intervals of hydrogen rejuvenation (12 wt.% Co on titania with 6 wt.% Al_2O_3 as binder (from ref. X.96).

ATTACHMENT I

FT Catalyst Promoter - Patents

1. J. J. C. Geerling, A. Hoek, H. M. Huisman, and P. W. Lednor, WO 9825870 A1, 06/18/98 (Shell International). A supported (e.g., titania) cobalt/manganese with a Co/Mn molar ratio of 7-14/1 - shows, at high GHSV and low Co/Mn ratios, a high activity and C₅+ productivity even at relatively high gas hourly space velocity (GHSV).
2. J. J. C. Geerlings, M. F. Goes, H. M. Huisman, J.-P. Lange, H. Oosterbeek, P. J. M. Paulus and D. Schadenhorst, WO 9700231 A1, 01/03/97 (Shell International). Co + Mn and/or V is supported on a carrier, e.g., TiO₂ is effective for use in a process for the manufacture of hydrocarbons from synthesis gas.
3. P. J. M. Rek and P. Blankenstein, EP 583837 A1, 02/23/94 (Shell International). This patent application provides a method for the preparation of a catalyst or catalyst precursor that comprises a refractory oxide, solvent and peptizing agent that are mixed and neutralized with salt of catalytic active component (e.g., Group VIII metals).
4. C. J. Kim, U.S. Patent 5,227,407, 07/13/93 (Exxon R&E Co.) A syngas with added water is passed over a catalyst containing Co, Ru, or their mixtures, preferably on a TiO₂ support, produces an increased amount of C₅+ and a decreased amount of CH₄, compared to conversions with the same catalyst without added water.
5. B. Sandra and A. L. Chaffee, WO 9305000 A1, 03/18/93 (Broken Hill Pty. Co. Ltd., Australia) A catalyst consists of Co and scandium incorporated into a zeolite.

6. D. Reinalda and P. Blankenstein, EP 510770 A2, 10/28/92 (Shell International).
A catalyst composed of a Group VIII metal (Fe, Co, Ni) on refractory oxide (e.g., alumina, silica, titania, zirconia or mixtures of these) and then extruded into shapes is suitable for producing hydrocarbons from syngas.
7. S. L. Soled, E. Iglesia and R. A. Fiato, U.S. Patent 5,162,284, 11/10/92 (Exxon Res. & Eng. Co.). Cu promoted Co-Mn spinel ($\text{Co}_{3-x}\text{Mn}_x\text{O}_4$ with $x = 0.5$ to 1.2) are effective for converting syngas to a product rich in low molecular weight alkenes. The synthesis includes the use of an α -hydroxy aliphatic carboxylic acid (e.g., citric or glycolic acid) and Cu = 0/1-5 g-atom% of Co + Mn.
8. J. W. Geus and E. Boellaard, EP 466268 A1, 01/15/92 (Shell International).
Alloys of 2 or more Group VIB, VIIB and VIII elements, in which the alloys (metals) have negative heat of formation and the metal may be in the form of carbide, are suitable catalyst or catalyst precursor for hydrocarbon synthesis from syngas.
9. J. T. Miller and C. A. Radlowski, CA 2018611 AA, 12/13/90 (Amoco Corp.).
Nitrates of Co, Zn and Na were precipitated at pH 10 and calcined and these solids are effective catalysts for the production of olefins or higher alcohols from synthesis gas.
10. Anon. UK, Res. Discl (1991), 323, 180. A honeycomb support for Co promoted with ZrO_2 or Pt or Pd is used to prepare a Fischer-Tropsch catalyst.
11. S. Eri, T. Riis, G. Marcelin and J. G. Goodwin, Jr., WO 9007377 A1, 07/12/90 (Statoil). Co with a second metal (Pt, Ir and/or Rh) on alumina support is used for hydrocarbon synthesis.

12. S. Eri, J. G. Goodwin, Jr., G. Marcelin and T. Riis, U.S. Patent 4,889,763, 11/14/89 (Statoil). Co, Re and alkali (K) are supported on alumina; a metal oxide promoter may also be present. The composite may be used to convert synthesis gas to hydrocarbons.
13. S. Eri and J. G. Goodwin, Jr., U.S. 4,857,559, 08/15/89 (Gas-to-oil, Inc., U.S.A.) Co-Re-alumina which may contain another metal oxide promoter is useful to produce hydrocarbons from synthesis gas.
14. J. G. Miller, G. M. James and J. A. Rabo, ZA 8806952, 05/30/89 (Union Carbide). Co containing LZ-210 zeolite that contains a Mo oxide promoter produce products that exhibit lower methane yield, higher C₅+ hydrocarbons, increased olefins and longer catalyst life..
15. S. L. Soled, R. A. Fiato and E. Iglesia, EP 319625 A1, 06/14/89 (Exxon Res. & Dev. Co.) A catalyst comprised of Co-Ru on TiO₂ support can be regenerated without removal from the reactor: it produces 7.9% CH₄ and 85.7% C₅+ at GHSV 1200 h⁻¹. Co and Ru are dispersed within the same crystallite.
16. S. Eri, J. G. Goodwin, Jr., G. Marcelin and T. Riis, U.S. 4,801,573, 01/31/89 (Statoil). Co-Re on alumina, to which a metal oxide promoter may be added, exhibits a higher activity than either Co or Re alone.
17. W. C. Behrmann, C. H. Mauldin, K. B. Arcuri and M. Herskowitz, EP 266898 A1, 05/11/88 (Exxon Res. & Dev. Co.). A catalyst consisting of a metal film of 0.02-0.25 mm thickness is deposited on the surface of a particulate support; Co and Re are repeatedly deposited on preheated TiO₂ substrate as thin layer (60-160 μm) to prepare the catalyst which is suitable for hydrocarbon production from

syngas. The composite has very high hydrocarbon productivity and low CH₄ selectivities.

18. E. Iglesia, S. L. Soled and R. A. Fiato, U.S. 4,738,948, 04/19/88 (Exxon Res. & Dev. Co.). Co-Ru is deposited on a refractory oxide, and then oxidized and reduced to form a catalyst with the Co and Ru in intimate contact. This catalyst produces 93 mol% C₅+ and 3.4 mole% methane whereas a similar catalyst without Re produces 85 mol% C₅+ and 7 mole% methane.
19. P. N. Dyer, R. Pierantozzi and H. P. Withers, U.S. 4,670,472, 06/02/86 (Air Products & Chemicals, Inc.). An inert carrier was treated with a Group IVB metal compound, then impregnated with decomposable metal compound (e.g., Co, Fe or Ru carbonyls) to produce a catalyst precursor. Reactions with air or water and calcination are specifically avoided. Instead the catalyst was contacted with the synthesis gas.
20. K. P. De Jong, J. H. E. Glezer and M. F. M. Post, EP 221598 A1, 05/13/87 (Shell International) Fe, Ni or Co is deposited on SiO₂ along with one or more Group VIII noble metal promoters and, in addition, may contain Zr. The specific example is Pt-Co-Zr-SiO₂ with 0.1:10:0.9:100 weight parts.
21. C. H. Mcateer and B. Nay, WO 8607350 A1, 12/18/86 (British Petroleum Co.) A catalyst with Co_aA_bL_{ac}CeO_x (A, alkali metal with a = 0-0.25%; b = 0-5%, x = number to satisfy equation) is prepared. A procedure for preparing a pellet also includes an activation procedure.
22. C. J. Kim and R. A. Fiato, U.S. 4,624,968, 11/25/86 (Exxon Res. & Dev. Co.) Fe/Ce/Zn/K, Re-Mn-K or Fe-Co-K catalysts are used in first stage and then the

exit gas is converted to heavier produces over Ru/TiO₂, Ru/SiO₂ or Ru/Al₂O₃ catalyst in a second stage.

23. J. H. Brophy, F. J. J. Font, M. Helena, D. J. H. Smith and C. D. Telford, WO8605775, 10/09/86 (British Petroleum Co.). Hydrocarbons are preferably produced by Fischer-Tropsch reaction over a Group VIII metal oxide or sulfide in presence of 1-40 mole% unsaturated hydrocarbon, preferably ethylene. Support utilized include: alumina, C, silica, zirconia, titania, MgO, ceria, gallia and can contain an acidic component such as a zeolite or amorphous silica-alumina.
24. H. Beuther, T. P. Kobylinski, C. L. Kibby and R. B. Pannell, U.S. 4,585,798, 04/29/86 (Gulf Oil). Co and Ru are impregnated by nonaqueous technique on alumina support and can contain another promoter (Ca, Mg, Th, or rare earth or rare earth mixtures).
25. D. Bode and S. T. Sie, EP 188304 A1, 07/23/86 (Shell International). Co + 0-100 wt. parts of element Zr, Ti, Cr and Ru are supported on alumina, silica or silica-alumina and the material formed to be suitable for fixed-bed catalyst.
26. P. K. Coughlin, WO 8600296 A1, 01.16/86 (Union Carbide Corp.). Co with or without Th (1-50 mol%) and an additive (Mo and/or W) on a zeolite or non-zeolite molecular sieve is used as catalyst for converting synthesis gas to hydrocarbons.
27. H. Beuther, T. P. Kobylinski, C. E. Kibby and R. B. Pannell, ZA 8505317, 03/26/86 (Gulf Res. & Dev. Co.) Diesel fuel is produced from synthesis gas using a Co(5-25%)-Ru(0.01-0.5) on a support. The support can be alumina or silica and is in the 10-110 μm size range. Data show diffusion limitations in large catalyst particles in fixed bed reactors but not with the small particles in the slurry reactor.

28. M. F. M. Post and S. T. Sie, EP 153781 A2, 09/04/85 (Shell International). In first step, syngas is converted to hydrocarbons using a $\text{Co}(3-60)\text{-Zr}(0.1-100)/\text{SiO}_2$ (100) under specified conversion levels, the water removed and the gaseous products passed to second step using a mixture of two catalysts [Co-Zr/silica and Cu-Zn/alumina].
29. J. K. Minderhoud, M. F. M. Post, S. T. Sie and E. J. R. Sudholter, EP 142887 A2, 05/29/85 (Shell International). A catalyst containing silica 100, Co (15-50) and 2nd metal (Zr, Ti, Ru or Cr) is prepared by sequential impregnations with Co and the 2nd metal.
30. J. K. Minderhoud, M. F. M. Post, S. T. Sie and E. J. R. Sudhoelter, EP 142888 A2, 05/29/85 (Shell International). A first stage Ni-Ca-K-alumina catalyst and a second stage Co-Zr-silica catalyst are employed.
31. J. K. Minderhoud and S. T. Sie, GB 2146350 A1, 04/17/85 (Shell International). Zr-Co-silica was used for hydrocarbon synthesis in the first stage of the process.
32. J. K. Minderhoud and M. F. M. Post, EP 127220 A2, 12/05/84 (Shell International). A three-step impregnation of silica with Zr and one-step impregnation with Co was followed by kneading/calcining to produce catalyst particles active for hydrocarbon synthesis from syngas.
33. J. K. Minderhoud, M. F. M. Post and S. T. Sie, EP 109702, 05/30/84 (Shell International). Zr- or Ti-promoted Co-silica are used to produce hydrocarbons.
34. A. Hoek, J. K. Minderhoud, M. F. M. Post and P. W. Lednor, EP 110449 A1, 06/13/84 (Shell International). a catalyst is prepared in which a Zr or Ti compound is added to silica by impregnation, then calcined and then impregnated with a Co compound, calcined and reduced.

35. H. Beuther, C. L. Kibby, T. P. Kobylinski, and R. B. Pannell, U.S. 4,413,064, 11/01/83 (Gulf Oil). Finely divided alumina is impregnated with a Co salt, the product is dried and then contacted with aqueous or nonaqueous solution of salts of Ru and Group IIIB or IVB metals is active for the production of hydrocarbons from synthesis gas.
36. T. P. Kobylinski, U.S. 4,088,671, 05/09/1978 (Gulf Res. & Dev. Co.). A process for the conversion of synthesis gas to hydrocarbons having only a minor amount of methane utilizes a catalyst consisting of a major amount of cobalt and a minor amount of ruthenium as the active catalytic components. A sub-claim indicates that the catalyst can contain an inert support. The standard cobalt catalyst was prepared following a recipe that is, or is similar, the standard German cobalt catalyst and consists of Co, Mg and Th on kieselguhr support. Cobalt can comprise from 1 to 50 wt.% of the finished catalyst. The molar ratio of cobalt to ruthenium in the finished catalyst can be from 5:1 to about 200:1. The active catalytic materials are "distended" on a suitable support material. Those metal oxides typically used can be employed to prepare the Co-Ru catalyst. Examples of suitable supports include oxides of the metals of Groups II, III, IV, V and VIB of the Periodic Chart [old style; Group VIB is obviously intended to be IVB as described in a following sentence]. The oxides of Group II, IIIA, and IVB are preferred, e.g., alumina, boria, zinc oxide, magnesia, calcium oxide, strontium oxide, barium oxide, titania, zirconia and vanadia. It is further stated that a combination of these metal oxides, e.g., silica-alumina, can be used. The support can be natural occurring or synthetic, and examples include: kieselguhr, carbon, attapulgite clays, diatomaceous earth, activated carbon, coke, charcoal,

and molecular sieves (both X and Y type). The method employed to deposit the catalytic metals onto the support is not critical, and any technique well known to those having ordinary skills in the art to distend the catalytic metals in a uniform thin layer on the catalyst support is suitable. The catalyst is normally dried, calcined and reduced in a gas such as flowing hydrogen. The interpretation of a phrase from a subclaim is critical: "...with a catalyst consisting essentially of a major amount of cobalt and a minor amount of ruthenium distended in a uniform, thin layer on a catalyst support..." One interpretation of the meaning of the phrase enclosed in quotes is that it includes "rim-loaded" catalysts. The patent covers operating temperatures from 60 to 450°C and pressures from atmospheric to 300 psig. In the body of the patent it is written that, "...using the catalysts of this invention can occur in a fixed, fluid or moving bed type of operation, and the type of operation would not appear to be critical." This patent expired after 17 years from the issue date so that it now falls within the public domain and does not restrict its use. A catalyst falling within this description was used in a bubble column reactor that was reported in a 1985 South African patent application.

ATTACHMENT II

FT Supports - Patents

1. P. Blankenstein, J. J. C. Geerlings, H. M. Huisman, P. W. Lednor and B. J. Van Liemt, WO 9811037 A1, 03/19/98 (Shell International). A catalytically active metal (e.g., Co) is supported on titania having a rutile/anatase ratio less than 2/3 and surface area $< 75 \text{ m}^2/\text{g}$ is used to prepare C_5+ hydrocarbons from synthesis gas.
2. L. A. Rivas, E. Peluso, D. Rojas, J. J. A. Garcia, U.S. 5,648,312, 07/15/97, (Intevep, S.A., Venez.). Spherical particles of a homogeneous mixture of two refractory inorganic carbides, nitrides or mixtures, with surface area $> 30 \text{ m}^2/\text{g}$ and a particle size $> 0.1 \text{ mm}$ can be used as a support Group IVB and VIII metals in a catalyst system active for the conversion of synthesis gas to C_2+ hydrocarbons.
3. R. Zennaro, A. Gusso and M. G. Clerici, EP 756895 A2, 02/05/97 (Agip Petroli S.P.A., Italy; Institut Francais Du Petrole). A method to prepare a catalyst utilizes an inert support and Co, Ru and a third element, scandium or yttrium. The process includes a sequence of steps for preparation and then calcination, reduction, and passivation steps.
4. J. J. C. Geerlings, M. F. Goes, H. M. Huisman, J.-P. Lange, H. Oosterbeek, P. J. M. Rek and D. Schadenhorst, WO 9700231 A1, 01/03/97, (Shell International). Co and Mn and/or V is supported on a carrier, eg, titania, and is used to convert synthesis gas to hydrocarbons.
5. R. L. Espinoza, J. J. Visagie, P. J. Van Berge and F. H. Bolder, EP 736326 A1, 10/09/96, (Sastech Proprietary Ltd.). A process for preparing Fischer-Tropsch

catalysts is prepared by impregnating alumina with an aqueous salt of Co, Fe and mixtures thereof. The sample is dried below atmospheric pressure, and then calcined.

6. D. Reinalda and P. Blankenstein, EP 510770 A2, 10/18/92, (Shell International). Hydrocarbons are produced by contacting a synthesis gas at 125-350°C and 5-100 bar pressure with a catalyst comprising a Group VIII metal (Fe, Co or Ni) on a refractory oxide carries (alumina, silica, titania, zirconia and mixtures thereof). The catalyst particles are helical lobed shape made by extrusion through a die plate such as a 2 mm helical trilobe.
7. S. L. Soled, E. Iglesia, R. A. Fiato and G. B. Ansell, U.S. 5,169,821, 12/08/92, (Exxon Res. & Eng. Co.). A stable high-temperature Fischer-Tropsch catalyst has the general formula $\text{Co/Ti}_x\text{M}_{1-x}\text{O}_2$ where $x = 0.01$ to 0.14 selected from Si, Zr, and Ta where titania is anatase. Activation of the composite includes drying and calcining followed by reduction of the Co.
8. D. Reinalda, P. Blankenstein and A. Derking, EP 510771 A1, 10/28/92, (Shell International). A process for the preparation of extruded SiO_2 -based catalysts, containing elements from Group VIIB or Group VIII and a promoter from elements in Group IVB is described.
9. A. H. Joustra and B. Scheffer, EP 455308 A1, 11/06/91 (Shell International). The preparation of alumina-based extrudates containing Co, Fe, or Ni is described.
10. E. Iglesia, H. Vroman, S. L. Soled, J. Baumgartner and R. A. Fiato, EP 434284 A2, 06/26/91 (Exxon Res. & Dev. Co.). Supported Co catalysts are prepared by depositing a metal on a suitable support, eg, silica. Rim-loaded catalysts are

obtained by contacting the support with a molten salt. Non-rim-loaded catalysts may be prepared in a similar manner.

11. D. Reinalda and J. Dars, EP 421502 A2, 04/10/91, (Shell International). A Co compound is applied on a porous inert support, dried and then calcined in an atmosphere with greater than 20 volume% NO_x.
12. C. H. Mauldin and K. L. Riley, U.S. 4,977,126, 12/11/90, (Exxon Res. & Eng. Co.). A film layer of catalytically effective amounts of Co is deposited on the peripheral outer surface of a porous inorganic oxide, especially TiO₂.
13. E. Iglesia, S. L. Soled and R. A. Fiato, U.S. 4,960,801, 10/02/90 (Exxon Res. & Dev. Co.). A catalyst with Co present on a TiO₂ support that contains up to 15 wt.% SiO₂ is described.
14. C. H. Mauldin and K. L. Riley, EP 370757 A1, 05/30/90, (Exxon Res. & Dev. Co.). A catalyst support with 0.1-20% of inorganic metal oxide binder (alumina, silica, zirconia or titania) is utilized. A Group VIII metal, preferably Co or Co plus additional metal or metals, is deposited on the support.
15. J. G. Miller and J. A. Rabo, U.S. 4,874,732, 10/17/89, (UOP). A catalyst having improved selectivity for C₅+ hydrocarbons consists of a Co containing acid zeolite that additionally contains Mn oxide or Mn oxide and Zr oxide promoters.
16. E. Iglesia, S. Soled and R. A. Fiato, U.S. 4,794,099, 12/27/88, (Exxon Res. & Dev. Co.). Silica (to 15%) or silica precursor is incorporated into a Co-containing catalyst on an inorganic refractory titania support. Re can also be present.
17. W. C. Behrmann, C. H. Mauldin, B. K. Arcuri and M. Herskowitz, EP 266898 A2, 05/11/88, (Exxon Res. & Dev. Co.). Metal is deposited alone or with a promoter as film on support.

18. K. P. De Jong, J. H. E. Glezer and M. F. M. Post, (Shell International). A Fischer-Tropsch catalyst contains Fe, Ni or Co deposited on silica with additional Group VIII metal(s). The catalyst may also contain Zr.
19. T. P. Kobylinski, C. L. Kibby, R. B. Pannell and E. L. Eddy, U.S. 5,605,679, 08/12/86, (Chevron Res. Co.). A Co-based catalyst is prepared by impregnation of Co carbonyl on alumina or silica and then activating in sequential steps of reduction in hydrogen, oxidation, and re-reduction in hydrogen.
20. P. F. Meier and F. Pennella, U.S. 4,623,669, 11/18/86, (Phillips Petroleum Co.). A metal is vaporized in the presence of a solvent and condenses to form a solid mixture; this is warmed to form a metal-solvent slurry which is then contacted with a support and then the solvent is removed. Co evaporation into toluene followed by deposition on a silica support was the example preparation.
21. H. Beuther, C. L. Kibby, T. P. Kobylinski and R. B. Pannell, U.S. 4,605,680, 08/12/86, (Chevron Research Co.). Alumina is used to support Co and one or more Group VIII or IVB metal oxide promoters.
22. E. J. R. Sudhoelter, EP 180269, 05/07/86, (Shell International). Co-silica catalyst preparation procedure is described wherein silica is obtained from a Si halogen, alkoxy and/or acyloxy).
23. A. I. Foster, R. W. Joyner, J. J. McCarroll, S. R. Partington, R. G. L. Spiers and S. R. Tennison, WO 8601499 A1, 03/13/86, (British Petroleum Co.). Co or Fe (with option of including Pt) is deposited on a C support.
24. D. Bode and S. T. Sie, EP 188304 A1, 07/23/86, (Shell International). Co, and one or more of Zr, Ti, Cr and Ru is deposited on a silica, alumina or silica-alumina support.

25. P. K. Coughlin, WO 8600296, 01/16/86, (Union Carbide Corp.). Co with Th promoter and 1-50 mole% (based on Co) of an additive (e.e, Mo and/or W) supported on a zeolite, SAPO or non-zeolite molecular sieve.
26. H. Beuther, T. P. Kobylinski, C. L. Kibby and R. B. Pannell, ZA 8505317, 03/26/86, (Gulf Res. & Dev. Co.). Co (5-25 WT.%) and Ru (or other promoters, 0.01-0.5 wt%) is deposited on a support. The average particle diameter is 10-110 micron size and is suitable for use as slurry phase conversion of synthesis gas to hydrocarbons.
27. V. L. Payne and C. H. Mauldin, U.S. 4,595,703, 06/17/86, (Exxon Res. & Eng. Co.). Co is dispersed on a TiO_2 or ThO_2 support that, when titania, has greater than 2:3 rutile-anatase ratio.
28. M. F. M. Post and S. T. Sie, EP 153781 A2, 09/04/85, (Shell International). A two step process for converting synthesis gas to diesel range fuels. In the first stage a Fischer-Tropsch catalyst containing Co (3-60)-Zr(0.1-100)- SiO_2 (100) so that conversion is in range $(F - 0.5)/(F + 2)(150) < C < (F - 0.5)/(F + 1)(250)$, where F is syngas flow and C is syngas conversion. After water removal, the gaseous products are separated and contacted in the second step with two catalysts (e.g., Co-Zr- SiO_2 (I) and Cu-Zn-alumina (II)).
29. J. K. Minderhoud, M. F. M. Post, S. T. Sie and E. J. R. Sudholter, EP 142887 A2, 05/29/85 (Shell International). Hydrocarbon steam reforming produces a syngas that is converted with a Fischer-Tropsch catalyst containing SiO_2 (100), Co (15-50) and a second metal (chosen from Zr, Ti, Ru or Cr) (> 0.1). The catalyst is prepared by sequential impregnation.

30. J. K. Minderhoud, M. F. M. Post, S. T. Sie and E. J. R. Sudholter, EP 142888 A2, 05/29/85, (Shell International). C₉+ hydrocarbons are manufactured in a two stage process consisting of steam reforming of C₁-C₄-hydrocarbons with a Ni-containing catalyst followed by Fischer-Tropsch synthesis with a Co-containing catalyst (e.g., Co:Zr:SiO₂ = 25:18:100).
31. J. K. Minderhoud and M. F. M. Post, EP 127220 A2, 12/05/84, (Shell International). Fischer-Tropsch catalysts were prepared by a three-step impregnation of silica with a solution of zirconium tetrapropoxide in a propanol-benzene, then aqueous cobalt nitrate, kneading and then calcination.
32. R. S. Sapienza, M. Sansone and W. A. R. Slegier, U.S. Patent Application 482372, 06/22/84, (United States). A catalyst for converting synthesis gas to hydrocarbons contains 0.1-10:10-70 (wt.%) Pd or Pt-Co-alumina where alumina does not show an XRD peak for alumina. The catalyst was prepared by impregnating a Pd/Al₂O₃ catalyst with Co₂(CO)₈ in the reactor and then heating with synthesis gas to the reaction temperature.
33. J. K. Minderhoud, M. F. M. Post and S. T. Sie, EP 109702 A1, 05/30/84, (Shell International). A catalyst with the composition 0.9:25:100 wt Zr-Co-silica was used for Fischer-Tropsch synthesis.
34. H. Beuther, C. L. Kibby, T. P. Kobylinski and R. B. Pannell, U.S. 4,413,064, 11/01/83, (Gulf Res. & Dev. Co.). A catalyst suitable for use in a fluidized reactor was prepared by impregnating finely divided alumina support with a Co salt, drying, and then contacting with a nonaqueous solution containing salts of Ru and a Group IIIB or IVB metal.

ATTACHMENT III

The Preparation of Cobalt Fischer-Tropsch Catalysts -

Literature from 1962

Cobalt Fischer-Tropsch catalysts have been widely investigated in recent years due to its high activity and selectivity for the synthesis of long-chain hydrocarbons. In this review, we summarize preparation methods of cobalt Fischer-Tropsch catalysts. The effect of precursors, promoters, support materials and pretreatment conditions are covered. These effects arise at the level of a catalytic site and reflect the influence of site structure, composition and electronic properties on the rate of the primary chain growth and the selectivity of catalysts. Such modifiers for metal catalysts have been hypothesized to act by the structural modification of the metal surfaces that is induced by a promoter (III.1-III.3), by blockage of the active catalytic sites by the modifier (III.4), by charge transfer between the modifier and the metal (III.5,III.6), by direct chemical interactions between the modifier and the active intermediates (III.7) and/or by the effect of the electrostatic field of the modifier ions (III.8-III.10). As to cobalt catalysts, work has been done on the promotion effect of potassium, zirconium, ruthenium, platinum, rhenium, etc.

The noble metal promoter has been suggested to have a number of different ways of affecting catalyst performance. It has been proposed that it acts as a source of hydrogen spillover (III.11), that it increases the reducibility of cobalt (many), that it preserves activity by preventing the buildup of carbonaceous deposits (III.12), that it exhibits cluster and ligand effects (III.13), and that it provides a combination of enhanced cobalt reducibility and dispersion (III.14). It has even been reported that the

addition of a second metal component may have no, or a detrimental, effect on CO hydrogenation activity (III.15).

Ruthenium promoters have been reported (III.13, III.16-III.20). Two papers (III.16,III.20) indicate the use of alumina as support material and the preparation of the catalyst using an incipient wetness impregnation method. Cobalt nitrate hexahydrate, ruthenium nitrosyl nitrate and ruthenium chloride were used as precursors. The incipient wetness impregnation was carried out in a single step followed by drying and calcination. Some catalysts, however, were prepared by sequential impregnation of cobalt and ruthenium with intermediate drying, calcination, or reduction in order to determine the ways that differences in catalyst preparation influence catalyst performance. Co-Ru/Al₂O₃ catalysts described in these references contained 20 wt% cobalt and 0.5 wt% ruthenium. Their results indicate that the addition of small amounts of ruthenium on alumina-supported cobalt catalysts facilitate the reduction of the cobalt. This conclusion was based on the lowering of the reduction temperatures during temperature programmed reduction (TPR) by approximately 100°C and essentially complete reduction of the Ru-promoted catalyst (CoRu/Al₂O₃) at 350°C compared to only a 60% reduction of the unpromoted Co/Al₂O₃ catalyst. In parallel, the amount of metal atoms exposed on the surface, determined by hydrogen chemisorption, increased by a factor of three upon ruthenium promotion.

Catalyst activity was obtained by the conversion of a helium diluted H₂/CO mixture (H₂/CO = 10; 20 cc/min H₂; 2 cc/min CO; total flow 100 cc/min; H₂ = 8 NL/hr•g-cat.; CO = 0.8 NL/hr•g-cat; total flow 40 NL/hr•g-cat). The catalyst bed consisted of 15 mg catalyst diluted with 15 mg of quartz powder. The reaction was conducted in a fixed-bed reactor at 220°C and 1.8 atm. The catalyst contained 20 wt.% cobalt and, if

present, 0.5 wt.% ruthenium. If the rate ($\mu\text{mole/gCo}\cdot\text{s}$) is assumed to be based on CO, we calculate that 25 $\mu\text{mole/gCo}\cdot\text{s}$ corresponds to 0.25 $\text{gCH}_2/\text{hr}\cdot\text{g-cat}$ and 50 $\mu\text{mole/gCo}\cdot\text{s}$ corresponds to 0.5 $\text{gCH}_2/\text{hr}\cdot\text{g-cat}$ (Figure III.1). From the data shown in Figure III.2, the temperature of reduction (300, 350 and 400°C) does not impact the reaction rate; however, the calcination temperature does and the catalyst calcined at 300°C is about twice as active as the material after calcination at 400°C.

An increase in surface exposed metal atoms was paralleled by an equivalent increase in the rate of CO hydrogenation, yielding practically constant turnover frequencies (Figure III.3). Steady-state isotopic transient kinetic analysis (SSITKA) results indicated constant intrinsic activities but an increase in the number of reaction intermediates at constant coverages when a Ru-promoted catalyst was compared to the unpromoted cobalt catalyst. There was little change in product selectivity. Promotion with more than 0.5% Ru improved the catalyst characteristics only marginally. From these results they conclude that ruthenium acts only as a reduction promoter for cobalt by increasing the reducibility and dispersion of the cobalt. These results for Ru promotion are compatible with those recently reported for Pt-promoted cobalt FTS catalysts (III.21).

As shown in Figure III.4, the presence of ruthenium increases the rate of hydrocarbon production by up to a factor of four. Iglesia et al. (III.13) reported that ruthenium promotion of silica- and titania-supported cobalt catalysts caused a synergistic effect since the specific rates for CO hydrogenation, expressed as turnover frequencies (TOFs) based on hydrogen chemisorption, increased with addition of small amounts of ruthenium. They attributed this improvement to the hydrogenation activity of ruthenium and its ability to decrease, or prevent, carbon formation on the surface of

cobalt. In contrast to Iglesia et al., Kogelbauer et al. (III.16) conclude that surface enrichment of ruthenium is unlikely for the alumina supported cobalt-ruthenium catalysts.

Belambe et al. (III.20) reported methane selectivities in the range of 70-85% for the cobalt catalysts tested in Goodwin's laboratory (Table III.1) and attributed this to the high H_2/CO ratio (=10) that they used. The Anderson-Schulz-Flory (ASF) alpha values obtained by Belambe et al. were in the range of 0.37 for the aged, steady-state catalysts and 0.4-0.42 for the fresh catalyst (Table III.1). Ruthenium appeared to inhibit the formation of highly irreducible cobalt species (cobalt oxide strongly interacting with the support to form cobalt aluminates) or to promote their reduction, indicated by the absence of the broad, high-temperature TPR feature observed with Co/Al_2O_3 and the greater degree of reduction. Calcination of Ru/Al_2O_3 or Co/Al_2O_3 precursors prior to a sequential impregnation of cobalt or ruthenium, respectively, impeded the intimate mixing of the metal components. Coimpregnation of the metal salts appeared to produce catalysts slightly more active for CO hydrogenation.

They (III.20) also investigated the effect of calcination and reduction temperatures on the activity of a Ru-promoted 20 wt% Co/Al_2O_3 catalyst for the CO hydrogenation reaction by steady-state reaction and SSITKA (III.20). While reduction temperature in the range 300-450°C had at most a negligible effect, calcination temperature was found to have a significant effect on the overall activity of this catalyst. The overall catalyst activity decreased with increasing temperature of calcination (Figure III.2). However, pretreatment temperatures did not affect the intrinsic activity of the catalyst sites. The decrease in CO hydrogenation rate with increasing calcination temperature was found to be attributable to a decrease in the number of surface active

sites due to a decrease in the reducibility of the catalyst. The SSITKA results, which showed no change in the surface residence time for CH_4 intermediates with increasing calcination temperature, as well as the TOF results, confirmed that there was no change in the intrinsic activity of the sites producing methane. Neither the reduction nor the calcination conditions had any effect on chain growth probability. Calcination temperature did have, however, a small effect on CH_4 selectivity.

A study of CO hydrogenation on La^{3+} -promoted Co/SiO_2 catalysts (La/Co atomic ratios of 0-0.75; Cab-O-Sil silica support) has been performed by Haddad et al. (III.21) using both global rate measurement and SSITKA. The prereduced and passivated base catalyst containing 20% cobalt was impregnated by incipient wetness with the appropriate amount of an aqueous solution of $\text{La}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ to obtain catalysts with La/Co atomic ratios of 0.0, 0.05, 0.1, 0.2, 0.3, 0.5 and 0.75. After impregnation, the catalyst was allowed to dry in an oven overnight at 90°C . Finally, it was re-reduced in hydrogen at 350°C for 22 h and passivated at 25°C .

Aqueous impregnation of Co/SiO_2 with La^{3+} led to a significant decrease in the number of intermediates leading to methane during CO hydrogenation (Figure III.5), but it did not alter the nature of the active sites (III.21). In a previous characterization paper (III.21a) La^{3+} promotion of Co/SiO_2 was shown to moderate strong Co-support interactions brought about by aqueous impregnation of the Co/SiO_2 and to enhance the reducibility of the cobalt oxide. La^{3+} addition to the Co/SiO_2 catalyst was found to lead to a significant increase in the activity for Fischer-Tropsch synthesis (on a per gram cobalt basis) (Figure III.6). It appears that the impregnation to produce the B-La0 (0 means no La^{3+} promoter) catalyst from the B catalyst caused a decrease in the amount of CO adsorbed and in the TON; the reason for this was not given. The SSITKA results

showed that the concentration of active intermediates leading to methane increased with increase in La/Co ratio. However, the TOF, the pseudo-first-order rate constant, the reactivity distribution function, and the activation energy were not affected by La³⁺ addition. Thus, it can be concluded that La³⁺ did not change the nature of the active sites, just their concentration. This increase in the concentration of active sites follows exactly the increase in surface Co⁰. La³⁺ promotion also caused the chain growth probability (Figure III.7) and the olefin/paraffin ratio (Figure III.8) to increase significantly at 220°C for H₂/CO=2.

Ali et al. (III.22) also investigated the influence of zirconia promotion of 20 wt% Co/SiO₂ on FTS using catalysts prepared in different ways and having different loadings of zirconia (up to 8.5 wt%). The catalysts were investigated using FTS (H₂/CO=2), H₂-D₂ exchange, and CO dissociation to provide insight into how zirconia modifies the cobalt properties. The Zr-promoted catalysts exhibited higher overall rates of FTS compared to unpromoted Co/SiO₂ (Figure III.9). The sequentially impregnated Co/Zr/SiO₂ catalysts appeared to be the most active. However, the coimpregnation method of preparation appeared to result in higher cobalt dispersion. While zirconia promotion did not appear to promote or inhibit hydrogen activation, hydrogen spillover may have been partly responsible for enhancing the activity of the sequentially impregnated Zr/Co/SiO₂ catalysts. Zirconia also possibly created an active interface with cobalt that increased catalyst activity by facilitating CO dissociation. Although high levels of promotion tended to increase the selectivity for higher hydrocarbons, zirconia appears to primarily function as an excellent rate promoter for Co/SiO₂.

Huffman et al. (III.23) studied the promotion effect of potassium on cobalt catalysts. The K-promoted Co/Al₂O₃ catalyst was prepared by impregnating the

passivated 9.0 wt% Co/Al₂O₃ catalyst with a solution of potassium nitrate in order to have an atomic ratio of K/Co=1. In situ XAFS spectroscopy studies were conducted at reaction conditions on the potassium-promoted cobalt catalysts supported on SiO₂ and Al₂O₃, and on similar samples without potassium. Measurements were conducted at temperatures up to 200°C under both reducing and simulated FTS reaction conditions. Potassium and cobalt K-edge XANES spectra indicate that potassium interacts with both the cobalt phase and the SiO₂ support, and that potassium promotion inhibits the reduction of the Co/SiO₂ catalyst in hydrogen at 200°C. However, under CO hydrogenation conditions in the presence of water vapor, the differences in degree of reducibility are less since the unpromoted catalyst becomes more oxidized. For the K-promoted Co/Al₂O₃ catalyst, Co K-edge XANES and EXAFS spectra show that cobalt is initially present as a mixture of Co₃O₄ and CoO. Under hydrogen at 200°C, these oxides are reduced to a mixture of CoO and cobalt metal. During reaction at 200°C in H₂/CO, the cobalt phases are reconverted to a mixture of Co₃O₄ and CoO. Without potassium, the cobalt in Co/Al₂O₃ is reduced almost completely to cobalt metal under hydrogen at 200°C and remains in that form even during reaction at 200°C in H₂/CO. Only a minor trace of CoO is observed.

Schanke et al. (III.24) undertook studies directed toward explaining the role of platinum as a promoter for hydrocarbon synthesis on alumina-supported and silica-supported cobalt catalysts. In addition to conventional measurements of kinetics and metal surface areas, direct information on reaction rates and surface coverage of reaction intermediates has been obtained by the use of SSITKA experiments. Al₂O₃ and SiO₂ supported catalysts containing 9 wt% cobalt and 0 or 0.4 wt% platinum were prepared by incipient wetness coimpregnation of the supports with aqueous solutions of

$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$. At $T = 483\text{K}$, $P = 1\text{ bar}$ and $\text{H}_2/\text{CO} = 7$, CO hydrogenation rates (based on weight of cobalt) of Pt-promoted catalysts were 3-5 times higher than those on their unpromoted analogues. The selectivity was not influenced by the presence of platinum. TPR-studies shown that the presence of platinum strongly influences the reducibility of the catalysts, with TPR-peaks shifting to lower temperatures for all catalysts. This effect is most pronounced on the Al_2O_3 supported catalysts, where the highly dispersed and otherwise difficult to reduce surface cobalt oxides are readily reduced at normal reduction temperature in the presence of platinum. The dispersion of metallic cobalt for platinum promoted catalysts increased compared to that on the unpromoted catalysts, with Al_2O_3 supported catalysts showing the largest effect due to the reduction of highly dispersed surface cobalt oxide. Apparent turnover numbers (based on H_2 -chemisorption) were higher for Pt-promoted catalysts than for their unpromoted analogues by a factor of two. Decoupling coverage and intrinsic reactivity effects on the apparent turnover number by the use of SSITKA revealed essentially constant true turnover numbers on all catalysts. Thus, the increased apparent turnover numbers on Pt-promoted catalysts are due to a higher surface coverage of reactive intermediates.

In another paper (III.15), they reported the preparation of Pt- and Re-promoted 8.7 wt% $\text{Co}/\text{Al}_2\text{O}_3$ (1.0 wt% platinum or 1.0 wt% rhenium) by impregnating Al_2O_3 with an aqueous solution of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ using the incipient wetness technique. The sample was dried and calcined for 2 h at 573 K. Portions of the calcined base catalyst were then modified by impregnating with an aqueous solution of $\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$ or Re_2O_7 . An investigation of the CO hydrogenation of the two promoted catalysts has been carried out at two different conditions: 473 K, 5 bar, $\text{H}_2/\text{CO}=2$ and 493 K, 1 bar, $\text{H}_2/\text{CO}=7.3$.

The addition of platinum or rhenium significantly increases the CO hydrogenation rate (based on weight of cobalt), but the selectivity was not changed by the presence of platinum or rhenium. The results show that the observed increases in the reaction rates are caused by increased reducibility and increased number of surface exposed Co-atoms. SSITKA with carbon tracing was used to decouple the effects of the concentration of active surface intermediates and the average site reactivity of intermediates during steady-state CO hydrogenation. The SSITKA results show that the concentration of active surface intermediates leading to CH₄ increased as a result of the addition of a noble metal promoter. However, the average site activity was not significantly affected upon rhenium or platinum addition.

Holmen (III.25) also studied the effect of small amounts of Re on the reduction properties of alumina supported cobalt catalysts by TPR. An intimate mixture of Co/Al₂O₃ and Re/Al₂O₃ catalysts showed a promoting effect of rhenium similar to that for coimpregnated Co-Re/Al₂O₃. A loose mixture of Co/Al₂O₃ + Re/Al₂O₃ did not show any effect of rhenium on the reduction of cobalt. However, when the loose mixture of Co/Al₂O₃ + Re/Al₂O₃ was pretreated with argon saturated with water before the TPR, a promoting effect of rhenium on the reduction of cobalt was observed. It is suggested that rhenium promotes the reduction of cobalt oxide by hydrogen spillover, and that no direct contact between rhenium and cobalt seems to be necessary in order to obtain the promoting effect as observed by TPR. It is also shown that the presence of a high temperature TPR peak at 1200 K assigned to cobalt aluminate is mainly a result of Co-ion diffusion during the TPR and not during calcination. It would appear that another possibility would be water assisted transport of rhenium onto the Co-Al₂O₃ particles.

Iglesia (III.13) has reported work on TiO_2 and SiO_2 supported Ru-promoted cobalt catalysts. The catalytic activity was obtained using a fixed-bed reactor with $\text{H}_2/\text{CO} = 2.05$, 453-523 K, 0.01-2 MPa and 2-10 g catalyst with an average diameter of less than 0.2 mm to avoid diffusional effects. Their Co-Ru/ TiO_2 catalysts were prepared by adding a ruthenium nitrate/acetone solution to an acetone slurry containing the pretreated, calcined, reduced and passivated Co/ TiO_2 catalyst, followed by evaporation of the acetone solvent while stirring. The cobalt and ruthenium contents were 11.6 and 0.14% wt., respectively, corresponding to an atomic Ru/Co ratio of about 0.0067. SiO_2 supported bimetallic Co-Ru/ SiO_2 catalyst was prepared from formerly prepared Co/ SiO_2 using the synthesis and pretreatment procedures described above for TiO_2 -supported catalysts. Cobalt and ruthenium contents were 23.0 and 0.26 wt.%, respectively, corresponding to an atomic Ru/Co ratio of about 0.0070. It seems the addition of small amounts of ruthenium to Co/ TiO_2 or Co/ SiO_2 catalysts (Ru/Co, 0.008 atm) increase their turnover rate (Figure III.10) and C_5+ selectivity (Figure III.11) for FTS. The methane make was much lower than Kogelbauer et al. (III.16) reported and the alpha-values were much higher. Also, deactivated bimetallic Co-Ru catalysts can be regenerated by a hydrogen treatment at the reaction temperature whereas monometallic cobalt catalysts cannot. On Co/ TiO_2 , ruthenium addition increases the turnover rates by a factor of three and C_5+ selectivities from 84.5 to 91.1%, without an apparent change in cobalt dispersion. Activation energies (88 ± 6 kJ/mol) and kinetic pressure orders ($n = 0.6-0.65$ for CO) are unaffected by ruthenium addition. These data suggest that the presence of ruthenium leads to higher cobalt site density during reaction without modifying the chemical reactivity of exposed cobalt surface atoms. Ruthenium appears to inhibit the deactivation of surface cobalt ensembles. Ruthenium

atoms at the surface of cobalt crystallites increase the rate of removal of carbon and oxygen species during reaction and during regeneration of deactivated cobalt catalysts. The resulting higher cobalt site density leads to higher apparent turnover rates and to enhanced readsorption of olefins. As a result, Co-Ru catalysts yield a heavier and more paraffinic product than monometallic cobalt catalysts with a similar initial dispersion. The observed bimetallic interactions require intimate contact between cobalt and ruthenium, a state that forms during oxidation of the bimetallic precursors at high temperature. This treatment induces migration of ruthenium oxide species and leads to mixed Co-Ru oxides. The reducibility and the carbon deposition rates on well-mixed bimetallic Co-Ru catalysts are very different from those of monometallic cobalt catalysts. Electron microscopy, X-ray absorption spectroscopy, and thermogravimetric studies confirm the intimate mixing required for catalytic rate and C₅+ selectivity enhancements, for faster reduction of the cobalt oxide precursor, and for inhibition of carbon deposits during reactions of H₂/CO mixtures.

Turney (III.19) prepared a Ru-promoted coprecipitated cobalt/ceria catalyst. A mixture of ammonium ceric nitrate and cobalt nitrate hexahydrate in water was slowly added to an aqueous solution of ammonium carbonate, while stirring vigorously and bubbling carbon dioxide through the reaction vessel. After addition, the pH dropped to 7.1; the resultant dark brown precipitate was collected by centrifugation and washed five times with 4 L aliquots of water and then twice with 2 L aliquots of acetone. Residual acetone was removed in vacuo at ambient temperature. Further drying at 120°C for 16 h in air and then calcination at 600°C gave a black powder. Promotion was effected by adsorption of Ru₃(CO)₁₂ from solution in *n*-heptane onto the support; on stirring under nitrogen for 2 h, the solution was fully decolorized, indicating complete uptake of the

ruthenium carbonyl. FTS using the catalysts indicates the addition of ruthenium lowers the reduction temperature of both Co_3O_4 and CeO_2 further, presumably via hydrogen spillover reduction. Consequently there is more Co^0 in the ruthenium-promoted catalyst than the unpromoted catalyst leading to higher activity.

Bianchi et al. (III.18) prepared a Ru-doped cobalt titanium silicate (ETS-10) catalyst by a slurry impregnation of the ion-exchanged ETS-10 with a solution of $\text{Ru}(\text{NO})(\text{NO})_3$ in pure ethanol. The result indicates that the presence of small amounts of ruthenium introduced by wet-impregnation leads a complete reduction of the surface cobalt species and an increase of CO conversion and of the selectivity to iso-products. Upon increasing the amount of ruthenium, a further increase of the CO conversion and an interesting decrease of the C_1 fraction was found.

Kiviaho et al. (III.17) prepared a Co-Ru/ SiO_2 catalyst from the carbonyl cluster. $\text{Co}_{4n}\text{Ru}_n\text{H}_n(\text{CO})_x/\text{SiO}_2$ and $(\text{Co}_4(\text{CO})_{12} + \text{Ru}_4\text{H}_4(\text{CO})_{12})/\text{SiO}_2$ catalysts were prepared and their TPR and FT-IR properties were studied. $\text{Co}_{4n}\text{Ru}_n\text{H}_n(\text{CO})_x/\text{SiO}_2$ and $(\text{Co}_4(\text{CO})_{12} + \text{Ru}_4\text{H}_4(\text{CO})_{12})/\text{SiO}_2$ catalysts were prepared from the carbonyl cluster and their TPR and FT-IR properties were studied by Kiviaho et al. (III.17). The FT-IR studies suggested that $\text{Ru}_4\text{H}_4(\text{CO})_{12}$, $\text{CoRu}_3\text{H}_3(\text{CO})_{12}$ and $\text{Co}_3\text{RuH}(\text{CO})_{12}$ clusters on silica were more stable in room temperature than $\text{Co}_4(\text{CO})_{12}$, $\text{Co}_2\text{Ru}_2\text{H}_2(\text{CO})_{12}$ and $\text{Co}_2\text{Ru}_2(\text{CO})_{13}$ clusters. The FT-IR measurements also indicated that all precursors decomposed during thermal treatment, but the distinct temperature of decarbonylation was not necessarily noticeable. On the other hand, in TPR, the CO desorption peak maxima for the precursors were 123°C for $(\text{Co}_4(\text{CO})_{12} + \text{Ru}_4\text{H}_4(\text{CO})_{12})$, 127°C for $\text{CoRu}_3\text{H}_3(\text{CO})_{12}$, 133°C for $\text{Co}_2\text{Ru}_2(\text{CO})_{13}$, 137°C for $\text{Co}_4(\text{CO})_{12}$, 144°C for $\text{Co}_2\text{Ru}_2\text{H}_2(\text{CO})_{12}$, 148°C for $\text{Co}_3\text{RuH}(\text{CO})_{12}$ and 185°C for $\text{Ru}_4\text{H}_4(\text{CO})_{12}$. Thus, the catalysts with 1:1 atomic ratio of

Co:Ru decarbonylated at different temperatures. The temperature of decarbonylation was lower for $\text{Co}_2\text{Ru}_2(\text{CO})_{13}/\text{SiO}_2$ than for $\text{Co}_2\text{Ru}_2\text{H}_2(\text{CO})_{12}/\text{SiO}_2$, i.e., cobalt influenced the decarbonylation more in the first case. In accordance, the CO hydrogenation activity and selectivity results for the decarbonylated catalysts suggested that $\text{Co}_2\text{Ru}_2(\text{CO})_{13}/\text{SiO}_2$ exhibited the characteristics of cobalt more than $\text{Co}_2\text{Ru}_2\text{H}_2(\text{CO})_{12}/\text{SiO}_2$ did.

Effects of activation on the surface properties of silica-supported cobalt catalysts were studied by Coulter and Sault (III.26). Drying and calcining effects for 16-19 wt% Co/SiO₂ FTS catalysts, prepared by impregnation with cobalt nitrate, have been examined using ultrahigh vacuum surface analysis and conventional catalyst characterization techniques. Drying in air at 110°C or under vacuum at 100°C and then calcining in air at 400°C causes large Co₃O₄ particles to form, which easily reduce under hydrogen at 300°C. In contrast, dried samples annealed under UHV prior to calcining exhibit dramatically different characteristics. The decomposition of cobalt nitrate during drying initiates the formation of a surface cobalt silicate. Prolonged air drying eventually converts the surface silicate into Co₃O₄, while vacuum drying disperses the nitrate precursors on the support, forming cobalt silicate islands. Annealing air-dried samples in UHV stabilizes the surface silicate against reduction or oxidation through the migration of Co²⁺ ions into the support to form a well-ordered bulk cobalt silicate. Annealing of vacuum dried samples to 200°C in UHV produces a continuous, conductive surface silicate that sinters upon heating to temperatures above 250°C. Analysis of species generated during the decomposition of the $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ precursor indicates that the concentration of gas phase CO near the surface determines the nature of the cobalt surface phase. The formation of an intermediate surface cobalt

silicate under specific activation conditions maximizes the amount of reducible cobalt surface area available for FTS reactions.

The precursor can significantly influence the property of the catalyst. Loosdrecht et al. (III.27) prepared alumina-supported cobalt catalysts from different cobalt precursors to study its influence on the ultimate metal particle size. Furthermore, the effect of the particle size on the catalytic performance (activity and selectivity) during FTS was investigated. The preparation by incipient wetness impregnation, using cobalt EDTA and ammonium cobalt citrate precursors, of low-loaded cobalt catalysts (2.5 wt%) resulted initially in very small cobalt oxide particles, as determined by XPS. The small oxide particles reacted during the thermal treatment in a reducing gas flow with the alumina support to form cobalt aluminate, which was neither active nor selective during FTS. The catalysts prepared with cobalt nitrate had larger particles that could be easily reduced to metallic cobalt. These catalysts were active under reaction conditions (fixed-bed reactor, 523 K, $H_2/CO = 2$, 30 ml/min, 1 atm). Higher-loaded cobalt catalysts (5.0 wt%) prepared using ammonium cobalt citrate showed a larger particle size than the lower-loaded catalyst prepared from the citrate precursor. The extent of reduction to metallic cobalt that could be achieved with the higher-loaded catalyst was significantly higher than that with the lower-loaded catalyst, as shown by magnetic measurements. Accordingly, the authors report that "the higher-load catalyst exhibited a reasonable activity and, in addition, an interesting and remarkably high selectivity toward higher hydrocarbons, and also a very high Schulz-Flory parameter." This statement must be viewed as a relative comparison since the methane selectivities varied from 36 to 64% and the alpha values were in the range of 0.45 to 0.69, low values for a cobalt catalyst.

The effect of the precursor on the characteristics of the Co/SiO₂ catalysts prepared from Co(NO₃)₂, Co(CO)₈ and Co₄(CO)₁₂ was determined by Niemela et al. (III.28). The near-surface reduction was clearly lower for the Co₂(CO)₈ derived catalyst than for the Co₄(CO)₁₂ based one. The hydrogen chemisorption, CO desorption, XRD and XPS measurements indicated that the dispersion of the metallic species decreased in the precursor order Co₂(CO)₈ > Co₄(CO)₁₂ >> Co(NO₃)₂. The TPD studies showed that CO was more strongly adsorbed on catalysts derived from carbonyls than on those based on nitrate, resulting in greater initial activity for CO hydrogenation. In pulsed CO hydrogenation reactions, the selectivity of the Co₂(CO)₈ derived catalyst differed from the other two. Thus, despite the well documented transformation of the Co₂(CO)₈ to Co₄(CO)₁₂ on the silica support, the supported catalysts derived from these two precursors exhibited distinct characteristics and reactivity.

The activity of the Co/SiO₂ catalyst in relation to pretreatment of the catalyst was investigated by Niemela et al. (III.29). With increasing reduction temperature (300-450°C), the extent of reduction increased. The increase was not, however, accompanied with increased chemisorption capacity. Namely, the hydrogen chemisorption was highest at a reduction temperature of approximately 300°C. Also, carbon monoxide adsorption was almost constant at 200-400°C, and decreased drastically when the catalyst was heated to higher temperatures. Thus, the results suggest that cobalt agglomerated at temperatures above 400°C. The activity for toluene hydrogenation correlated well with the hydrogen uptake for reduction temperatures above 300°C. Also, the CO hydrogenation activity (235°C; 5 bar, H₂/CO/Ar = 3/1/3, GHSV = 2600 h⁻¹) of the catalyst increased with increasing temperature of reduction (400-450°C) due to the decrease in the number of active sites (figure III.12). These

results are in contradiction to the results of Moon and Yoon (III.30) who obtained a higher extent of reduction and catalytic activity by increasing the reduction temperature in the range 325-525°C. Johnson et al. (III.31) also obtained increasing activity (expressed as CO turnover frequency) with increasing percentage of reduction, although the specific activity of the well reduced catalyst sample did not depend upon cobalt dispersion.

Iglesia (III.32) found that catalyst productivity and selectivity to C₅+ hydrocarbons are critical design criteria in the choice of FTS catalysts and reactors. Cobalt-based catalysts appear to provide the best compromise between performance and cost for the synthesis of hydrocarbons from CO/H₂ mixtures. Optimum catalysts with high cobalt concentration and site density can be prepared by controlled reduction of nitrate precursors introduced via melt or aqueous impregnation methods. FTS turnover rates are independent of cobalt dispersion and support identity over the accessible dispersion range (0.01-0.12) (Figure III.10) at typical FTS conditions. At low reactant pressures or conversions, water increases FTS reaction rates and the selectivity to olefins and to C₅+ hydrocarbons. These water effects depend on the identity of the support and lead to support effects on turnover rates at low CO conversions. Turnover rates increase when small amounts of ruthenium (Ru/Co < 0.008 atm) are added to cobalt catalysts. C₅+ selectivity increases with increasing cobalt site density because diffusion-enhanced readsorption of α -olefins > β -hydrogen abstraction steps and inhibits chain termination. The readsorption of α -olefins merely has the effect of reversing the predominant chain termination pathways of small surface chains (β -hydrogen abstractions) by reinitiating surface chains that continue to grow and ultimately desorb as larger hydrocarbons. In effect, termination of alkyl chains via β -hydrogen abstraction becomes increasingly

reversible as olefin concentration or residence time increases; the readsorption reaction also becomes faster as reactive olefins are retained longer within liquid-filled catalyst pellets. This well known secondary reaction leads to an increase in the selectivity to C₅+ hydrocarbons and to lower selectivities to methane and olefins as bed residence time increases. Clearly, readsorption effects become more influential as olefin concentrations increase with increasing bed residence time and CO conversion. Severe diffusional restrictions, however, can also deplete CO within moderate diffusional restrictions. Diffusional constraints depend on pellet size and porosity and on the density and radial location of cobalt sites within catalyst pellets. Slurry bubble column reactors and the use of eggshell catalyst pellets in packed-bed reactors introduce design flexibility by decoupling the characteristic diffusion distance in catalyst pellets from pressure drop and other reactor constraints.

Catalytic rates and selectivity can reflect the intrinsic behavior of a metal surface. Sometimes, this surface chemistry changes because metal crystallites of different size expose surface ensembles with unique structures (III.33); strong interactions with a metal oxide support can also perturb the electronic density and structure of metal crystallites (III.34). The effect of titania, silica, alumina, zirconia and ZSM-5 on the specific activity and selectivity properties of cobalt for carbon monoxide hydrogenation has been studied by different authors under different conditions.

Bessell (III.35) examined a range of cobalt catalysts supported on kieselguhr, silica, alumina, bentonite, Y-zeolite, mordenite and ZSM-5 for catalytic activity and product selectivity for FTS at 240°C, 2 MPa using a GHSV of 1000 h⁻¹ in a microreactor. These results were correlated with catalyst reducibility and adsorptive properties, as well as support acidity, surface area and structure. In order to maximize the activity of

cobalt-based Fischer-Tropsch catalysts, it is necessary to choose high surface area supports and to obtain high cobalt dispersions. However, possible interactions between cobalt and the support must be taken into account as they can lead to lower catalyst activity. This was evidenced by the alumina, Y-zeolite and mordenite supported catalysts which did not undergo complete reduction under standard conditions due to the formation of irreducible surface species or ion exchanged cobalt within the support. Incomplete reduction, while producing a more dispersed catalyst, will limit the availability of active cobalt sites. Pore structure of the support is also important as pore diffusion or blocking effects can prevent reactants accessing active cobalt sites. All supports examined showed similar methane, carbon dioxide and higher hydrocarbon selectivities, and in all cases carbon dioxide selectivity was low. However, the nature of the higher hydrocarbons depended very much on the acidity of the support. The low acidity kieselguhr, silica, alumina and bentonite supports produced the traditional straight chained Fischer-Tropsch products, and are thus the preferred type of support if a straight chained product, such as a wax or diesel fuel, is desired. If gasoline production is targeted, zeolite supported catalysts are to be preferred as a lighter, more highly branched, and at sufficiently high temperatures aromatic, product results. However, the primary formed Fischer-Tropsch products must have access to the zeolitic acid sites if these secondary isomerization and aromatization reactions are to occur. This places some constraints on the channel system and ion exchange properties of the zeolite in question.

Reuel and Bartholomew (III.36) investigated the effect of support and dispersion on the CO hydrogenation activity/selectivity properties of cobalt. Specific activities and selectivities of unsupported cobalt and cobalt supported on alumina, silica, titania,

carbon, and magnesia carriers for CO hydrogenation were measured in a single-pass differential reactor at low conversion, 1 atm, and 175-350°C. The results indicate that specific activity and selectivity of cobalt vary with support, dispersion, metal loading, and preparation method. The order of decreasing CO hydrogenation activity at 1 atm and 225°C for catalysts containing 3 wt% cobalt is Co/TiO₂, Co/SiO₂, Co/Al₂O₃, Co/C, and Co/MgO (Figure III.13). The specific activity of cobalt decreases significantly with increasing dispersion (Figure III.14). Product selectivity is best correlated with dispersion and extent of reduction (Figure III.15), i.e., the molecular weight of hydrocarbon products is lower and the CO₂/H₂O ratio is higher for catalysts having higher dispersions and lower extent of reduction. This effect may be due to stable oxides in the well-dispersed, poorly reduced catalysts, which catalyze the water-gas-shift reaction thereby increasing the H₂/CO ratio at the surface. In the Co/Al₂O₃ system, activity and selectivity for high molecular weight hydrocarbons increase very significantly with increasing cobalt loading. A 15% Co/Al₂O₃ is 20 times more active than 3% Co/Al₂O₃; moreover, 86 wt% of its hydrocarbon fraction is in the C₅-C₁₂ (gasoline) range compared to 18 wt% for 3% Co/Al₂O₃.

Silica is a very popular support for cobalt; it exhibits high surface area and it does not readily form spinels during the reduction process. However, according to Goodwin's results (III.37), the formation of cobalt silicates in Co/SiO₂ has been found to occur during FTS, whether conducted in gaseous or the liquid phase. In order to explore the role of vapor in causing this formation, the Co/SiO₂ catalyst was studied using conditions simulating those present during FTS. It was found that, depending on exposure time and gas phase concentration, a loss of the catalytically active phase and the formation of cobalt silicates occurred. The cobalt silicates formed were not

completely reducible even during TPR to 900°C. The formation of silicates occurred rapidly for the in situ reduced catalyst and even more rapidly in the presence of hydrogen. The presence of air retarded this effect. On the contrary, when the cobalt was present as the oxide, hydrothermal treatment had little effect. It is concluded that the presence of cobalt metal is necessary for Co-silica reactions to occur forming both 'reducible' and 'nonreducible' (<900°C) cobalt silicate. The results point out a type of catalyst change which can occur during reaction. The authors did not indicate how Co_o can react to form a cobalt silicate.

Khodakov et al. (III.38) studied the reducibility of cobalt species that are present in silica-supported Fischer-Tropsch catalysts using in situ XRD, in situ EXAFS, and FTIR spectroscopy with carbon monoxide as a molecular probe. Crystalline cobalt phases in the oxidized catalysts were characterized using XRD. In the oxidized samples with a large concentration of amorphous phase, EXAFS showed the presence of small oxide clusters including several cobalt atoms. It was found (in-situ XRD, EXAFS) that calcination of oxidized cobalt catalysts under an inert atmosphere resulted in a selective transformation of Co₃O₄ to CoO at 623-673 K. FTIR spectroscopy, with CO as a molecular probe, revealed the presence of different sites associated with cobalt after the reduction of the catalysts with hydrogen at 723 K: cobalt metal sites, Co²⁺ ions in the crystalline phase of CoO, and Coⁿ⁺ species in an amorphous phase. The results (XRD, EXAFS, FTIR) showed that the hydrogen reduction properties of particles of cobalt oxide on silica depended on the size of the Co₃O₄ crystallites. The ease of reduction to metal decreased from larger (200-700Å) to smaller (60Å) particles.

The long-term performance of Co/SiO₂ catalysts in CO hydrogenation was investigated by Neimela and Krause (III.39). The catalysts were prepared from nitrate

(N) and carbonyl (CO) precursors. The activity in terms of conversion of carbon monoxide was determined over a reaction time of 120 h. The activity was obtained using a fixed-bed reactor, 0.5 MPa, 235-290°C, Ar:CO:H₂ = 3:1:3 and GHSV = 5200 h⁻¹. The conversion decreased rapidly during the first five hours (Figure III.16), and thereafter at a moderate rate that was related to dispersion, i.e, the higher the dispersion the higher the rate of decrease. These catalysts produced 58-65 mole% methane and had alpha values in the range of 0.69-0.81. The active sites were blocked by wax and coke formed during the reaction, although some agglomeration of particles probably took place on the Co(CO)/SiO₂ catalysts. More carbon was accumulated on Co(CO)/SiO₂ during the reaction suggesting a need for frequent regeneration. The reduction-oxidation-reduction treatments indicated, however, that the regenerability of the Co(CO)/SiO₂ in terms of hydrogen uptake is poor, although the amounts adsorbed still remained higher than those for Co(N)/SiO₂.

The influence of water on alumina-supported cobalt catalysts has been studied by Schanke et al. (III.40). The deactivation of supported cobalt catalysts was studied in a fixed-bed reactor using synthesis gas feeds containing different concentration of water vapor. Supporting model studies were carried out using H₂O/H₂ feeds in conjunction with XPS and gravimetry. Rapid deactivation occurs on Re-promoted Co/Al₂O₃ catalysts when H₂/CO/H₂O feeds are used, whereas unpromoted Co/Al₂O₃ shows more stable activity (Figure III.17). The results from the gravimetric studies suggest that only a small fraction of the bulk cobalt metal initially present reoxidizes to cobalt oxide during reaction. However, the XPS results indicate significant reoxidation of surface cobalt atoms in highly dispersed cobalt phases, which is likely to be the cause of the observed deactivation. Rhenium is shown to have a marked effect by decreasing the extent of

reoxidation of alumina-supported cobalt catalysts and a smaller decrease in the catalytic activity.

Lapidus and co-workers (III.41-III.43) studied the physical properties and FT performance of 10% cobalt catalysts supported on alumina, silica and alumina-silica, respectively. They found that properties of impregnated cobalt catalysts depend on the nature of the support and on the temperature of pretreatment. The decomposition of dried 10% Co/Al₂O₃ and 10% Co/SiO₂ in an inert gas proceeds in two steps: water evolution and decomposition of cobalt nitrate. In a reducing atmosphere, the endothermic decomposition was accompanied by exothermic reduction of cobalt nitrate, and the whole process strongly depended on the nature of the support. On SiO₂, the formation of cobalt surface compounds with the support was much more limited than on Al₂O₃. The amount of adsorbed CO increases with calcination temperature, while both the degree of cobalt reduction and the cobalt dispersion decrease. CO was adsorbed in four different states on the 10% Co/Al₂O₃ catalyst: as linear forms on Co²⁺, Co. δ .⁺, and CoO, bridged form on CoO. Their relative amounts depended on the temperature of pretreatment. Catalyst pretreatment with a CO and hydrogen mixture under hydrocarbon synthesis conditions causes a certain modification of the metal surface which leads to variations of the CO adsorption states. The influence of the nature of the support and the pretreatment temperature on the activity of cobalt catalysts in FTS at atmospheric pressure are presented. Pretreatment by calcination in air led to a decrease in cobalt reducibility and dispersion. The degree of reduction was higher with Co/SiO₂ than with Co/Al₂O₃ at all calcination temperatures. Except for the dried samples, cobalt dispersions were higher with Co/Al₂O₃. The variations in the catalytic properties of Co/Al₂O₃ and Co/SiO₂ in FTS with the pretreatment temperature differed

for both supports. When the calcination temperature was increased, the total hydrocarbon yield decreased over Co/SiO_2 catalysts and increased over $\text{Co/Al}_2\text{O}_3$ catalysts. The C_{5+} fraction selectivities over $\text{Co/Al}_2\text{O}_3$ catalysts increased with the pretreatment temperature, whereas over Co/SiO_2 catalysts, they remained practically constant. The resistance of cobalt catalysts to the action of air was higher with samples previously used in Fischer-Tropsch synthesis than with freshly reduced ones. For freshly reduced $\text{Co/Al}_2\text{O}_3$ catalysts, an increase of catalytic activity was found up to a certain level after repeated doses of air were passed through the catalyst bed. The nature of the oxide phases are thought to be responsible for the variation of catalytic properties. On the Co/SiO_2 catalyst surface, the formation of Co_3O_4 supposedly reduces the total hydrocarbon yield. In spite of the decrease of cobalt dispersion, the Co-support surface compounds cause an increase in the total hydrocarbon yield and the C_{5+} fraction selectivity on the $\text{Co/Al}_2\text{O}_3$ catalysts.

The physicochemical properties of 10% $\text{Co/SiO}_2\text{-Al}_2\text{O}_3$ catalysts prepared by impregnation were studied by temperature programmed reduction, thermoanalysis and CO adsorption (III.41-III.43). The temperature at which the catalyst was pretreated has a great influence on its adsorption capacity for CO. Both reduced and unreduced samples calcined in air at relatively high temperatures adsorbed CO, but the reduced ones adsorbed much larger amounts. The adsorption capacity tended to increase with increasing pretreatment temperature. The character of CO temperature programmed desorption profiles and the proportions of the individual adsorption forms depend on the pretreatment temperature and the degree of cobalt reduction. CO was adsorbed in three forms on species originating in Co-support interactions, metallic cobalt, and on Co_3O_4 . Calcination in air caused a decrease of both cobalt reduction and the activity for

hydrocarbon synthesis. While the yield of gaseous products remained constant, liquid yield decreased substantially with increasing pretreatment temperature, reaching a maximum value when the degree of cobalt reduction was approximately 40-50%. The average carbon number decreased with increasing cobalt reduction. The catalytic properties of $\text{Co/SiO}_2\text{-Al}_2\text{O}_3$ are resemble more closely those of Co/SiO_2 than of $\text{Co/Al}_2\text{O}_3$, but $\text{Co/SiO}_2\text{-Al}_2\text{O}_3$ catalysts are less efficient in polymerization than either Co/SiO_2 or $\text{Co/Al}_2\text{O}_3$. The hypothesis, suggesting that the adsorption centers of weakly bonded CO were involved in the production of liquid hydrocarbons and that the cobalt oxide species act directly in this synthesis, was confirmed.

A particularly interesting scheme is to react synthesis gas mixture over a bifunctional catalyst (III.44-III.46). The catalyst would be a combination of Fischer-Tropsch catalyst and a shape-selective zeolite. For example, the combination of metal oxides with the medium pore (ca. 6.0 Å) ZSM-5 zeolite (III.47-III.50) and the use of metal nitrate or organometallic impregnated ZSM-5 (III.51-III.55) catalysts have been shown to produce gasoline range hydrocarbons containing a high percentage of aromatics from synthesis gas. Physical and chemical properties as well as the activity and selectivity of Co/HZSM-5 zeolite bifunctional catalysts have been studied by Calleja (III.56) for conversion of synthesis gas. These catalysts were prepared by incipient wetness impregnation with different conditions of drying, calcination and reduction. The cobalt content in the catalyst and the effect of thorium, as a promoter, were also studied. The catalysts were characterized and tested in a fixed bed continuous reactor system. The results show that drying is the most important step in the preparation, having more active catalysts with fast drying conditions, probably due to the formation of smaller cobalt particles. The interaction between the metal and the zeolite surface seems to

contribute significantly to the catalyst activity. Maximum activity of the catalyst is obtained with 1.5 wt% of thorium, resulting in an increase of C_{6+} selectivity. This was explained in terms of a shift in chemisorption properties of the catalyst. The basic character of the promoter affects the zeolite acidity, decreasing the aromatic proportion in the liquid hydrocarbon fraction. [It is not clear how either ThO_2 or Rh^{4+} can exchange could do this. For example, exchange of a zeolite with La^{3+} does not appreciably change the number of acid sites of a zeolite.] Finally, the optimum bifunctional catalyst selected in this study is compared with a physical mixture of a commercial Fischer-Tropsch catalyst and HZSM-5 zeolite. The results achieved under the usual reduction conditions with both catalysts show that, for the same value of conversion, selectivity towards C_{6+} hydrocarbons was notably greater for the optimum catalyst. Although the amount of aromatic hydrocarbons was slightly lower, the percentage of C_{6+} hydrocarbons was about two-fold higher. Also, an increase could be observed in the olefinic nature of C_3 hydrocarbon fraction obtained using the selected catalyst. The most important reason for these differences may be a decrease in the acidity of the zeolite due to the basicity of ThO_2 , which reduces aromatization reactions of light alkenes. Therefore, the selected catalyst yields a higher liquid hydrocarbon fraction compared to physical mixture catalyst. Moreover, the mixture of hydrocarbons had an acceptable composition to be used as high octane number fuel.

Yin et al. (III.57) studied CO hydrogenation with PdCo/NaY catalysts. NaY-encapsulated Pd-Co bimetallic catalysts of various Co/Pd ratios and pretreatment conditions were used for carbon monoxide hydrogenation. Preparation conditions have an overwhelming effect on the active phases and the catalyst selectivity. In Pd/NaY and bimetal samples with very a low extent of cobalt reduction, the formation of palladium

carbide is detected by XRD. On these catalysts, methane is formed when particles are very small, but after some agglomeration, methanol is the dominant primary product of CO hydrogenation; secondary reactions (MTG) on strong Brønsted-acid sites lead to dimethyl ether and heavier hydrocarbons. For bimetallic PdCo/NaY samples, calcination and reduction conditions are critical for the formation of PdCo alloy particles, which prevents the formation of palladium carbide, and methane selectivity is high. For higher cobalt contents, alloy particles are obtained following reduction at high temperature; these samples show a signature reminiscent of Fischer-Tropsch catalysts.

McMahon et al. (III.58) studied dispersed cobalt-containing zeolite Fischer-Tropsch catalysts. Microwave discharge methods were used to prepared highly dispersed cobalt clusters in zeolites. Ferromagnetic resonance, electron microscopy, and hydrogen chemisorption experiments have been used to determine the particle sizes of the cobalt clusters. These materials were also studied as Fischer-Tropsch catalysts. Catalytic results suggest that these cobalt zeolite catalysts show high selectivity for the production of low-molecular-weight olefin. Evidence of shape selective catalysts with a cut off at the C₆ chain length has also been observed according to their analysis. McMahon et al.'s data indicate that CO hydrogenation on Co/zeolite catalysts is a structure-sensitive reaction. These highly dispersed catalysts are not as active as catalysts with larger cobalt particles but show higher selectivities toward light hydrocarbons than cobalt-alumina catalysts. FTIR, SEM, and hydrogen chemisorption experiments indicate that the cobalt clusters are extremely small. H₂ chemisorption experiments indicate a 100% dispersion and a particle size of about 9 Å prior to catalytic experiments. At 512 K, the hydrocarbon product is 26% C₂-C₄ olefins. A tail-off in Anderson-Schulz-Flory plots at C₆-C₉ is indicative of a shape-selective

effect. However, in a later review, Bartholomew (III.59) provided data obtained by Ungar and Baird that is still unpublished that conclusively show that because of the holdup of heavy hydrocarbons in the zeolite structure, one must wait for a longer time period than most of the reported data to ensure that steady-state products are obtained.

Stencel et al. (III.60) prepared a metal-impregnated Co/ZSM-5 catalysts with $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ using an incipient wetness technique. These catalysts were shown to contain highly dispersed, ion-exchanged, non-reducible Co^{2+} species in the interior of the ZSM-5 particle, and large, reducible cobalt oxide crystallites on the exterior as determined from the number of pyridine molecules that coordinately bond to each of these ions, estimated using infrared data. The crystalline forms of cobalt on the surface of the ZSM-5 are identified and their sizes estimated after O_2 calcination, H_2 reduction, and $\text{CO}+\text{H}_2$ exposure. These data are then scrutinized for correlations of chemical and physical properties of the Co/ZSM-5 catalysts with conversion activity and selectivity for synthesis of hydrocarbons from $\text{CO}+\text{H}_2$ gas. The use of surface sensitive and bulk experimental techniques have enabled the differentiation of two distinct cobalt species in Co/ZSM-5 catalysts. Cobalt interior to the ZSM-5 is in an irreducible, ionic Co^{2+} form created during ion exchange for H^+ , cobalt exterior to the ZSM-5 is in the form of large Co_3O_4 crystallites that are reducible under hydrogen at 350°C to hcp cobalt metal and CoO . By varying the preparation methods, either of these cobalt forms can be obtained. It may now be of interest to study the conversion of other reactants over these types of catalysts and possibly to investigate the effect of particle size of the exterior-located cobalt on $\text{CO}+\text{H}_2$ conversion activity and selectivity.

Investigation of bifunctional zeolite supported cobalt Fischer-Tropsch catalysts has been done by Bessell (III.61). ZSM-5, ZSM-11, ZSM-12 and ZSM-34 were

examined as supports for cobalt bifunctional Fischer-Tropsch catalysts in order to determine the influence of zeolite pore structure on the synthesis. All supports produced reasonably active catalysts, with the activity increasing with the channel size of the zeolite support (i.e, in the order of ZSM-34 < ZSM5, ZSM-11 < ZSM-12 supported catalysts). Lack of observable differences in methane and higher hydrocarbon selectivities indicated that this increased activity was not due to an electronic cobalt-support effect. It was more likely a result of increased cobalt dispersion due to an enhancement of some small cobalt crystallite formation within the larger-channeled zeolites. The absence of a channel-size dependent cut-off in the product distributions indicated a lack of shape selective behavior, and that significant hydrocarbon chain growth was occurring on cobalt crystallites on the zeolite surface. Ammonia TPD measurements indicated that the acidity of these zeolites, in terms of both acid strength and acid site concentration, decreased in the order ZSM-34 > ZSM-5 > ZSM-11 > ZSM-12. Contrary to initial expectations, the hydrocarbon products became lighter, and contained less n-alkanes, as the acidity of the zeolite was reduced (which was in the same order as when the channel size of the zeolite was increased). This indicated that for this strongly acidic series of zeolites, accessibility to internal acid sites was more important in influencing the degree of secondary acid catalyzed restructuring reactions of the primary Fischer-Tropsch products than was the strength or concentration of these acid sites.

Metal dispersion and support effects on FTS rate and selectivity were studied at conditions that favor the formation of C₅+ hydrocarbons (>80% selectivity) by Iglesia et al. (III.62). On cobalt, hydrocarbon synthesis rates are proportional to metal dispersion (0.0045-0.095) and independent of the metal oxide support (SiO₂, Al₂O₃, TiO₂, and ZrO₂-

modified SiO_2 and TiO_2). Site-time yields ($1.6\text{--}3.0 \times 10^{-2} \text{ s}^{-1}$) are independent of cobalt dispersion and support (473 K, 2.0 MPa, $\text{H}_2/\text{CO}=2.1$). Dispersion and support influence C_5+ selectivity slightly; these changes reflect transport-enhanced secondary reactions and not modifications of intrinsic chain growth kinetics. Specifically, transport restrictions imposed by the physical structure of the support and by a high site density within catalysts pellets increase the residence time and the readsorption probability of reactive α -olefins and lead to higher C_5+ yields and more paraffinic products.

FTS site-time yields and intrinsic chain growth kinetics depend only weakly on cobalt dispersion and on the oxide support (SiO_2 , Al_2O_3 , TiO_2). Dispersion and support effects on C_5+ selectivity arise from changes in the extent of α -olefin readsorption as changes in site density and support structure modify the rate of intrapellet olefin removal (III.63).

Fu and Bartholomew (III.64) determined the activities and selectivities of cobalt/alumina catalysts for CO hydrogenation as a function of metal loading, reduction temperature, and preparation. Specific activities and average carbon number of the hydrocarbon product were found to significantly vary with metal loading, reduction temperature, and preparation. These changes were also found to be linearly correlated with changes in dispersion indicating that CO hydrogenation on $\text{Co}/\text{Al}_2\text{O}_3$ is structure-sensitive (Figure III.18). The changes in specific activity with dispersion can be explained by variations in the distribution of low and high coordination sites and by changes in the nature of adsorbed CO species available for reaction. High specific activity is apparently favored on sites to which CO is strongly coordinated. Variations in the average carbon number of the product can be explained by changes in the rate of

termination relative to the rate of propagation. High-molecular-weight products are favored by catalysts having high rates of propagation and low rate of termination.

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Table III.1										
Effect of Calcination Temperature on CO Hydrogenation (reduction temperature = 300°C, H ₂ /CO = 10, T = 220°C, P = 1.8 atm) (from ref. III.20)										
	% CO conversion		Rate ^d (μmole/g Co _{TOT} /S)		CH ₄ Selectivity (%)		α		TOF ^e x 10 ² (1/s)	
T _c (°C) ^a	Initial ^b	S-S ^c	Initial	S-S	Initial	S-S	Initial	S-S	Initial	S-S
Uncalcined	9.7	7.5	44.0	32.2	70	75	0.42	0.37	---	---
200	15.1	11.1	68.6	50.4	86	84	0.40	0.36	---	---
250	12.3	9.2	55.9	41.9	86	80	0.41	0.36	3.0	2.2
300	10.9	8.4	49.8	38.2	73	76	0.40	0.38	2.9	2.3
350	8.2	6.4	37.2	29.2	70	74	0.42	0.37	3.0	2.3
400	6.4	5.1	29.2	23.0	68	73	0.41	0.37	3.3	2.6
a. Calcination temperature. b. After 5 min. of reaction. c. After 7 hr. of reaction. d. Error in rate measurement was ± 5%. e. Based on total hydrogen chemisorption.										

Figure III.1. Time-on-stream behavior of the overall rate of CO hydrogenation for the catalyst reduced at 300°C and calcined at various temperatures (from ref. III.20).

Figure III.2. Effect of pretreatment temperatures on overall catalyst activity of Ru/Co/Al₂O₃ (from ref. III.20).

Figure III.3. Effect of pretreatment temperatures on intrinsic activity of Ru/Co/Al₂O₃ for methane formation (from ref. III.20).

Figure III.4. Rates of F-T synthesis at 220°, 1 atm. and H₂/CO = 2 versus time-on-stream for selected catalysts (in inset d = dried, c = calcined, r = reduced, Cl = prepared from RuCl₃) (figure from ref. III.16).

Figure III.5. Influence of La^{3+} content on the fraction of methane produced by a Co/SiO_2 catalyst (220°C , 1 atm., $\text{H}_2/\text{CO} = 2$) (from ref. III.23) Plot from table 2 of reference.

Figure III.6. Initial CO hydrogenation reaction for $(\text{La})\text{Co}/\text{SiO}_2$ catalysts (220°C , 1 atm., $\text{H}_2/\text{CO} = 2$) (from ref. III.23).

Figure III.7. Dependence of the chain growth probability (α) on the La^{3+} content for a Co-SiO₂ catalyst (220°C, 1 atm., $\text{H}_2/\text{CO} = 2$) (from ref. III.23). drawn from table 2.

Figure III.8. C₂-C₅ olefin/paraffin ratios for La-promoted Co/SiO₂ catalysts (220°C, 1 atm., $\text{H}_2/\text{CO} = 2$) (from ref. III.23).

Figure III.9. Overall rate vs time-on-stream during FTS (220°C, 1 atm., $\text{H}_2/\text{CO} = 2$) (from ref. III.24).

Figure III.10. Effects of cobalt dispersion and support on Fischer-Tropsch synthesis rates (473 K, $\text{H}_2/\text{CO} = 2.1$, 2.0 MPa, 50-60% CO conversion: (a) metal-time yields and (b) site-time yields (from ref. III.13).

Figure III.11. C₅+ selectivity on Co/TiO₂ and Co-Ru/TiO₂ (Ru/Co = 0.0067 at.) catalysts (473 K, 2.0 MPa, H₂/CO = 2.05, 11.6 wt.% Co) (from ref. III.13).

Figure III.12. The effect of reduction temperature on the activity of Co/SiO₂ hydrogenation at 235°C, 5 bar, 1g of catalyst, GHSV of 2600 h⁻¹ and H₂:CO:Ar = 3:1:3 (from ref. III.29).

Figure III.13. The activity of the indicated catalysts for CO hydrogenation at atmospheric pressure (drawn using data in C. H. Bartholomew, R. B. Pannell and J.L. Butler, *J. Catal.*, 65 (1980) 335).

Figure III.14. Percentage dispersion vs CO turnover frequency at 225°C for impregnated, precipitated, and evaporatively deposited catalysts (G, Co/SiO₂; F, Co/Al₂O₃; Δ, Co/TiO₂; ◇, Co/C) (from ref. III.34).

Figure III.15. Average carbon number of hydrocarbons produced at 225°C and 1 atm for 3 and 10 wt.% supported cobalt catalysts as a function of dispersion. (Δ , Co/SiO₂ (impregnated); $\square$, Co/Al₂O₃ (impregnated); $\diamond$, Co/TiO₂ (impregnated); $\circ$, Co/C (evaporatively deposited) (from ref. III.34).

Figure III.16. The activity of Co/SiO₂ at 235°C for 120 h of reaction time (from ref. III.37).

Figure III.17. Observed reaction rate relative to the initial rate for hydrocarbon formation as a function of time during simulated high conversion conditions. p_{o,H_2O} = partial pressure of water at reactor inlet. Feed composition: 50 mole% H_2 + CO, $H_2/CO=2$, balance N_2+He or $N_2 + He + H_2O$. CO conversion before addition of water: 20-28%. (a) Catalyst: 21%Co-1%Re/ γ - Al_2O_3 (Puralox). $T=493K$, $P=13bar$. (b) Catalyst: 20%Co/ γ - Al_2O_3 (Vista-B). $T=493 K$, $P = 8 bar$. (from ref. III.38).

Figure III.18. Correlations of dispersion with average carbon number for $\text{Co}/\text{Al}_2\text{O}_3$ catalysts of different loading and reduction temperature. (Δ , different reduction temperatures; $\circ$, different loadings) (from ref. III.61).

ATTACHMENT IV

Fischer Tropsch - Examples of Activation

EX-SITU

1. Oukaci et al. [R. Oukaci, J. G. Goodwin, Jr., G. Marcelin and A. Singleton, ACS Fuel Chem Preprint, 39, (1994) 1118] reported that the catalyst is first reduced ex-situ in a fluidized bed assembly and then transferred into a glove box for weighing and subsequent transfer into the slurry bubble column reactor.
2. Beuther et al. reported a procedure known as ROR [H. Beuther, T. P. Kobylinski, C. E. Kibby and R. B. Pannell, South Africa Patent Application No. 855317, July 15, 1985.] in which a reduction in hydrogen, oxidation, and rereduction (ROR) procedure was utilized. The rereduction was conducted the same as the first reduction. The reduction procedure was conducted so that the water vapor pressure did not exceed 1% of the exit gas. The catalyst particles were then suspended in a liquid medium but details of catalyst transfer not given nor were the details of any in-situ treatment prior to the synthesis.
3. Iglesia et al. [E. Iglesia, S. Soled, R. Fiato; Cobalt-ruthenium catalysts for FT synthesis and process for their preparation; patent 4,738,948 (Apr. 1988).] claim a hydrocarbon synthesis catalyst prepared by a process that comprises an impregnation of a refractory support comprising titania with solutions of catalytically active amounts of cobalt and ruthenium salts, drying the impregnated support, reducing the cobalt and ruthenium, treating the reduced metals with an oxygen containing stream at conditions sufficient to form oxides of cobalt and oxides of ruthenium and reducing the cobalt and ruthenium oxides. It appears

that this procedure is either the same as or very similar to the ROR procedure utilized by Beuther et al. (IV.1).

4. Nay et al. [B. Nay, M. R. Smith and C. D. Telford, "Catalyst treatment;" U.S. Patent 5,585,316, December 17, 1996.] claimed a process for reducing a catalyst containing cobalt, suitable for use in a Fischer Tropsch process for converting synthesis gas into hydrocarbons, which comprises pretreating said cobalt catalyst at 200-600°C with a gas containing molecular oxygen to produce an oxidized cobalt catalyst, a majority of said cobalt being in an oxide form, and then contacting said oxidized cobalt catalyst at elevated temperatures with a gas containing carbon monoxide substantially free of hydrogen, to produce a reduced cobalt containing catalyst. In one example, a 10% Co on ZnO and one portion treated at 500°C in air for 6 hr and then hydrogen for 9 hr at 320°C. The other portion was treated with air for 50 hr and then with CO for 3 hr at 250°C.

Conversion was obtained in fixed bed at 30 bar, GHSV 1250 h⁻¹.

Catalyst Treatment	Hr. on Stream	Mean Bed Temp (°C)	CO Conv %	% CH ₄	CO ₂	C ₅ +
Air/H ₂	214	214	87	7.5	2.5	76.8
Air/CO	213	212	87	4.6	1.9	91.0

During the early work at Air Products, catalysts were activated in syngas. To accomplish this the catalyst precursor was heated to 180°C in a nitrogen flow at atmospheric pressure. At 180°C, the flow was switched to the synthesis gas (CO/H₂ = 1) and then heated to the reaction temperature. At the reaction temperature, the pressure was increased to the one used for the synthesis. Later in their work, they compared the impact of activation in pure H₂ or syngas (CO/H₂ = 1). For a 4%Co-

zirconia promoted alumina catalyst, they found that the sample activated in hydrogen had a significantly higher activity and higher yield of liquid fuels (Figure VI.1; Table VI.1).

IN-SITU

The reduction procedure used by the U.S. Bureau of Mines [6. H. E. Benson, J. H. Field, D. Bienstock, R. R. Nagel, L. W. Brunn, C. O. Hawk, J. H. Crowell and H. H. Storch, "Development of the Fischer-Tropsch oil-recycle process," Bureau of Mines Bulletin 568, 1957.] was conducted at atmospheric pressure. To begin the reduction the temperature was raised to 360°C as rapidly as possible, maintaining a flow of about 40 GHSV. At 360°C the hydrogen flow was increased to 500 to 1,000 GHSV, and was maintained for four hours. The flow was then reduced to 20 GHSV and the temperature reduced to 150°C. Process oil was then added to the reactor, nitrogen replaced the hydrogen flow and the pressure was increased to about 40 psig. When the reflux and readdition of process oil stabilized, the nitrogen flow was replaced by synthesis gas. The pressure was slowly increased which in turn slowly increased the temperature inside the reactor. During 48 h. the temperature remained below 175°C and the gas contraction held to a maximum of 50%. The temperature was increased to 180°C during 24 h. after which the induction period had been completed and the temperature was adjusted to obtain maximum productivity.

Mitchell [W. N. Mitchell, "Activation of hydrocarbon synthesis catalyst;" U.S. patent 5,292,705 (Mar. 1994).] claimed a method for activating an essentially fresh, reduced cobalt containing FT catalyst which comprises treating the catalyst with hydrogen or a hydrogen containing gas in the presence of hydrocarbon liquids for a period sufficient to increase substantially the initial catalyst productivity.

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Table VI.1		
Effect of syngas vs. hydrogenation activation on the hydrocarbon selectivity using a 4% Co on Zr/Al ₂ O ₃ catalyst utilized in a slurry CSTR.		
	Syngas	H ₂
Space velocity, NL/gcat/hr	1.6	2.0
CO/H ₂	1.6	1.5
Pressure, psig	300	300
Temperature, °C	250	258
Hydrocarbon, wt. %		
C ₁	11.5	7.2
C ₂₋₄	10.4	10.8
C ₅₋₁₁	29.2	34.1
C ₁₂₋₁₈	15.3	27.9
C ₁₉₋₂₃	12.5	8.6
C ₂₄₊	21.1	11.4
C ₅₋₂₃	57.0	70.6

Figure IV.1. Productivity, based upon 2,500 bbl/day and assumed reactor filling, of the Sasol slurry reactor versus percentage of iron in the slurry.

ATTACHMENT V

Productivity - Slurry Phase

I. Iron Catalyst

H. Kölbel, "Chemische Technologie. Band 3: Organische Technologie I, Carl Hansen Verlag, München, 1959, p. 439.

Kg Product/m³ Reactor/day = 1,000 to 2,000 in the large pilot plant [60 m³].

0.47 - 0.94 g/g catalyst/hr

Experimental was 0.44 g/g catalyst/hr

Sasol

The reactor is 5 m diameter and 22 m tall. Assuming that only 2/3rd of the total volume is available for synthesis, the reactor volume is about 288 m³. The productivity is 2,500 bbl/d which is 16,561 L/hr and, assuming a density of 1 g/cm³ for the product, this corresponds to 16,561 kg/hr. The productivity/reactor volume is then 57.8 kg/hr/m³. Assuming various iron content per reactor volume produces a productivity of 2.89 g/gFe/hr for 0.02 fraction of iron whereas a loading of 0.2 iron gives a productivity of 0.289 g/gFe/hr (Figure V.1).

II. Cobalt Catalyst

La Porte

Run design for LaPorte Run 3-4

Slurry concentration 24-25 wt.% catalyst, reactor temperature 250-260°C;
reactor pressure = 710 psig (48.3 atm), reactor productivity = 150g hc/L/hr.
Assume density of slurry is 1.25 kg/L

0.5 g hc/g catalyst/hr

Exxon

R. M. Koros, "Bubble column, tube slurry process and apparatus," U.S. Patent 5,384,336, January 24, 1995.

At 65% CO conversion with $H_2/CO = 2.1$, 5 cm/s, reaction temperature of 183°C or higher, space velocities of 2800 to 3600 hr^{-1} , the productivities ranged from 450 to 750.

This gives a productivity of 0.28 to 0.47 g hc/cm³/hr. If the bulk density is 2.7g/cm³ as given [W.C. Behrmann et al, U.S. Patent 5,545,674, August 13, 1996] this corresponds to a productivity of **0.104 to 0.174 g/g catalyst/hr.**

ATTACHMENT VI

Early Slurry Reactors

A unique slurry reactor involved an arrangement of trays, each containing catalysts, that were contained in a cylindrical vertical reactor that was fitted at the top with a reflux condenser and an arrangement for removal of liquid at the bottom of the reactor (figure VI.1) (VI.1,VI.2) Experiments were conducted in a 7-tray reactor, 4.5 cm diameter and 60 cm tall, with up flow of gas.

A tube containing cells, a bundle of tubes, is employed to effect the conversion wherein the catalyst bed is completely submersed in a liquid. An example of one version of this reactor is shown in figure VI.2 (VI.3). Preheated oil is pumped into the outer shell and allowed to descend to the bottom where it is carried, together with the reactant gas, through the reactor tube containing the catalyst. Unconverted gases, the cooling oil and products pass overhead, are cooled and pass to a separator to produce gaseous and liquid product streams as well as recycle cooling oil.

Another reactor is constructed along the lines of a modern multi-tray bubble cap distillation tower. Thus, a reactor is fitted with a number of trays that contain the catalyst with bubble caps arranged to allow vapors, unconverted feed gases and vapor phase products, to be distributed to keep the catalyst in suspension (figures VI.3 and VI.4) (VI.4) Some bubble caps are fitted with downcomers that allow nonvolatile liquid to descent to the bottom of the reactor. In an example, 0.75 lb of catalyst was suspended in one gallon of oil (about 10 % slurry) and charged to a reaction chamber containing 50 bubble trays.

Another variation was provided (figure VI.5 and VI.6) (VI.5). In this version the cooling liquid could be added at several levels in the reactor so as to maintain a better control of the temperature during startup and synthesis.

Benson et al. (VI.6) report that after the preliminary work by F. Duftschmid, E. Linckh and F. Winkler as described above, a pilot plant with a reactor of 0.2 m diameter and 6 m height (about 200 L) was constructed during 1936 and 1937 at pressures of 100 atm and then at 15 to 20 atm. In 1938, a larger plant with a 0.5 m diameter and 6 m tall (1,500 L) was operated.

The U.S. Bureau of Mines constructed and operated a pilot plant that utilized oil-
recycle in a reactor with a 3 inch (7.6 cm) and 8 ft. (2.44 m) tall (VI.6). After several runs during 1946-47 with co-current downflow of gas and liquid over cobalt catalysts, a run was made with the cobalt catalyst completely submerged in liquid and co-current upflow of gas and liquid. After it had been demonstrated that the unit could be operated with the cobalt catalyst, the later runs were made with an iron catalyst. The composition of the cobalt catalyst was Co:ThO₂:MgO:kieselguhr = 100:7:12:200. The cobalt catalyst was reduced at atmospheric pressure in the reactor. The temperature was raised to 360°C as rapidly as possible using a hydrogen flow of 10 ft³/h and then the hydrogen flow was increased to 200 to 400 ft³/h and the reduction continued for 4 h. Since the catalyst bed occupied about 0.25 ft³, the GHSV was about 800 to 1600 h⁻¹ during the reduction at 360°C. Following reduction, the hydrogen flow was reduced to 5 ft³/h and the temperature reduced to 150°C. Nitrogen replaced hydrogen at this point and the pressure was increased to 40 psig. Oil was then admitted to the reactor. After the oil was added, syngas flow of GHSV = 100 was started. The temperature was slowly increased from 150°C by increasing the pressure in small increments, which decreased

the rate of evaporation of the cooling oil. The temperature was maintained below 175°C, maintaining a gas contraction of less than 50%, during 48 hours. The temperature was increased to 180°C during the next 24 h., after which the induction was considered complete. The conditions were then adjusted as required to obtain maximum productivity.

Kölbel and Ackermann (VI.7, VI.8). obtained patents for an apparatus for carrying out gaseous catalytic reactions in liquid medium. The reactions included Fischer-Tropsch synthesis.

It is stated that the "[Fischer-Tropsch] synthesis according to known processes is feasible without trouble in a reaction space of up to 20 cm [7.9 in] diameter. With increasing horizontal diameter of the reaction space the amount of gas conversion decreases and it is always more difficult to maintain a constant gas conversion. The larger the horizontal diameter of the reaction space, the more the liquid substance leans toward changing from stationary state to a state of vertical rotation. The liquid flows downwardly along the surface of the wall and flows along the bottom to the middle of the reaction space, whereby it is drawn out by the gas bubbles leaving at the middle of the bottom. The compressed central gas stream flows along with the liquid toward the top whereby the firmly compressed gas bubbles combine to form large elongated gas bubbles. Only at the upper reversal point of the liquid, in the vicinity of the surface of the column of liquid, the gas spreads out horizontally across the transverse section and the large gas particles are partially decomposed (Figure VI.7)."

Kölbel and Ackermann illustrated the problem with figure VI.7. As shown, the liquid flows upwardly in the interior of the reactor tube and flows downward along the

wall side of the reactor. They indicated several disadvantages accrue from this situation, including:

1. decreased gas conversion,
2. occurrence of secondary reactions,
3. increased catalyst damage, and
4. increased catalyst aging.

These authors state that, for reactions like Fischer-Tropsch synthesis where the gas composition changes with conversion and where the products admix with the unconverted gas, "...the gas conversion should be complete as possible on passing the gas through once..." The authors indicate that, prior to their patent, none of the available operations permit "...maintaining the liquid medium and the suspended catalyst stationary and nevertheless permitting the gas bubbles in uniform size and distribution to pass vertically through the liquid medium at equalized velocity..." The authors indicate that the disadvantages of the liquid and catalyst circulation, as shown in figure VI.7, can be overcome in a cylindrical reactor with a horizontal diameter of more than 30 cm (11.8 in) and up to 3 m or more (9.8 ft or more) and more than 1.5 m (4.9 ft) in height, and a gas headspace above the liquid at least as large as the reactor diameter. To provide within the reaction zone a stationary catalyst and liquid condition, the large reactor shell is subdivided into similar, vertical shafts which are open at top and bottom that have liquid-tight casings and a diameter of at least 5 cm (2 in) (figure VI.8). The shafts should terminate above the expanded liquid level; i.e., in the free gas space. Because of the flows in the bottom of the reactor, it is stated that each of the shafts, in the center as well as at the wall region, receive the same amount gas. While there is circulation of the liquid in the sump (bottom of reactor in figure VI.8), "...there

are formed in the shafts extremely stationary liquid columns whose expansion depends on the amount of gas."

The authors indicate that in certain cases, as in the Fischer-Tropsch reaction, it may be an advantage to allow the temperature to rise toward the top of the reactor, and provisions are described which would allow for this to occur. Thus, as the partial pressure of the reactants decrease, the higher temperature will be able to compensate, completely or partially, for the partial pressure decrease.

References

- VI.1 F. Duftschmid, E. Linckh and F. Winkler, "Production of valuable hydrocarbons and their derivatives containing oxygen," U.S. Patent 2,159,077, May 23, 1939.
- VI.2 F. Duftschmid, E. Linckh and F. Winkler, "Preparation of products containing valuable hydrocarbons or their derivatives, U.S. Patent 2,207,581, July 9, 1940.
- VI.3 F. Duftschmid, E. Linckh and F. Winkler, "Synthesis of hydrocarbons," U.S. Patent 2,287,092, June 23, 1942.
- VI.4 E. B. Peck, "Method of controlling exothermic reactions, U.S. Patent 2,161,974, June 13, 1939.
- VI.5 F. Duftschmid, E. Linckh and F. Winkler, "Synthesis of hydrocarbons," U.S. Patent 2,318,602, May 11, 1943.
- VI.6 H. E. Benson, J. H. Field, D. Bienstock, R. R. Nagel, L. W. Brunn, C. O. Hawk, H. H. Crowell and H. H. Storch, "Development of the Fischer-Tropsch Oil-Recycle Process," Bureau of Mines Bulletin 568, 1957.
- VI.7 H. Kölbel and P. Ackermann, U.S. Patent 2,853,369, Sept. 23, 1958.
- VI.8 H. Kölbel and P. Ackermann, U.S. Patent 2,868,627, Jan. 13, 1959.

Figure VI.1. Schematic reactor fitted with catalyst trays for the preparation of hydrocarbons from synthesis gas in slurry reactor (from ref. VI.1.).

Figure VI.2. Schematic of slurry reactor tube subdivided into cells to modify liquid flow patterns (from ref. VI.3.).

Figure VI.3. Reactor fitted with catalyst trays, each containing bottle caps, to effect slurry phase synthesis of hydrocarbons (from ref. VI.4).

Figure VI.4. Schematic of bubble caps and gas transport columns for trays in reactor shown in figure VI.3 (from ref. VI.4).

Figure VI.5. Schematic of slurry reactor with capability of adding preheated liquid as several levels within the reactor (from ref. VI.5).

Figure VI.6. Schematic of slurry reactor with recycle of oil to the reactor (from ref. VI.5).

Figure VI.7. Schematic of oil recirculation within slurry reactor (figures VI.1 and VI.2) and the elimination of recirculation by adding shafts (tubes) (figure VI.3) (from ref. VI.7).

Figure VI.8. Schematic of slurry reactor with shafts (open at top and bottom) to subdivide reactor shell to establish reactor zone with stationary catalyst and liquid condition (from ref. VI.8).

Attachment VII

Tube-in-Shell Fischer-Tropsch Reactor

1. W. C. Behrmann, C. H. Mauldin and L. E. Pedrick, **Exxon**, U.S. Patent 5,382,748. The reactor consists of 2-4 inch tubes that are 39.8 ft tall [5.08-10.2 cm x 12.1 m]
2. R. M. Koros, **Exxon**, U.S. Patent 5,384,336; January 24, 1995; filed November 30, 1993. The reactor uses of plurality of reactor tubes (L/D at least 10) in a shell. [Example used 6inch x 50 foot (15.2 cm x 15.2 m) single tube].
3. T. M. Stark, **Exxon**, U.S. 5,409,960; April 25, 1995; filed June 15, 1994. The patent covers the use of pentane rather than steam for heat removal.
4. G. B. Lorentzen, A. Westvik and T. Myrstad; **Statoil**, U.S. Patent 5,520,890; May 28, 1996; filed August 18, 1994. This patent is based on data in U.S. Patent 4,801,573 and presents calculations with no experimental data. The optimum tube diameter is stated to be one which exactly matches heat exchange surface to the synthesis.

ATTACHMENT VIII

Cooling Coils in or outside the Fischer-Tropsch Reactor Shell

1. H. Kölbel, P. Ackermann and Fr. Engelhardt, Erdöl Kohle, 9 (1956) 225;
Rheinpreussen-Koppers. This report is based on extensive work at Rheinpreussen-Koppers that started in the 1930s. It utilized an iron catalyst and a reactor with dimensions of 1.55 m diameter and 8.6 m height. It used external wax/slurry separation, including filtration, gravity settling and distillation. It also included ex-situ catalyst regeneration.
2. B. Jager and R. Espinoza, Catal. Today, 23 (1995) 17; **Sasol**. The work at Sasol has been scaled from early laboratory work to a 5 m x 22 m reactor that produces 2,500 bbl/day using iron catalyst. Smaller scale work with a 3m diameter pilot plant using a cobalt catalyst has been reported. The commercial plant uses internal separation of wax/slurry.
3. H. Beuther, T. P. Kobylinski, E. E. Kibby and R. B. Pannel, South Africa Patent 855317, July 15, 1985; **Gulf Oil, now Shell**. The work utilized a reactor with external wax-catalyst slurry separation and ex-situ catalyst regeneration. Reactor diameter was not specified - one could reasonably make the assumption that this patent covers **all** reactor diameters. Patent demonstrated the higher productivity of the slurry reactor because of (1) smaller catalyst particle and (2) better temperature control and a lower methane make. The patent also contains data showing the impact of diffusion on the activity, methane selectivity and the C₅+ selectivity when the catalyst is utilized in a fixed-bed reactor.
4. S. J. Hsia, U.S. Patent 5,260,239; November 9, 1993; filed December 18, 1992.

No examples with experimental data. Utilizes downcomer-conduit means of catalyst mixing/transport in reactor and/or ex-situ rejuvenation vessel as means of catalyst rejuvenation on a continuous basis.

5. W. C. Behrmann, C. H. Mauldin and L. E. Pedrick, U.S. Patent 5,382,748; January 17, 1995; filed December 18, 1992.

Utilizes downcomer(s) to effect liquid recirculation to effect uniform distribution of catalyst in the suspension; a single 3 inch pipe can provide an upward liquid velocity of 2-3 cm/sec in a 4 foot diameter reactor.

6. M. Chang, U.S. Patent 5,332,552;; July 26, 1994; filed December 18, 1992.

A means of catalyst/slurry recirculation that utilizes concentric shells to provide means for recirculation transport of slurry from the top to bottom of reactor with the additional provision of catalyst rejuvenation on a continuous or at interval basis.

7. C. D. Ackerman, U.S. Patent 5,527,473, June 18, 1996; filed January 9, 1995;

Not Assigned to Company.

A slurry reactor with means of internal wax/catalyst slurry separation.

8. E. Rytter, P. Lian, T. Myrstad, P. T. Roterud and A. Solbakken, U.S. Patent 5,422,375; June 6, 1995; February 24, 1993.

Experimental data using a 4.8 cm x 2 m tube filled with cobalt-alumina catalyst slurry and liquid withdrawn through internal filter during 400 hours of operation. They claim a process using multiphase Fischer-Tropsch synthesis.

9. M. Chang, U.S. Patent 5,242,613; October 12, 1993; filed December 18, 1992.

An improvement of the mixing to improve catalyst distribution by introducing a secondary-suspending liquid, e.g. pentane, above the gas distributor but in the bottom 20% of the column. This is a variation, and may be the same, as used by the Bureau of Mines operation in the 1950s.

10. E. Herbolzheimer and E. Iglesia, U.S. Patent 5,348,982, September 20, 1994; filed May 20, 1993.

This patent claims a method for optimally operating a large diameter (greater than 15 cm) for Fischer-Tropsch synthesis over a **supported cobalt catalyst** in which particles are fluidized in the liquid phase by bubbles of the gas phase. Derivations are made to define the flows that balance catalyst settling by gravity to catalyst uplift due to the gas bubble velocity. To many, this is a patent based on earlier textbook examples of bubble column operation. It would appear that the region in figure 7 that is considered for optimal performance falls completely, or mostly, within the flows used or described by Kölbel and Ralek.

11. L. E. Pedrick, C. H. Mauldin and W. C. Behrmann, U.S. Patent 5,268,344, December 7, 1993; filed December 18, 1992; **Exxon**.

One or more vertical draft tubes that are fully immersed in the liquid are used for catalyst mixing and for rejuvenation using pure, or nearly pure, gaseous hydrogen and injecting the rejuvenate catalyst into the top of the reactor.

12. M. W. McEwan and M. B. Teekens, U.S. Patent 4,139,352, February 13, 1979; filed March 14, 1978; **Shell Oil Company**.

An improved process and apparatus is described for the slurry phase Fischer-Tropsch synthesis. The process utilizes a catalyst but the catalyst is not specified. The slurry reactor separates unconverted gas and gaseous products

from the catalyst slurry at the top of the reactor. The catalyst slurry passes through a downcomer fitted with coolers and is returned to the bottom of the reactor. Excess liquid can be removed at the top of the downcomer as can catalyst which requires regeneration.

ATTACHMENT IX

Review of Air Products Fischer-Tropsch Synthesis Work

During the 1980s, Air Products & Chemicals worked on several aspects of the Fischer-Tropsch synthesis. These included the development of novel Fischer-Tropsch slurry catalysts and process concepts, the design of a Fischer-Tropsch pilot plant, the hydrodynamics of bubble column reactors, and the development and operation of the LaPorte Fischer-Tropsch facility (IX.1-IX.7). Their patents concerning the preparation of Fischer-Tropsch catalysts contain the following: "The invention was made under DOE Contract No. [one of two contracts] and is subject to government rights arising therefrom."

The focus of the work was on the use of the low H_2/CO synthesis gas ratios expected from coal gasification. However, a limited number of runs with a H_2/CO ratio that would be typical of the gasification of natural gas were made.

The work on the preparation, characterization and performance of cobalt and ruthenium catalysts focused on the use of carbonyl clusters with the expectation that these would lead to highly dispersed supported metal catalysts. As part of this study a baseline catalyst was prepared by the "normal" procedure using a cobalt nitrate precursor and aqueous impregnation techniques.

The workers utilized a number of catalyst supports. These included: $\gamma-Al_2O_3$ (Catapal SB, $217\text{ m}^2/\text{g}$, $45\text{ }\mu\text{m}$), silica (Davison 952, $339\text{ m}^2/\text{g}$, $70\text{ }\mu\text{m}$), $MgO \cdot 3.6SiO_2$ (Florisil, $298\text{ m}^2/\text{g}$, $75\text{ }\mu\text{m}$) and titania (Degussa P-25, $50\text{ m}^2/\text{g}$, $2\text{ }\mu\text{m}$). These supports were used to prepare the catalysts shown in Table IX.1a and IX.1b.

A common impregnation procedure was used to prepare four batches of a catalyst with a formulation of $Co_2(CO)_8/Zr(OPr)_4/Al_2O_3$ in which the metal precursor to

support ratio was held constant (3.55-3.81 wt.% Co with the Co/Zr ratio 0.55). This base case catalyst, including one larger batch, exhibited similar activity and product selectivity, showing that the preparative method was reproducible.

The catalysts covered in the patents (IX.4-IX.6) are prepared using a decomposable salt or organic compound of cobalt, iron or ruthenium. One claim is (IX.5):

"1. Method of making a catalyst comprising the following steps:

- (a) treating an inert, inorganic metal oxide catalyst base material with a nonaqueous solution of a decomposable salt or organic compound of a group IVB metal and removing said nonaqueous solution;
- (b) impregnating the product of Step (a) with a nonaqueous solution of a decomposable salt or organic compound of a Fischer-Tropsch metal catalyst from the group consisting of cobalt, iron or ruthenium, and removing remaining said nonaqueous solution; and
- (c) exposing the product of Step (b) to a reducing atmosphere; all while maintaining said material and said products under conditions sufficient to avoid hydrolysis, oxidation, and calcination thereof."

A number of catalyst formulations were prepared by the patented technique. Fischer-Tropsch synthesis activity and selectivity were obtained in a fixed-bed reactor (screening test) and for those formulations exhibiting a high activity in a 1-liter continuous stirred tank reactor. The conditions used for the screening studies were 240-280°C, CO/H₂ feed = 0.55 - 2.0, 300 psig (2.0 MPa) and a space velocity of 1.0-2.0 NL/g cat/hr.

The $\text{Co}_2(\text{CO})_8/\text{Zr}(\text{OPr})_4/\text{SiO}_2$ (3.5% Co, 6.6% Zr) catalyst was found to be the most active system in the slurry reactor and also gave the best liquid fuel selectivity. The Schulz-Flory pattern was found for the products obtained using this catalyst. The bulk activity ranged from 16 to 54 mole syngas/kg cat/hr. The gasoline range ($\text{C}_5\text{-C}_{11}$) products accounted for 20 to 45% of the products and the diesel range ($\text{C}_{12}\text{-C}_{18}$) products were 17 to 32%. This catalyst was tested in an extended slurry-phase run that achieved 6 months on stream with a 10% loss in activity.

A comparison was made for 4% cobalt Zr-alumina catalysts in which the dominant difference was the cobalt compound used in the preparation of the catalyst: cobalt carbonyl in an organic solvent and cobalt nitrate in aqueous solution. The specific activity of the nitrate derived catalyst is significantly lower than the one derived from the carbonyl compound when the conversion is effected at 240°C in the CSTR (Table IX.2). However, when the conversions are compared at 260°C, there is less difference between the two conversions; one possibility to account for this is that significantly more sintering of the cobalt occurred for the carbonyl derived catalyst at this higher temperature.

The activity of the $\text{Co}_2(\text{CO})_8$ -based catalysts decreased with changing supports as follows: $\text{SiO}_2 \gg \text{TiO}_2 > \text{Al}_2\text{O}_3 > \text{MgO} \cdot \text{SiO}_2$ (figure IX.1). The Co/TiO_2 catalyst was found to exhibit an unusually high selectivity for C_{3-5} olefins. Zirconium was found to be the better promoter, compared to Ti, for enhancing activity and selectivity, with the optimum Co/Zr ratio being between 0.5 and 1.0.

As the cobalt loading was increased from 4 to 14 wt%, the catalytic activity remained constant and then eventually declined.

The supported Ru catalyst exhibited initially a high activity but the catalyst deactivated rapidly in the slurry reactor. Thus, not much data were obtained with this catalyst.

They found that the following kinetic expression best fitted the data they obtained over a wide range of conversions:

$$- (r_{CO+H_2}) = kC_{H_2}/(1 + k C_{H_2O}/C_{CO}C_{H_2}). \quad [1].$$

However, it was not possible to discriminate with great confidence among the kinetic equations tested during the study.

Catalyst Activation

The activation of supported metal carbonyl catalysts is frequently done by thermal decomposition under vacuum or inert gas atmosphere (IX.8). During the early work at Air Products, catalysts were activated in syngas. To accomplish this the catalyst precursor was heated to 180°C in a nitrogen flow at atmospheric pressure. At 180°C, the flow was switched to the synthesis gas (CO/H₂ = 1) and then heated to the reaction temperature. At the reaction temperature, the pressure was increased to the one used for the synthesis. Later in their work, they compared the impact of activation in pure H₂ or syngas (CO/H₂ = 1). For a 4%Co-zirconia promoted alumina catalyst, they found that the sample activated in hydrogen had a significantly higher activity and higher yield of liquid fuels (figure IX.2a,b; Table IX.3).

Catalyst Promoters

The Air Products work included a comparison of the promotional effects of zirconia and titania for both silica and alumina supports. The titania promoted cobalt catalyst on both alumina and silica supports showed lower catalytic activity than a

similar zirconia promoted catalyst. The bulk activity at 240°C for the alumina supported cobalt was 20 % lower with the titania promoter; with the silica supported cobalt this was 40% lower. The titania promoter also produced more methane and light hydrocarbons than the zirconia promoted cobalt catalyst. Similar activity trends were obtained in both the fixed-bed and slurry reactors; however, the differences in the selectivity were less noticeable in the slurry reactor.

Cobalt Metal to Promoter Metal Ratio

In this study the cobalt to promoter ratio for the silica support was conducted with precursors which contained the same level of cobalt but with a variable amount of promoter. Four catalysts were prepared and the compositions are shown below:

<u>Weight % Cobalt</u>	<u>Weight % zirconium</u>	<u>Co/Zr</u>
4.0	4.8	1.2
4.4	2.3	0.53
4.6	0.1	0.15
4.2	0.0	0.0

The effect of the Co/Zr ratio in the gas-phase reactor on the bulk and specific activities for this series are shown in figures IX.3 and IX.4. It appears that the optimum ratio for bulk activity occurs at about Co/Zr = 1; however, for the specific activity it occurs at about Co/Zr = 0.5, the base case catalyst ratio. The usage ratio appears to increase as the zirconium content increases. The base case catalyst provided the highest yield of liquid fuel, C₅-C₁₈.

Three of the catalysts, Zr/Co = 0, 0.53 and 1.9, that were evaluated in the fixed-bed reactor were also evaluated in the CSTR (figure IX.5). Just as in the fixed-bed

reactor, the optimum activity was obtained for the base case catalyst with a Zr/Co = 0.53 ratio.

Metal Loading

Metal loadings of 3.5, 11.0 and 14.4 wt.% Co on silica were evaluated. For the base case (3.5 wt% Co) the Zr/Co ratio was 0.53 but this ratio was not used for the catalysts with the higher cobalt loadings. One reason for using the higher Zr/Co ratio for the two higher Co loadings was to be able to make a comparison with the Co/Zr/silica catalyst that is used by Shell Oil for their Shell Middle Distillate Synthesis (SMDS). There was little change in the bulk activity in increasing Co content from 3.5 to 11.0; however, at all temperatures there was a significant decline in activity upon further increasing the Co content to 14.4 wt.% (figure IX.6). Selectivity to liquid fuels declined as the Co loading increased.

Significant increases were observed for the bulk density with increasing Co loadings: 0.394 g/cc for 3.5 % Co, 0.564 g/cc for 11.0% Co, and 0.883 g/cc for 14.4% Co. Thus, as the experiments were conducted in the fixed-bed reactors, the amount of catalyst contained in the 10 cc catalyst volume increased significantly and this may have been a major factor in determining the bulk activity shown in figure IX.6.

In the slurry reactor tests of the 3.5 and 11.0% Co catalysts, the activity at both 240 and 260°C declined as the Co content increased in contrast to the fixed-bed reactor runs (figure IX.7).

Product Selectivity

Satterfield et al. (IX.9) reviewed the literature with respect to product distributions for slurry Fischer-Tropsch reactor operation, particularly with iron catalysts. It was concluded that product hydrocarbon selectivities follow a predicted Anderson-

Schulz-Flory (ASF) distribution characterized by the chain growth probability factor, α , and that previously reported deviations are probably due to experimental artifacts. Fixed-bed temperature gradients, insufficient time to reach steady-state, volatilization of certain fractions, and condensation of high molecular weight material are some of the experimental problems that can give misleading selectivity results. These considerations are for deviations which produce chain-limiting Fischer-Tropsch product distributions; most agree that deviations which produce more high-molecular weight products than predicted by ASF are valid (IX.10). Air Products workers sought to avoid the problems previously encountered by their close attention to experimental details, and by determining product distributions over long-term slurry phase operations with good quantitative mass balances (IX.11).

With the fused iron United Catalysts, Inc. C-73 catalyst, a good fit to the ASF distribution was obtained (figure IX.8). However, for slurry catalyst A2 (later shown to be a cobalt-zirconia-silica catalyst) there was an enhanced product deviation from the ASF distribution for the C_{18} - C_{35} region when the catalyst was operated at 2.21 MPa. The effect of pressure in determining this product enhancement can be seen by comparing curves a and b in figure IX.8.

Another catalyst, B, also shows a deviation from ASF (figure IX.9). There was a significant deviation from the ASF distribution for the C_9 - C_{25} products when operating with a feed of $H_2/CO = 0.5$. The yield of 67.3 wt% product obtained in the C_9 - C_{25} products represents a 25 wt% increase over what was considered to be the limit of 54.1% imposed by the ASF distribution.

An adequate explanation for these deviations obtained early in the experimental program has not been offered. These and similar catalysts usually provided "standard"

ASF distributions based on the data reported. This implies that some experimental operational problem was responsible for this unusual, and highly desirable, deviation from ASF distribution.

Ruthenium Catalyst

A Ru/Zr/alumina ($\text{Co}_2(\text{CO})_8$) was a promising catalyst when tested in the fixed-bed reactor. The fixed-bed activity was 26.7 mol syngas/kg cat/hr (comparable to the Co base case catalyst) and a high specific activity of 0.48 mol/mol Ru/min. Methane production was high at about 20%. Slurry phase testing of this catalyst indicated a significantly lower catalytic activity (8 mol syngas/kg cat/hr).

A Ru/Zr/silica catalyst was also tested and it exhibited a much higher activity (70 mol syngas/kg cat/hr; 0.834 mol CO/mole Ru/min at 240°C; 81 mol syngas/kg cat/hr and 1.05 mol Co/mol Ru/min at 260°C) than the similar catalyst using alumina as a support. The Ru catalyst produced higher molecular weight products than a similar Co catalyst. Methane selectivity was low, never exceeding 5.3%.

The performance of the Ru/Zr/silica catalyst was poor in the CSTR. Initially showing a high activity at 240°C (43 moles syngas/kg cat/hr), it had declined to 4 moles syngas/kg cat/hr after only 280 hours on stream.

These preliminary results led the workers to concentrate their further efforts on their cobalt catalysts.

Improving Water-Gas-Shift (WGS) Activity

Since both the Ru and Co catalysts exhibited very low WGS activity, attempts were made to modify the catalyst to increase the WGS activity. A physical mixture of the base case catalyst and a commercial Cu/Zn/alumina low temperature shift catalyst was employed. The addition of the shift catalyst caused a decrease in the Fischer-

Tropsch synthesis without increasing the WGS activity. A Co/Fe/alumina catalyst was prepared using the carbonyl compound of Co and Fe. There was a 53% increase in the usage ratio indicating increased WGS; however, the bulk activity declined by 40%. A Fe/Co/Zr/silica catalyst showed only a slight increase (14%) in usage ratio and a slight decrease in bulk activity. Thus, the exploratory effort to increase the WGS activity failed.

Extended Runs in CSTRs

A run of nearly 6 months was made with a Co/Zr/silica catalyst (4.43% Co, 7.58% Zr) (IX.12). This catalyst displayed remarkable stability. During the first 1012 hours it was utilized at 240°C, 300 psig, CO/H₂ = 0.5 and space velocity = 1.8 l/g cat/hr, and then from 1012 to 2188 hours at 260°C, 300 psig, CO/H₂ = 1 and space velocity = 2.0 L/g cat/hr. The productivity declined from 52.7 to 46.9 mol syngas/kg cat/hr during 1012 hours (figures IX.10 and IX.11) and then declined slowly during operation from 1012 to 2188 hours (figures IX.12 and IX.13). During the second period the product selectivity remained nearly constant (figure IX.14).

After 2188 hours, a series of changes from the base case conditions, 260°C, 300 psig, space velocity 2.0 L/g cat/hr and CO/H₂ = 1.0, were made for the CO/H₂ ratio and the space velocity to generate data for kinetic studies. At intervals, the conditions were returned to the base case to obtain data to correct for the slow catalyst aging. A series of tests were made at two feed set of conditions. In one instance, the impeller speed was altered using constant feed conditions and in the other the space velocity was varied by adding a nitrogen flow, maintaining the same partial pressure of hydrogen and carbon monoxide by increasing the total pressure. Both variations show that mass transfer effects can be neglected.

At 3964 hours, the temperature was increased to 280°C to repeat the series of kinetic measurements. At this temperature the methane production was very high (up to 56.4%) and the wax production very low. At the end of the experiment, the reactor contained only solid, indicating that the operations at the higher temperature had caused the reactor to lose essentially all of the liquid through vapor pressure and/or hydrogenolysis effects.

Cobalt Dispersion

Hydrogen chemisorption was measured to obtain a measure of the metal dispersion of the cobalt and ruthenium catalysts. Air Products reports indicate that they were disappointed with the low dispersions that they obtained; however, the 10-12% dispersion values they obtained for 11 and 14% Co on silica are about as high as reported by later workers. In general, the silica supported Co exhibited a higher dispersion than the alumina supported cobalt at a similar metal loading (Table IX.4). The hydrogen chemisorption was considered to decrease along with the catalytic activity as the cobalt loading was increased for the silica supported cobalt catalysts. The dispersions obtained by the Air Products workers agree with those reported by Reul and Bartholomew (IX.13). Chemisorption was measured at higher temperatures because this led to higher surface areas.

Olefin Reincorporation

In a screening study, ethene was added to the syngas feed for runs with the $\text{Co}_2(\text{CO})_8/\text{Zr}(\text{OPr})_4/\text{Al}_2\text{O}_3$ catalyst (5.07% Co; 4.39% Zr). Under the reaction conditions employed, the CO conversion should have been 20% or less. When 10 or 20 volume percent ethene was added to the feed, the major result was the production of ethane. The oxygenate production did increase slightly (from 0.2 to 2.4 wt%) but the majority of

this fraction was propanol, the product of hydroformylation. The catalyst underwent significant (20% conversion) deactivation during the addition of ethene. The conclusion is that ethene did not undergo significant incorporation; rather it was hydrogenated to ethane.

Kinetic Study

A program was developed to obtain kinetic data from the experimental data (figure IX.15). Experimental data from two runs were made with a catalyst formulation that was essentially the same as the base case catalyst but a more active $\text{Co}_2(\text{CO})_8/\text{Zr}/\text{SiO}_2$ catalyst (4.9% Co; 9.3% Zr). Henry's Law was assumed to apply and to allow for calculation of vapor partial pressures. Henry's Law data was taken from Peter and Weinert (IX.14) and liquid densities were calculated using correlations proposed by Deckwer (IX.15). Mass transfer from bulk liquid to catalyst surface was considered to negligible, based upon the experimental data.

The authors fit the data to five kinetic expressions (to correlate with equations in reference 13, A=2, B=1, C=3, D=4):

$$- r_{\text{CO}+\text{H}_2} = k C_{\text{H}_2} / (1 + K C_{\text{CO}_2} / C_{\text{CO}}) \quad [2]$$

$$- r_{\text{CO}+\text{H}_2} = k C_{\text{H}_2} / (1 + K C_{\text{H}_2\text{O}} / C_{\text{CO}}) \quad [3]$$

$$- r_{\text{CO}+\text{H}_2} = k C_{\text{H}_2} / (1 + K_1 C_{\text{CO}_2} / C_{\text{CO}} + K_2 C_{\text{H}_2\text{O}} / C_{\text{CO}}) \quad [4]$$

$$- r_{\text{CO}+\text{H}_2} = k C_{\text{H}_2} / (1 + K C_{\text{H}_2\text{O}} / C_{\text{CO}} C_{\text{H}_2}) \quad [5]$$

$$- r_{\text{CO}+\text{H}_2} = k C_{\text{H}_2}^a C_{\text{CO}}^b \quad [6]$$

For the run with the catalyst similar to the baseline catalyst, the data at high H₂/CO feed ratios and at high space velocities were best described by the first order rate equation:

$$-r_{\text{CO}+\text{H}_2} = kC_{\text{H}_2}^a C_{\text{CO}}^b \quad [7]$$

where a = 1.1 and b = 0. For low H₂/CO data, equation 3 fits the data better:

$$-r_{\text{CO}+\text{H}_2} = k C_{\text{H}_2} / (1 + KC_{\text{H}_2\text{O}}/C_{\text{CO}}) \quad [8]$$

where k = 0.349 and K = 0.425. The activation energy was in the range of 33-44 kJ/mole.

For the more active catalyst, none of the five equations were able to be used to fully describe the data. They concluded that equation 3 provided the better fit to the data and transformed the equation to a linear form:

$$C_{\text{H}_2} / -r_{\text{CO}+\text{H}_2} = (K/k) C_{\text{H}_2\text{O}}/C_{\text{CO}} + (1/k). \quad [9]$$

The data are plotted using equation 7 and is shown in figure IX.16 for 240, 260 and 280°C. From the intercept, the rate constant, k, is derived with values ranging from 0.328 to 0.775 cc/g cat/sec. This allows K to be determined from the slope and values ranging from 0.466 to 0.302 are obtained. An activation energy of 51 kJ/mole was obtained from the Arrhenius plot.

The authors write that, at that time, relatively few kinetic studies of the Fischer-Tropsch reaction using cobalt catalysts have been made (IX.17-IX.22). From the available literature, activation energies for cobalt catalysts are in the range of 67-117 kJ/mole; for iron catalysts they range from 37 to 105 kJ/mole. The activation energies obtained by the Air Products workers for these catalysts are surprisingly low.

The Air Product workers analyzed the kinetic data obtained during run hours 2188 and 3964 in the extended run described above. It was assumed that the deactivation led to a linear decrease in conversion during the kinetic measurements. They concluded that Equation 5, which included water inhibition, fit the data better than the other equations; a plot of the data using the linearized form of Equation 5 is shown in figure IX.17. It had been reported by Huff and Saterfield (IX.23) that this equation describes data with high water concentration quite well. After Equation 5, the data was best fit by equation 6. The rate constant obtained using Equation 5, based upon fresh catalyst activity, are $K = 5.24 \times 10^9 \exp(-23,254/RT)$ cc/g cat/sec and $K = 1.55 \times 10^{-3} \exp(-6,250/RT)$ mol/cc. The Arrhenius plot returned an activation energy of 97 kJ/mole, and this value agrees much better with those reported earlier for cobalt catalysts.

Slurry Reactor Hydrodynamics Studies

The final report (IX.24) provides a detailed summary of the literature to that date (about 1983) and experimental data obtained in cold flow simulators of 12.7 and 30.5 cm diameter (1.52 and 4.75 m height, respectively) that was conducted at Air Products. With the simulator, phase holdups, phase dispersion coefficients, and interphase heat and mass transfer coefficients were measured. The measured heat and mass transfer and phase dispersion correlations were found to conform to the literature, while the phase holdup correlations were different from the literature. The product distributions from Air Products' catalyst testing program were combined with the hydrodynamic studies to make predictions of space-time yields of product fuel fractions in large-scale bubble column reactors.

Based upon the study, they concluded:

1. Both hydrodynamic and kinetic effects are important to the proper design of the bubble column reactor.
2. For solid particles below 60 μm , the slurry can be modeled as a pseudo-single phase. Larger size solid particles were distributed in accordance with Cova's sedimentation-diffusion model (IX.25).
3. Of those studied, the most important independent variable affecting the reactor performance was the superficial gas velocity, followed by solid particle loading. The type of liquid had a small effect on the column hydrodynamics. The parameters that had little or no effect in the range studied included the presence of heat transfer internals, solid type, distributor hole size, and superficial slurry velocity.
4. Staging the bubble column system to provide more plug flow behavior of the gas was predicted to result in a 5% increase in conversion rates, assuming the same bubble size, about 0.23 cm, as in the unstaged column. On the other, if the average bubble diameter is decreased to 0.07 cm, the conversion rates are expected to increase by 25%.
5. The gas holdup obtained in the cold flow systems was lower than measured by Deckwer (IX.26) and Mobil (IX.27) but in agreement with results of Satterfield (IX.28) and with the correlations from Air Products' slurry phase methanol project (IX.29).
6. Adding seven, 5.7 cm o.d. x 1.42 m heat transfer internals to the 30.5 cm column had no effect on column hydrodynamics.

7. The heat transfer results agreed with Deckwer's correlation (IX.30) but, unlike Deckwer, the heat transfer rates continued to increase beyond a 10 cm/s superficial gas velocity. Heat transfer tubes would therefore take only a small fraction of the internal volume of a Fischer-Tropsch slurry bubble column reactor.
8. Mass transfer results agreed with Akita and Yoshida (IX.31) and Hikita et al. (IX.30-IX.33).
9. Liquid dispersion results agreed with Kato et al. (IX.34), indicating that above a superficial gas velocity of 3 cm/s, the slurry was well-mixed.

The Air Products workers wrote, "One of the more important aspects of gas flowing through a tubular reactor is its availability at the reaction site. This is ultimately related to the interfacial area between the liquid and gaseous phases. In a two-phase, gas-liquid system, the interfacial area, a , is related to the gas volume fraction, ϵ_G , and mean bubble size, d_{SB} , by

$$a = 6 \epsilon_G / d_{SB} \quad [10]$$

Both the mean bubble size, also known as the Sauter mean diameter, and the volume fraction, which is typically referred to as gas holdup or void fraction, are values which are extremely important to optimum reactor design."

The Air Products work followed three steps:

1. Hydrodynamic data were obtained in a 5" ID x 5' (12.7 cm ID x 1.52 m) cold flow simulator.
2. Scale hydrodynamic study to 12" ID x 15.5' (30.5 cm ID x 4.75 m) column.
3. Incorporate kinetic data from catalyst studies with hydrodynamic correlations into a computer model and use this to predict the conversion rates and space-time yields that would be obtained in actual Fischer-Tropsch slurry reactor operation.

Using the model, the heat, mass and momentum transfer parameters which most affect the bubble column design were better quantified.

In the slurry reactor, either mass transfer resistance or kinetic resistance is expected to dominate. Gas holdup, average bubble size and mass transfer coefficient are the important dependent variables that impact mass transfer resistance. Two important factors for kinetic resistance are solids dispersion and liquid dispersion, both affecting catalyst loading, and thereby reactor productivity. Heat transfer rate is also important since this will determine the fraction of the reactor volume required for heat exchangers, and not available for production. The Air Products work attempted to quantify the above mentioned parameters (Table IX.5).

The workers reviewed work prior to 1982 concerning gas-liquid-solid systems. They indicate that Kara (IX.35) found that solid particles promote bubble coalescence and hence the onset of the churn-turbulent regime. However, reports of solids decreasing or increasing gas-holdup can be found in the literature. Kurten and Zehner (IX.36) report Sittig's work on bubble breakup caused by solids. It was shown that bubble breakup occurs when the inertia forces of the solid particle exceed the bubble surface tension forces:

$$(\pi/6)(\rho_s/2) d_s^3 u_{SG}^2 > (\pi/4) \sigma d_s^2 \quad [11]$$

which, when rearranged, shows that bubble breakup can occur when the Weber number is greater than 3:

$$We = (\rho_s d_s u_{SG}) / \sigma \geq 3 . \quad [12]$$

This indicates that below the critical Weber number the solid will not cause bubble breakup.

Since for a particle of about 4 or about 100 μm , a bubble rise velocity > 0.1 or 0.65 m/sec , respectively, is needed for the particle to induce bubble breakup, it is not anticipated that Fischer-Tropsch slurry column will experience bubble breakup due to the presence of solid catalyst particles. In fact, it is expected that bubble coalescence will occur, decreasing gas holdups.

Deckwer et al. (IX.15) studied gas holdup in 4.1 and 10 cm ID columns in the bubbly flow regime (1 to 4 cm/sec) using a hydrogenated Fischer-Tropsch liquid and up to 16 wt.% of > 5 micron alumina particles and obtained the empirical correlation:

$$\epsilon_G = 0.053 j_G^{1.1} \quad [13]$$

where j_G is the superficial velocity of the gas. It was suspected that foaming occurred in the measurements reported by Deckwer et al. (IX.15). Kuo (IX.27) obtained data for the same system showed that with a sintered plate gas distributor he obtained foaming but that no foaming and a much smaller gas holdup was obtained with a distributor with larger openings. Bukur (IX.37) used the same wax as Deckwer and Kuo and obtained a means of eliminating the formation of a foam region. In the absence of a foam region, Bukur obtained a gas holdup that was comparable to those of Pilhofer and Bach (IX.38) and the results obtained by Air Products.

It was concluded that gas holdup was mostly a function of gas velocity and varies to the first power. Slurry density, or weight loading, has the second largest impact on gas holdup. The larger column (30.5 cm) had a lower gas holdup than the 12.7 cm column at the higher gas velocities. It was considered that this was due to more bubble coalescence in the taller column and that the data obtained in the larger diameter column, being more reliable, would be used in the computer simulation of an operating commercial Fischer-Tropsch reactor.

The gas bubble diameter was obtained over a wide range of conditions. The bubble diameter, d_{SB} , relationship with the gas holdup, the gas liquid interfacial area is related to the Sauter mean bubble diameter and gas holdup by

$$a = 6 \epsilon_G / d_{SB} . \quad [14]$$

The uncorrected bubble chord lengths were in the range from 0.28 to 0.44 cm. The measured values are slightly larger than the true values because the experimental approaches caused bubble acceleration/elongation during the measurement. The corrected bubble diameters ranged from 0.22 to 0.35 cm and the bubble velocity ranged from 26.3 to 32.7 cm/sec, both range over fairly narrow values. Since the bubble size should be smaller in Fischer-Tropsch liquids than in water, they concluded that the Calderbank (IX.39) correlation suggested a Sauter diameter size of 0.23 cm for a Fischer-Tropsch type system and this produces

$$a = 6 \epsilon_G / 0.23 = 26.09 \epsilon_G \quad [15]$$

which was used in the computer model.

The overall mass transfer coefficient, $K_L a$, is the product of the mass transfer rate per unit area, K_L , and the interfacial area, a . Air Products workers measured $K_L a$ because of the variation in the reported values. This variation was primarily due to variation in the reported gas holdup and average bubble size; however, there is also variation in the reported values of K_L . They obtained an empirical correlation for $K_L a$:

$$K_L a = (0.30 \epsilon_G^{1.06} d_p^{0.05}) / W^{0.08} \quad [16]$$

where W = weight fraction of solids. Gas velocity was considered to be the primary factor in estimating $K_L a$.

Liquid dispersion relates to how well mixed the liquid phase is and how much solid can be suspended. The Air Products workers discussed this in terms of two extremes:

1. Ideal mixing, continuous stirred tank reactor (CSTR) behavior where any liquid molecule can move to any other part of the column from one instant to the next, and
2. Plug flow reactor (PFR), where any molecule will move in concert with the other neighboring molecules, entering and leaving the column at the same time.

The axial liquid dispersion coefficient, E_z , provides one way to quantify where a particular reactor lies between these two extremes (CSTR and PFR). E_z will be zero for PFR and infinity for CSTR behavior. In practice, when E_z is greater than $10^{-2} \text{ m}^2/\text{sec}$, a well-mixed behavior exists. Knowing E_z , one can plot a sample's concentration as a function of time at a fixed point within the column; such a plot is a residence time distribution (RTD) curve.

A model that is used to describe the sample concentration at any time is Fick's Law:

$$dC/dt = E_z d^2C/dZ^2 . \quad [17]$$

Using the appropriate boundary conditions, an approximate analytical solution which describes the RTD curve at any point within the column was given by Ohki and Inoue (IX.40):

$$dC/dt = E_L d^2C / dZ^2 . \quad [18]$$

For the boundary conditions where a tracer impulse is inserted at any longitudinal location:

$$dC/dt)_{0,T} = dC/dZ)_{L,T} = 0 \quad [19]$$

where L = extended bed height and

$$C(Z,0) = \begin{cases} 0, & 0 \leq Z < Z_1 \\ C_0, & Z_1 \leq Z \leq Z_2 \\ 0, & Z_2 \leq Z \end{cases} \quad [20]$$

$$C/C_0 = 1 + 2 \sum_{n=1}^{100} [\cos(n\pi Z/L) \exp(-n^2 \pi^2 E_L t / L^2)] \quad [21]$$

Little difference is obtained if the summation is to infinity, the exact solution, or stops at 100.

The experimental program to address the dispersion issue and to obtain the RTD curve utilized the injection of a sodium chloride solution into water, detecting the movement of the sodium chloride, the tracer, by conductivity measurements at various heights in the column.

The energy dispersion is greatest at the gas distributor inlet and least at the gas disengagement zone at the top of the reactor. However, E_z was not height dependent was not evident since one dispersion coefficient was sufficient to characterize the entire column. The results of the liquid dispersion runs at Air Products were in agreement with the work of Kato and Nishiwaki (IX.41):

$$Pe = (13 Fr) / (1 + 6.5 Fr^{0.8}) \quad [22]$$

where Pe is the Peclet number $((V_G d_c) / E_z)$ and Fr is the Fraud Number $(V_G / g d_s)^{1/2}$.

From their experimental work, they obtained data to show that a uniform distribution of 0.5-5 micron sized particles was obtained. With larger particles there was, as expected a distribution of particles along the column height, with more at the bottom than the top. They concluded that nonagglomerating catalyst particles less than 60 microns should be suitable for Fischer-Tropsch bubble column batch operation, as no unsuspended solids were observed.

Heat transfer was studied by placing tubes with heaters in the bubble column. It was noted that the agitation produced by the gas phase within the reactor produces heat transfer coefficients that are higher than those produced by gas or slurry alone. The heat transfer surface needed for internal use is less than required for an external exchanger.

The report ends with an engineering evaluation that utilizes the model proposed by Deckwer et al. (IX.42). The substitution of the Air Products correlations for those in Deckwer's model showed little effect at low gas velocities. At 9 cm/sec the space-time yield was doubled (Tables IX.6 and IX.7). A major reason for this was that the lower gas holdup allowed for more catalyst per unit volume. In the bubble column operation there exists an optimum gas holdup which will maximize column space-time yield. Gas holdups higher than this optimum will be reaction rate-limited while those lower than this will be mass transfer-limited. The optimum gas holdup will be affected by the bubble size (b_{SB}), intrinsic kinetic rate (K_o), catalyst weight loading (W), the rate of mass transfer across the gas-liquid interface (K_L), and the usage ratio (U). The optimum gas holdup is given by the expression:

$$\alpha_{opt} = 1 / [1 + (6 K_L (1 + U) / K_o W d_{SB})^{1/2}]. \quad [23]$$

Using this equation allows one to calculate the relative space-time yields for a variety of K_o , W and D_{SB} (Table IX.8).

The Air Products workers compared the space-time yield for a bubble column reactor and for a series of staged reactors. In the first method of calculating the space-time yield, a number of idealized CSTRs are simulated with almost complete recycle of the liquid and catalyst but no recycle of the gas phase. This model would be equivalent to the recirculating cell model used in the literature. In the second method, the extent of backmixing of the gas phase was modeled by applying an axial dispersion model (IX.43).

In this model, a low dispersion coefficient refers to many CSTRs in series, while a high dispersion coefficient refers to very few CSTRs in series. Carberry (IX.44) showed that the two methods are related so that:

$$N = V_G L / 2D \quad [24]$$

Since the Deckwer computer model incorporates the axial dispersion model for the gas, liquid and catalyst phases, this approach was chosen.

Results of simulating the Rheinpreussen-size column as several stages as having the same total volume as the original single-stage column (figure IX.18) are shown in Table IX.9. Thus, a 5% increase in space-time yield is obtained by using 5 CSTRs but a further increase does not lead to a further increase in yield (figure IX.19).

Design of LaPorte Plant

As part of the work, a design for a pilot plant to be located at La Porte, Texas adjacent to an Air Products plant was completed (IX.45). The bubble Fischer-Tropsch reactor was sized to operate in the churn-turbulent flow regime, in which commercial-scale reactors will operate. The study indicated that this flow regime could be achieved

with an effective reactor diameter of five inches. However, it was recognized that the exact diameter of the transition from the quiescent to churn turbulent regime is an unknown function of the slurry viscosity and surface tension. To achieve a 40-50% conversion of the synthesis gas in a single pass at a superficial gas velocity of 0.3 ft/sec would require a 30 foot expanded slurry height.

The reasons for the choice of flow regime were described. Concurrent up-flow bubble columns can operate in any one of three flow regimes (IX.15) and these are illustrated in figure (IX.20) together with an indication of the Air Products cold flow work, the LaPorte design and the Rheinpruessen work. The bubbly flow or quiescent regime occurs at velocities less than typically 0.15 ft/sec. Bubbles are of uniform size and do not interact or coalesce to any substantial degree. At higher velocities, the bubbles do not rise uninfluenced by neighboring bubbles and the churn turbulent regime is entered. Coalescence occurs, yielding larger bubbles and faster rise velocities. Because of coalescence, gas holdup does not increase as quickly with gas flow rate in the churn turbulent regime as in the bubbly flow regime. Where the coalesced bubble would be larger than the diameter of the column, the slug flow regime is reached. Slug flow is undesired because of the low gas/liquid interfacial area and the tendency for the slurry to be lifted out of the reactor along with the gas.

The choice of flow regime was dictated by two economic factors. For a given reactor volume:

1. The highest space time yield or production rate per unit volume is optimal.
2. A tall column is preferred to a short one.

The higher the space-time yield, the smaller the reactor volume required for a given production. The simulations with the Deckwer model and the Air Products

hydrodynamic and catalytic data showed that, in every case, the optimum gas velocity for a maximum space-time yield falls within the churn turbulent regime. It was concluded that the value of 9.1 cm/sec (0.3 ft/sec), although slightly below the optimum, would still allow a reasonable conversion for the reactor height chosen.

Air Products workers wrote, "For a commercial plant with multiple trains, it is advantageous to have as few reactor vessels as possible. In the quiescent regime only about 15' of reactor height is required to achieve 90+% conversion of syngas. By increasing the gas velocity into the churn turbulent regime, 90+% conversion of syngas is not achieved until a height of 60'. For equivalent STY's, it is more economical to have N vessels at 60' than to have four times that number of vessels, each with a height of 15'." (IX.45).

The slurry reactor was designed to operate in a fluidized-bed mode. Once charged, the slurry will not be added or removed except for removal of high molecular weight products that form during reactor operation. Gas will flow up the column and exit out the column top.

The design was implemented at the La Porte location and the plant has been modified during the years of operation. To date, four runs, two with an iron catalyst and two with cobalt catalyst, have been conducted.

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Table IX.1a.

Compositions (wt.% of catalyst) and specific catalytic activity (mol CO/mol metal/min) for catalysts prepared using an alumina support during the Last Three-Year DOE Contract (reference IX.1).

Co	Zr	Ti	K	Fe	Mn	Act.
3.6	6.6					0.25
4.4	1.8					0.31
3.4	6.6				1.6	0.31
2.8	4.9					0.48
1.4				0.51		0.40
1.2			0.3	0.4		
4.7 ^a						0.25
3.5		8.6				0.23
2.6				0.85		0.34
2.4			0.02	0.79		0.27
3.9	5.0					0.24
5.1 ^a	4.4					0.20
4.2 ^a	7.1					0.20
4.0	6.4					0.21
10.8	8.5					0.26
3.5	6.6					0.51
3.7	7.3			0.72		0.26

a. Cobalt added as cobalt nitrate.

Table IX.1b.

Compositions (wt.% of catalyst) and specific catalytic activity (mol CO/mol metal/min) for catalysts prepared using an silica support during the Last Three-Year DOE Contract (reference IX.1).

Co	Zr	Ti	K	Fe	Mn	Act.
4.4		4.0				0.24
3.7	7.2					0.23
4.6	7.5					0.43
4.0	3.3					0.83
3.5						0.31
	7.3			2.4		n.d.
4.0	4.8					0.44
4.4	2.3					0.32
4.6	2.3					0.32
4.2						0.14
4.1	6.8					0.31
11.0	7.4					0.15
14.4	10					0.07

Table IX.2				
Effect of Co source on activity and selectivity of 4% Co on Zr/alumina catalyst tested in the slurry phase using a CSTR at 300 psig, CO/H ₂ = 1.0 and 2.0 NL/g cat-hr. (from reference IX.1)				
Cobalt Source	Carbonyl	Carbonyl	Nitrate	Nitrate
	240°C	260°C	240°C	260°C
Bulk activity, mol syngas/kg cat/hr	35.3	38.5	15.8	29.9
Specific activity, mol CO/mol Co/min	0.29	0.32	0.09	0.21
Selectivity, Wt. %				
C ₁	7.9	10.4	10.9	16.5
C ₂₋₄	13.7	15.0	6.5	11.1
C ₅₋₁₁	37.0	44.5	12.9	26.5
C ₁₂₋₁₈	23.4	25.8	19.8	23.8
C ₁₉₋₂₃	8.9	2.0	21.9	10.6
C ₂₄₊	9.1	2.3	28.0	11.5
TOTAL FUELS, C ₅₋₂₃	69.3	72.3	54.6	60.9

Table IX.3		
Effect of syngas vs. hydrogenation activation on the activity and hydrocarbon selectivity using a 4% Co on Zr/Al ₂ O ₃ catalyst in a slurry CSTR (from reference IX.1)		
	Syngas	H ₂
Space velocity, NL/gcat/hr	1.6	2.0
CO/H ₂	1.6	1.5
Pressure, psig	300	300
Temperature, °C	250	258
Hydrocarbon, wt. %		
C ₁	11.5	7.2
C ₂₋₄	10.4	10.8
C ₅₋₁₁	29.2	34.1
C ₁₂₋₁₈	15.3	27.9
C ₁₉₋₂₃	12.5	8.6
C ₂₄₊	21.1	11.4
C ₅₋₂₃	57.0	70.6

Table IX.4			
Metal dispersion for Co and Ru Catalysts (from reference IX.1)			
Catalyst	BET Surface Area, m ² /g	Metal Surface Area, m ² /g	Dispersion, %
3.5%Co/Zr/SiO ₂	316	1.9 (a)	6
4.0%Co/Zr/Al ₂ O ₃	209	0.3 (b)	1
4.1%Co/Zr/SiO ₂	210	1.9 (a)	7
11.0%Co/Zr/SiO ₂	302	8.1 (a)	12
10.8%Co/Zr/Al ₂ O ₃	n.d.	5.4 (a)	7
14.4%Co/Zr/SiO ₂	145	9.3 (a)	10
4.0%Ru/Zr/SiO ₂	325	1.6 (b)	8
(a) Hydrogen chemisorption performed at 100°C			
(b) Hydrogen chemisorption performed at 35°C.			

Table IX.5	
Slurry Reactor Design Variables Considered in the Air Products Study (reference IX.21)	
DEPENDENT VARIABLES	
Gas Hold-Up	Mass Transfer
Bubble Size	Liquid Dispersion
Solids	Heat Transfer
INDEPENDENT VARIABLES	
Slurry Medium: Paraffin, water	
Superficial Gas Velocity: 1.52 - 15.2 cm/sec	
Superficial Slurry Velocity: 0 - 3.0 cm/sec	
Solid: Silica, Iron Oxide	
Solid Size: 1 - 5 μm , 45 - 53 μm , 90 - 106 μm	
Solid Concentration: 0, 10, 20, 30 Wt. %	
Distributor Hole Size: 0.9, 3.2, 12.8 mm	
Heat Transfer Internals: None, Plain	

Table IX.6			
Rheinpreussen Simulation using Deckwer Correlations (from reference IX.1)			
REGIME	CHURN TURBULENT		
CATALYST	Base Case	Cat. A	Cat. B
Inlet gas velocity, cm/sec	9.00	9.00	9.00
Gas holdup	0.385	0.512	0.526
Interfacial area, cm ² /cm ³	32.66	43.44	44.66
Temperature, °C	260.2	259.7	260.2
Rate Constants			
Preexponential factor (sec wt.% in slurry) x 10 ⁵	1.12	90.3	115
Activation energy, kJ/mol	70	94.7	94.7
Inlet ratio, mol CO/mol H ₂	1.5	1.5	1.98
Usage ratio, mol CO/mol H ₂	1.5	1.5	0.65
Hydrogen conversion, %	80.4	34.9	49.8
Relative mass transfer resistance	0.106	0.021	0.035
Space-time yield, mol CH ₂ /hr	2937	1065	1022
Constants in Case Study			
Reactor length, ft (cm): 26.25 (800)			
Reactor diameter, in (cm): 59 (150)			
Contraction factor: -0.5			
Particle diameter, μm: 50			
Reactor pressure, psig (bar): 174 (12)			
Weight fraction catalyst in slurry: 0.20			
Specific heat transfer area, cm ² /cm ³ : 0.10			

Table IX.7				
Rheinpreussen Simulation using Air Products Correlations (from reference IX.1)				
REGIME	CHURN TURBULENT			
CATALYST	Base Case*	Cat. A	Cat. B#	Cat. B with Shift
Inlet gas velocity, cm/sec	9.00	9.00	9.00	9.0
Gas holdup	0.385	0.149	0.171	0.146
Interfacial area, cm ² /cm ³	32.66	36.06	41.43	35.39
Temperature, °C	260.2	260.4	260.4	261.1
Rate Constants				
Preexponential factor (sec wt.% in slurry) x 10 ⁵	1.12	90.3	115	115
Activation energy, kJ/mol	70	94.7	94.7	94.7
Inlet ratio, mol CO/mol H ₂	1.5	1.5	1.98	1.98
Usage ratio, mol CO/mol H ₂	1.5	1.5	0.65	1.98
Hydrogen conversion, %	80.4	55.9	62.9	58.5
Relative mass transfer resistance	0.106	0.043	0.069	0.048
Space-time yield, mol CH ₂ /hr	2937	2042	1273	2135
Constants in Case Study				
Reactor length, ft (cm): 26.25 (800)				
Reactor diameter, in (cm): 59 (150)				
Contraction factor: -0.5				
Particle diameter, μm: 50				
Reactor pressure, psig (bar): 174 (12)				
Weight fraction catalyst in slurry: 0.20				
Specific heat transfer area, cm ² /cm ³ : 0.10				
*Operating conditions at Rheinpreussen #Cold flow model gas holdup correlation				

Table IX.8						
Optimum gas holdup, gas velocity*, and space-time yield (STY) ($K_L = 0.0205$ cm/s; $U = 2$) (from reference IX.1)						
CASE	$K_o, \text{sec}^{-1} \text{wt}\%^{-1}$	W, %	d_B, cm	α opt, vol %	V_G cm/sec	STY
1	1.4×10^{-3}	20	0.07	6.8	2.13	1.00
2	1.4×10^{-3}	60	0.07	11.2	12.75	2.72
3	6.1×10^{-3}	60	0.07	20.9	36.43	9.42
4	1.4×10^{-3}	20	0.30	13.1	5.29	0.87
5	1.4×10^{-3}	60	0.30	20.7	36.00	2.17
*Using Air Products cold flow gas holdup correlation						

Table IX.9				
Rheinpreussen simulation for staged reaction systems (from reference IX.1)				
NUMBER OF STAGES	1	20	5	20
DISPERSION COEFF., cm^2/s	72.130	128.8	572.5	143.8
Gas Holdup	0.145	0.148	0.158	0.158
Interfacial area, cm^2/cm^3	4.148	12.717	4.514	4.527
Hydrogen Conv., %	66.1	85.1	69.2	69.2
Rel. Mass Transfer Resistance	0.556	0.310	0.542	0.541
Space-Time Yield, mol CH_2	2,417	3,128	2,529	2,530
Improvement Ratio	1.000	1.294	1.046	1.047
CONSTANTS IN CASE STUDY				
Reactor Length, ft (cm): 26.25 (800)				
Reactor Diameter, in (cm): 59 (150)				
Contraction Factor: -0.5				
Particle diameter, m: 50				
Reactor Pressure, psig (bar): 174 (12)				
Weight Fraction Catalyst in Slurry: 0.20				
Specific Heat Transfer Area, cm^2/cm^3 : 0.30				
Inlet Gas Velocity, cm/sec: 9				
Temperature, C: 260.0				
Preexponential Factor (see wt% in slurry): 3.45×10^7				
Activation Energy, kJ/mol: 9417				
Inlet Ratio, mol CO/mol H_2 : 1.98				
Usage Ratio, mol CO/mol H_2 : 1.98				

Figure IX.1. Activity of CO₂(CO)₈-based catalysts, fixed bed reactor (240°C, CO/H₂ = 1.0, GHSV = 1000 hr⁻¹, 300 psig).

Figure IX.2a. Effect of syngas versus hydrogen activation on conversion.

Figure IX. 2b. CO/Zr ratio effect on activity.

Figure IX.3. Effect of Co/Zr ratio on bulk activity (gas phase, $\text{CO}/\text{H}_2 = 1$, $\text{SV} = 1000 \text{ hr}^{-1}$, 300 psig).

Figure IX.4. Effect of Co/Zr ratio on specific activity (gas phase, $\text{CO}/\text{H}_2 = 1$, $\text{SV} = 1000 \text{ hr}^{-1}$, 300 psig).

Figure IX.5. Effect of Co/Zr weight ratio on slurry-phase activity of Co/Zr/silica catalysts.

Figure IX.6. Effect of cobalt loading on bulk activity of Co/Zr/SiO₂ Catalyst (fixed bed reactor, CO/H₂ = 1, 1000 hr⁻¹, 300 psig).

Figure IX.7. Effect of Co loading on Co/Zr/SiO₂ performance.

Figure IX.8. Hydrocarbon Schulz-Flory distribution of slurry catalyst A2.

Figure IX.9. Hydrocarbon Schulz-Flory distribution of slurry catalyst B.

Figure IX.10. Bulk activity maintenance - extended slurry test 8862-1-31 Co/Zr/SiO₂, 240°C, CO/H₂ = 0.5, 1.8 L/g/hr, 300 psig.

Figure IX.11. Conversion maintenance - extended slurry test 8862-1-31 Co/Zr/SiO₂, 240°C, CO/H₂ = 0.5, 1.8 L/g/hr, 300 psig.

Figure IX.12. Bulk activity maintenance - extended slurry test 8862-1-31 (Co/Zr/SiO₂, 260°C, CO/H₂ = 1.0, 2.0 NL/g/hr, 300 psig).

Figure IX.13. Conversion maintenance - extended slurry test 8862-1-31 (Co/Zr/SiO₂, 260°C, CO/H₂ = 1.0, 2.0 NL/g/hr, 300 psig).

Figure IX.14. Hydrocarbon selectivity — extended slurry test 8862-1-31 (Co/Zr/SiO₂, 260°C, CO/H₂ = 1.0, 2.0 NL/g/hr, 300 psig).

Figure IX.15. Kinetic data analysis program ($\rho = 0.758 - 0.555 \cdot (T_k - 373)$) (ref. 12);

$$He_{H_2} = 34.162 \cdot \exp(739.485/T_k) \cdot 14.23 \text{ psia/mol/kg oil (ref. 11); } He_{CO} = 44.583/T_k \cdot \exp(433.391/T_k) \cdot 14.23; He_{CO_2} = 119.925 \cdot \exp(-438.926/T_k) \cdot 14.23; He_{H_2O} = 275.113 \cdot \exp(-1122.92/T_k) \cdot 14.23.$$

Figure IX.16. Fitting $Co_2(CO)_8/Zr(OP_R)_4/SiO_2$ data.

Figure IX.17. $Co_2(CO)_8/Zr(OP_R)_4/SiO_2$ activation energy.

Figure IX.18. Staged reaction systems.

Figure IX.19. Hydrogen conversion vs. column height.

Figure IX.20. Bubble column flow regimes.

ATTACHMENT X

Review of Exxon Patents

Edwin N. Givens

and

Burtron H. Davis

ATTACHMENT X

Review of Exxon Patents

INTRODUCTION

It is quite apparent from searching the patent literature that Exxon has been actively involved in conducting research on conversion of synthesis gas to fuels and chemical products for many years. They have used CO as a chemical reactant for producing olefins and alcohols in addition to preparing liquid fuels. Since the mid 1970s the number of patents that have been assigned to Exxon and the types of examples contained in those patents reflect an increasing interest in converting synthesis gas to hydrocarbons. The earlier patents that were obtained during this period contain numerous examples of synthesis gas conversion at ambient pressures that gave very small CO conversions, typically less than 10%. More recently, the data reflect a more sophisticated evaluation of catalysts and the beginning of a string of patents that relate to improvements in equipment and operation. The latter are a result of the operation of a sizable pilot facility at their Baton Rouge Laboratory. These patents have addressed many of the finer points of reactor design.

The search was focused on synthesis gas conversion, i.e. the Fischer-Tropsch reaction, and limited to U. S. patents that were assigned to Exxon that were abstracted by Derwent through mid-1995. There are apparently numerous other patents that were issued to Exxon that relate to CO conversion which are not included, such as those related to conversion of CO to hydrocarbons or alcohols. Exxon's approach to developing a patent portfolio in this technology area is unlike most of their competitors, in that they have obtained an extensive number of composition of matter patents. Supplementing these patents are a large number of process related patents that apply

to either methods for preparing these materials or the use of these compositions in the conversion of synthesis gas. In some of the composition of matter patents that are of interest for synthesis gas conversion, the claimed materials are used for hydrocarbon conversion without mention of their use as catalysts for the FT reaction. Based upon the addresses of the inventors in these various patents, it is clear that significant work on the FT reaction has been going on at Exxon's New Jersey and Baton Rouge laboratories. Although there is overlap in the type of work that was being done in these laboratories, it appears from the timing of the patents that the approaches that were being taken were quite independent. Those differences were apparent from the discussion in the patents regarding various elements of catalyst composition and the claims that are made regarding those compositions.

The Exxon patent portfolio includes a large number of patents on iron and iron-containing catalysts. The majority of these cases relate to compositions that have spinel structures that are isostructural with Fe_3O_4 but contain one or two additional metal atoms, with iron usually being the dominant metal. In these patents, the spinel structures are expressed interchangeably either as $\text{M}_x\text{N}_{3-x}\text{O}_4$ or as $\text{M}_{3-x}\text{N}_x\text{O}_4$, where M is almost exclusively Fe. For consistency, the first format is used exclusively throughout this discussion. Other iron-related catalysts are also covered including catalysts in which the iron, as the oxide, is used as a substrate, and others in which the iron is deposited on other substrates.

There is extensive coverage for catalysts in which titania and titania containing materials are used as metal supports. These include combinations of titania with vanadium, tantalum and niobium oxides (Group Vb) which are used either as intimate mixtures or as coatings on the surface of titania. All of these supports apparently give

rise to unique metal-support interactions that had not hitherto been reported. Other coverage was obtained for titanias that are coated with silica. Some of these patents specify titanias having rutile as the dominant crystalline phase which is favored at high temperatures. One case claims an anatase based catalyst that was stabilized through addition of silicon, zirconium and tantalum. In many of these cases, the catalyst is formed by impregnating the oxides with metals from Group VIII, of which cobalt or ruthenium are the most common. In other cases, addition of rhenium, thorium, cerium, copper, hafnium, zirconium, and uranium is claimed. Although many of the catalysts that are covered in these patents fall into one of the above categories, they have also obtained coverage in several related areas. Catalysts comprising ruthenium or combinations of several Group VIII metals on manganese oxide are covered as are cobalt-manganese spinels. Coverage of catalysts comprising Group VIII metals supported on various oxide supports was obtained which specifically apply to FT type processes.

In almost all of these cases the use of an alkali promoter is also covered, either in the main claim or a dependent claim. Almost without exception, potassium is specified as the alkali metal of choice, although in a few rubidium has been specifically mentioned. Most of the patents specify that the catalysts can be used in either a fixed-bed or a slurry type process, although in some cases they can be applied to both. Generally, powder catalysts are specified for slurry operations while sintered spinel type catalysts apply to fixed-bed type operations. There are, however, cases which claim that the catalysts are useful for either slurry or fixed-bed type operations.

The third area of significant coverage includes various process improvement patents that relate to process equipment or operation, most of which have been

obtained in recent years. These include 2-stage processes, modified feeds, modified reactor designs, methods of reactor operation and methods of catalyst pretreatment. Many of these patents contain data that were taken from highly sophisticated pilot plant operations, some of which were quite large in size.

Iron

A number of patents were issued to Exxon related to the use of iron in FT synthesis. Most apply to catalysts in which the iron is in combination with other metals. However, two patents were issued that apply to the use of iron alone. These were catalysts that were prepared using a laser technique in which volatile iron compounds were thermally decomposed to form iron carbides having particle diameters of less than 0.1 μm . Most of the iron containing catalysts that are covered in these patents relate to spinels in which Fe is combined with different metals in the spinel structure, including cobalt, manganese, zinc, and titanium. Various promoters are also added, including cerium, copper and potassium. Two patents covered catalysts in which thallium was deposited on an iron support, while others covered catalysts prepared by depositing Fe salts onto supports. One covers an Fe/TiO₂ catalyst that was prepared by converting an impregnated Fe salt to the carbided form. Another covered catalyst prepared by decomposing Fe and Co carbonyl compounds in the presence of CO which deposited them onto finely divided supports which were then reduced in H₂.

Particulate Iron Catalysts

A patent issued to Rice et al. (X.1) claims compositions comprising finely divided particles of iron and carbon in absence of Si produced in a reaction zone in the presence of laser radiation under such conditions of laser flux density, power adsorption, concentration of iron reactants, and pressure sufficient to give non-

pyrophoric particles having diameters from 1-100 nm. The iron reactants are selected from iron carbonyls, iron acetylacetonate and ferrocene. A related patent issued to Rice et al. (X.2) claims the same compositions which are subsequently impregnated with $\geq 2\%$ of a promoter selected from a group of salts and oxides of alkali and alkaline earth metals. These patents specify these compositions can be used in either slurry or fixed bed FT reactions. Data were presented in the examples for a fixed-bed catalyst in which the claimed composition was deposited on a refractory MgO support. Laser generated Fe carbide, either with or without K, was found to be considerably more active than Fe carbides generated from either Fe_3O_4 or from mixtures of $\text{Fe}(\text{CO})_5$ and C_2H_4 in the presence of $\text{SiH}_2(\text{CH}_3)_2$ (see Table X.1). The Fe_3O_4 and silane generated carbides have lower CO conversions and higher methane yields while the catalysts of these inventions produce more olefins in the $\text{C}_2\text{-C}_4$ fraction.

A catalyst was illustrated which was prepared by reacting Fe_3O_4 until all of the iron was converted to a carbide phase which was predominantly Fe_5C_2 and Fe_3C . The iron carbide phase was dispersed in a matrix of 40 to 70 wt.% of amorphous carbon. The comparison of the activated Fe_3O_4 catalyst and the laser generated catalyst is for activity for CO conversion on a volume of gas/volume of catalyst basis. The laser generated sample contained 5-15 wt.% of amorphous carbon phase. If we take into account (1) the difference in density of amorphous carbon and iron carbide (factor of 2) and (2) the difference in the amount of amorphous carbon (factor of about 5-8), we calculate that the material produced by the laser technique will contain 10 to 20 times as much iron as the material prepared from Fe_3O_4 . Thus, while the material prepared using the laser technique is about two times as active as the material derived from Fe_3O_4 when the comparison is based on volume of catalyst, it is estimated by us to be 5

to 10 times less active on the basis of the iron content. Furthermore, it has been shown that, under reaction conditions utilized for slurry phase synthesis, a significant fraction of the iron carbide is gradually converted to Fe_3O_4 (X.3) during synthesis. Thus, the relative advantage of the catalyst generated by the laser technique depends upon how it is compared to the precipitated catalyst.

Spinels Containing Fe

The first patents assigned to Exxon that apply to the use of spinel or spinel-derived compositions for converting synthesis gas appeared in 1985. These materials were generally prepared by one of two methods and they had distinctly different morphological features. In one case, high surface area materials were prepared by co-precipitation of salts coupled with moderate heating. These materials have been used directly as slurry catalysts. The second method of preparation involves sintering of metal/metal oxide mixtures at much higher temperatures to give low-surface-area, fused materials, which after grinding and sizing are used directly in fixed bed applications. Hydrogen reduction of either of these products at temperatures of 400°C leads to alloys, which when treated with CO, give high surface area carbides containing considerable carbon inclusion. The reduced and carbided spinels are then used as catalysts in either slurry or fixed-bed applications.

A number of different combination of metal spinels have been patented in this series, all of which, except one, contain iron. In all the Fe cases, the claims cover spinel compositions that allow the use of high concentrations of Fe. From an economical standpoint, this is favorable since the cost of co-metals is generally greater than for Fe. The different Fe-containing combinations that are covered, most of which are promoted with potassium, are:

- ! Fe-Co, either with or without added Cu,
- ! Fe-Mn containing Cu,
- ! Fe-Zn containing Ce or Cu,
- ! Fe-Zn-Ti and/or Mn with Ce and
- ! Co-Mn with Cu.

The only non-Fe containing spinel that was covered was a Co-Mn spinel that is promoted with Cu. This catalyst is discussed with the manganese supported catalysts.

Fe-Co Spinels. Both high and low surface area spinels are covered. High surface area spinel compositions and reduced and carbided iron-cobalt alloy compositions derived from the spinels that are isostructural with Fe_3C and $\chi\text{-Fe}_5\text{C}_2$ are covered in a patent issued to Soled and Fiato (X.4). Because of their fine particle size, the preferred use of these materials is in a slurry process which is covered in a patent issued to Soled and Fiato (X.5). High surface area copper promoted Fe-Co spinel compositions are covered in a patent issued to Soled and Fiato (X.6) while their use as a catalyst in a slurry process is covered in Soled and Fiato (X.7). Low-surface area Fe-Co spinel compositions are claimed by Fiato et al. (X.8) and their use as catalysts in a fixed-bed process is claimed by Fiato et al. (X.9). The use of the carbided and reduced form of these low-surface area Fe-Co spinels in a slurry phase process is claimed by Fiato and Soled (X.10). No patents were found that contain claims related to low-surface area Cu-promoted Fe-Co spinels.

Fe-Mn Spinels. High surface area K and Cu promoted Fe-Mn spinels are covered in a patent issued to Fiato and Soled (X.11). The use of this spinel as catalyst in a slurry process is covered in Fiato and Soled (X.12) and in a fixed-bed process in Iglesia et al. (X.13). The corresponding low surface area spinels derived from sintering

mixed oxides was covered in a prior patent issued to McGrath and Rubin (X.14) and assigned to Kellogg. An alternative method for forming Fe-Mn alloys directly at low temperature without going through the spinel is covered by Soled et al. (X.15).

Fe-Zn Spinels. Two patents comprising compositions of Fe and Zn using different promoters were issued. In one patent compositions comprising sintered combinations of metal oxides of Fe and Zn promoted with Ce and K are covered in Gates and Fiato (X.16). In the other, compositions containing Fe and Zn promoted with Cu and K are covered in Soled et al. (X.17).

Fe-Zn Spinels with Ti and/or Mn. Compositions comprising sintered combinations of metal oxides of Fe, Zn, Ti, and/or Mn promoted with K and Ce are claimed in Fiato et al. (X.18).

Fe-Co Spinels

Seven patents assigned to Exxon relate to Fe-Co spinels, five of which were issued either from applications filed on December 14, 1983, or were continuations-in-part of applications filed on that day. Cross reference was also made to applications which apparently never issued as patents. The series of seven patents that did issue fit into three different groups with at least two patents being in each group. One of the groups relates to Cu promoted Fe-Co spinels while the other two groups relate to Fe-Co spinels that are prepared by two different methods. In one group the spinels are prepared by sintering mixtures of metal-metal oxides while in the other, spinels are prepared by precipitating metal oxides from the respective metal salt solutions. In each of these three groups, two of the patent specifications are identical differing only in their claims. In the one group that includes a third patent, the specification differs only slightly from the other two. For each of the three groups, one patent is a composition of

matter case for a specific Fe-Co containing spinel and the other(s) claims either a fixed-bed or slurry process that employs the claimed catalyst composition.

The empirical formula of the spinels claimed in these cases can be written as $\text{Fe}_x\text{Co}_{3-x}\text{O}_4$ where compositions having x-values ≥ 2.4 or 2.7 are claimed. Prior art existed for structures having x values of 2, i.e. Fe_2CoO_4 (X.19). Among the various spinel compositions that were patented, there appears to be a pattern of obtaining coverage for both slurry and fixed-bed type FT processes. In the case of the Fe-Co spinels, specific claims are made to fixed-bed processes using catalysts derived from spinels prepared by sintering metal-metal oxide mixtures. These are classified as having low surface areas (less than $5 \text{ m}^2/\text{g}$). For slurry processes, patents were issued that claim use of catalysts derived from both low surface area spinels as well as those prepared by precipitating metal oxides from the respective metal salt solutions. This latter group is classified as high surface area spinels having surface areas greater than $5 \text{ m}^2/\text{g}$. In these Fe-Co spinel cases, patents were not found that claim the use of high surface area spinels in a fixed-bed process, although such claims were obtained for Fe-Mn spinels, which are discussed below.

High surface area spinel compositions are covered in a patent issued to Soled and Fiato (X.4) that claims Group 1A or IIA promoted high surface area spinels having compositions $\text{Fe}_x\text{Co}_{3-x}\text{O}_4$ with x-values ≥ 2.4 and BET surface areas $>5 \text{ m}^2/\text{g}$. A second composition in this same patent, given in claim 20, comprises reduced and carbided iron-cobalt alloy that is isostructural with Fe_3C and has a BET surface area $>5 \text{ m}^2/\text{g}$. A third independent claim covers compositions that are isostructural with $\chi\text{-Fe}_5\text{C}_2$ having surface areas $>5 \text{ m}^2/\text{g}$ that are produced by carbiding iron-cobalt alloy which is isostructural with alpha Fe and has a BET surface area $>5 \text{ m}^2/\text{g}$, which is produced by

reducing the high surface area spinel composition. Therefore, compositions are claimed that include the spinel, the reduced alloy and the resulting carbided alloy. The specification is even broader in that it anticipates the application of the spinel, the alloy and the reduced-carbided spinel in either a fixed-bed or slurry-type process. The corresponding process related patent issued to Soled and Fiato (X.5) claims a slurry process that uses the catalyst that is claimed by Soled and Fiato (X.4). The two specifications are identical except for the claims. Although there is a slight difference in the spinel compositions that are claimed in these two cases, in that Soled and Fiato (X.4) claim spinels having Fe/Co ratios $\geq 4/1$ while Soled and Fiato (X.5) claims Fe/Co ratios $\geq 7/1$, this would not likely have any real impact on the application of the invention.

Low surface area Fe-Co spinel compositions are covered in a patent issued to Fiato et al. (X.8) that claims hydrocarbon synthesis catalyst compositions comprising an unsupported, Group Ia or IIa metal salt promoted low-surface area iron-cobalt spinel, an initial empirical formula $\text{Fe}_x\text{Co}_{3-x}\text{O}_4$, where x is ≥ 2.625 , a powder X-ray diffraction pattern isostructural with Fe_3O_4 and having an initial BET surface area $< 5 \text{ m}^2/\text{g}$. Various dependent claims are included such as the use of diluents like silicas, aluminas, titanias, oxides of La, Ce, Cr, and Mn and mixtures including zeolites, glasses, etc. K_2CO_3 is claimed as a promoter and potassium promoted compositions are claimed that are substantially carbided by contact with CO/H_2 at elevated temperatures. Two process patents were issued that are related to use of low-surface area spinel compositions in synthesis gas conversion reactions. One patent, issued to Fiato et al. (X.9), claims a process for synthesizing hydrocarbons containing C_2 - C_6 olefins by contacting a fixed-bed of catalyst, having the initial spinel composition specified in Fiato et al. (X.8), with

synthesis gas. The specifications of Fiato et al. (X.8) and Fiato et al. (X.9) are identical, except for different claims. The second process patent issued to Fiato and Soled (X.10) claims a slurry process utilizing the carbided and reduced unsupported spinel of Fiato et al. (X.8), which reflects the need to *ex situ* pretreat the spinel before placing it in the slurry reactor.

Catalyst preparation

The following method was used to illustrate the preparation of several of the high surface area spinels. A solution containing Fe and Co nitrate salts and an ammonium α -hydroxy carboxylic (glycolic) acid was evaporated and the recovered solid was heated at 350°C for 2 hours and then impregnated with K_2CO_3 and dried. The material, prior to impregnation with potassium, had a very small particle size, an x-ray diffraction pattern isostructural with Fe_3O_4 , and surface area $>100\text{ m}^2/\text{g}$. The specification refers to prior art for the preparing of Fe_2CoO_4 ¹⁹ that involved evaporating aqueous solutions of metal glycolates, lactates, and tartarates to dryness. The prior art apparently limited claims to Fe/Co ratios > 4 .

The invention was illustrated for various low-surface area spinels prepared by sintering mixtures of metal oxides and metals in combinations having the stoichiometric composition necessary to provide the correct empirical formula. Sintering is done first in an inert or vacuum atmosphere at temperatures preferably from about 800 to 900°C for about 8 to 24 hours. The material is then exposed to air and heated an additional 24 hours until the x-ray diffraction pattern of the material is isostructural with Fe_3O_4 . Sintered pellets are crushed, sieved and then impregnated with aqueous potassium carbonate to a 1% K loading providing a material having a surface area of 0.25-0.30 m^2/g .

Reduced and carbided slurry catalysts are prepared starting with both high and low-surface area spinels. The preparation starting with low-surface area spinel is described in Fiato and Soled (X.10) and the preparation from high-surface area spinel is described in Soled and Fiato (X.4). In both cases, the respective spinel powders were reduced at 400°C in H₂ for 4 hours to produce an alloy, which was passivated with dilute oxygen. These materials had surface areas of 3 and 8 m²/g and x-ray diffraction patterns isostructural with alpha iron. The active catalyst was produced by carbiding the alloys in dilute synthesis gas and passivating with dilute oxygen to give products having x-ray diffraction patterns isostructural with chi Fe₅C₂ and BET nitrogen surface areas of 118 and 173 m²/g. The resulting catalysts contained 60-70% carbon and had the composition Fe_{2.85}Co_{0.15}O₄/1 wt.% K.

The form of the active catalyst generated by these two different preparative methods was not differentiated from each other. Both, after reducing and carbiding, give materials that are isostructural with chi-Fe₅C₂ or Fe₃C, apparently contain sizable amounts of carbon, and have surface areas >100 m²/g.

Slurry Catalysts. A number of examples were provided in the five cases which illustrate the use of catalysts derived from spinels for converting synthesis gas. Catalysts to be used in slurry reactors were pretreated in various ways before being placed in the slurry reactor and exposing them to synthesis gas at reaction condition. The methods of pretreatment included:

- ! Adding the spinel to the slurry reactor and reducing in H₂ before exposure to synthesis gas;
- ! Reducing and carbiding the spinel *ex situ* before introducing into the reactor;

! Reducing the spinel in H_2 to form the alloy before introducing into the reactor.

Conversion and product distribution data were provided for each of the respective catalysts and compared with data obtained on a high surface area $Fe_3O_4/1\%K$ catalyst that was prepared in the same manner as the high surface area spinel.

There was a big difference in the activities of the *in situ* treated spinel slurry catalysts. The high surface area Fe-Co spinel oxide that was reduced in situ with flowing H_2 (1 atm) for 1 hour at $200^\circ C$ gave 60% CO conversion, whereas both the high surface area Fe spinel and the low-surface area Fe-Co spinel that were pretreated in the same way were inoperable. They gave CO conversions of only 8 and <4%, respectively (see Table X.2). *Ex situ* treatment had little effect on CO conversion of the high surface area spinel derived catalyst which gave essentially the same CO conversion as the *in situ* treated spinel, namely 64 and 60%, respectively. By contrast, *ex situ* treatment of both the low-surface area Fe-Co spinel and Fe spinel catalysts improved their activity, giving 42 and 65% CO conversion, respectively. Apparently insufficient carbided catalyst was formed in the *in situ* pretreatment of the low-surface area spinel, whereas the *ex situ* treatment was sufficiently severe to convert the low-surface area spinel to the carbided form. In the comparisons that were provided, the Fe-Co spinels produced more C_5+ hydrocarbons and less C_2-C_4 olefins than the Fe spinel catalysts. Although data with a 2/1 H_2/CO synthesis gas mixture in Table X.2 on *ex situ* treated catalysts indicate a difference between the CO conversion of the reduced-carbided low- and high-surface-area Fe-Co spinel derived catalysts, i.e. 42 and 64% conversion, respectively, other data with a 1/1 H_2/CO synthesis gas mixture showed no difference in activity (see Table X.3). The latter data indicate that the *ex situ*

reduced and carbided high- and low-surface-area Fe-Co spinel derived catalysts, as well as the activity of the *ex situ* reduced and carbided high-surface-area Fe spinel catalysts, have essentially the same activity. The activity of the *ex situ* low-surface-area Fe-Co spinel and the lack of activity for the *in situ* treated low-surface-area spinel appears to be one reason why Fiato and Soled (X.10) claim a slurry process utilizing only the carbided and reduced low-surface area spinel.

Alloys active for CO conversion are formed by reducing the high-surface-area Fe-Co spinel *ex situ* with H₂ at 350°C for 12 hrs followed by further reduction with H₂ at 400°C for 24 hrs. CO conversions with either 1/1 and 2/1 H₂/CO synthesis gas mixtures were higher than the correspondingly reduced Fe-only spinel, as shown in Table X.4. Although the correspondingly reduced high surface area Fe-only spinel was not quite as active as the Fe-Co alloy, its selectivity for CO₂ production was much smaller. The hydrocarbon selectivity of the Fe-Co spinel was greater and its methane and C₅+ selectivities were less than for the Fe-only spinel. In this series of patents, no claims were made nor information provided on alloys produced from reduced low-surface area Fe-Co spinels.

Fixed-Bed Catalysts. Only catalysts prepared from low surface area Fe-Co spinels were used as fixed-bed catalysts. Although high-surface area spinel derived catalysts were anticipated for use in fixed-bed reactors, no claims nor examples were found that relate to such usage. An example was provided in which low-surface area Fe_{2.85}Co_{0.15}O₄ spinel was reduced at 500°C with a mixture of 90% H₂ in N₂ at 100 psig for 5-7 hrs before exposing to synthesis gas. It was more active for CO conversion than a comparably prepared and treated Fe₃O₄/1%K spinel, as shown in Table X.5. At a run temperature that was 35°C lower than the control sample, the Fe-Co conversion of

CO was higher than for the Fe-only catalyst at the same space velocity. Both CO₂, hydrocarbon yields and olefin content in the C₂-C₄ fraction were higher for the Fe-Co catalyst while the C₅+ and C₆+ products were greater for the control.

In all the Fe-Co spinel patents, there was only one example of a spinel having an Fe-Co concentration that did not fall within the claimed limits. That spinel, having an x value of 2.20, falls below the 2.4 value specified in the claims. The CO conversions and hydrocarbon yields were essentially the same for this catalyst as for those that fell within the claimed limits, i.e. x values either ≥ 2.4 or >2.625 , both of which were used in different patents (see Table X.6). Regardless, all of these catalysts had Fe/Co ratios that were greater than 2 (x value 2.0), which was consistent with the prior art value discussed above.

In almost all of the patents regarding the FT reaction that are assigned to Exxon, only a few discuss the exotherm that is observed in any of the experimental reactors. In one of the patents, assigned to Fiato et al. (X.8) claiming Fe-Co spinel derived materials as catalysts for fixed-bed FT reactors, the exotherms observed in those reactors are discussed. Actual maximum bed temperatures are given for runs in which furnace temperatures were from 225 to 290°C. In these runs made with a cobalt spinel having an x value of 2.625 (Fe_{2.625}Co_{0.375}O₄/1 wt.% K), exotherms of 8 to 44°C were observed at 240°C and 290°C, respectively (see Table X.7). Over this range the corresponding CO conversion increased from 31% to 97%. The CO conversion follows the same trend as does the difference between the furnace and bed temperatures. At the higher temperature, the hydrocarbon selectivity deteriorated resulting in increased conversion to methane, whereas at the lower temperature the olefin selectivity was higher, i.e. 55.3% versus 37.1%, and the C₆+ yield was also higher. The effect of furnace

temperature at 235 and 270°C for a $\text{Fe}_{2.85}\text{Co}_{0.15}\text{O}_4$ /1 wt.% K spinel, where $x = 2.85$, is also shown in Table X.7. In this case the actual bed temperatures were not reported but can be assumed to be about the same as for runs made at the same temperature. The CO conversion and CO_2 and hydrocarbon yields for the $x = 2.85$ spinel were essentially the same as for the $x = 2.625$ spinel. At high conversion, hydrocarbon selectivity of the $x = 2.85$ spinel was better giving less methane, more C_6+ , and more C_2 - C_5 olefin yields. This provides further evidence that lower cobalt concentration provides better yields.

Copper promoted Fe-Co spinels. Two patents claim Cu promoted Fe-Co spinels as slurry phase catalysts. A patent issued to Soled and Fiato (X.6) claims compositions comprising a reduced-carbided Cu-promoted Fe-Co alloy, produced by contacting a Cu-promoted Fe-Co alloy with a carbiding atmosphere, which was prepared by reduction of a Group Ia or Group IIa metal salt promoted Fe-Co spinel possessing a BET surface area greater than $5 \text{ m}^2/\text{gm}$. The spinels correspond to high surface area spinels prepared by precipitating the Fe and Co nitrate salts, as presented in Soled and Fiato (X.4). A corresponding patent issued to Soled and Fiato (X.7) which, except for the claims, is identical to Soled and Fiato (X.6) claims a slurry process using a catalyst comprising an unsupported Cu-promoted Fe-Co spinel having an initial BET surface area $>5 \text{ m}^2/\text{g}$ and a Fe/Co ratio $\geq 4/1$.

Copper promoted spinels are prepared by impregnating Fe-Co spinel with an aqueous solution of cupric nitrate, drying, and then impregnating with an aqueous solution of K_2CO_3 followed by a final drying to give a composition of $\text{Fe}_{2.85}\text{Co}_{0.15}\text{O}_4$ /(1 wt.% K, 1 wt% Cu). *Ex situ* carbided catalysts were prepared by reducing the spinel in a 40% H_2 , 20% CO and 40% He containing stream at 400°C for 24 hrs. After cooling to

room temperature, the oxygen (1%) passivated sample gave an X-ray diffraction pattern isostructural with Fe_5C_2 , had a BET surface area of $150 \text{ m}^2/\text{g}$, and contained 40-50% carbon. Corresponding Co-free and carbided spinels were also prepared by the same method.

Examples were included which illustrate the use of these spinels as catalysts in a slurry reactor both in *in situ* unreduced as well as *ex situ* carbided forms. CO conversion for the *in situ* reduced catalysts followed the sequence Cu/K-promoted Fe-Co spinel > K-promoted Fe-Co spinel > Cu-free Fe spinel (see Table X.8). However, data were not provided that showed relative selectivities for hydrocarbon versus CO_2 formation. The CO conversion activities of the *ex situ* carbided-reduced Fe and Fe-Co spinels were quite similar as were the methane and $\text{C}_2\text{-C}_4$ olefin selectivities. The olefin concentrations (52-59%) in the C_{10} fractions from these catalysts were quite high.

Iron - Manganese Spinels

A composition of matter and three process related patents assigned to Exxon cover iron-manganese spinels. Two cases that were originally filed on December 20, 1983 were abandoned and refiled in December 1985. Both applications resulted in patents that issued in 1986. Apparently at some time during the application process, claims for a fixed-bed process were split from the slurry bed process application and refiled as a separate application. The latter fixed-bed application was subsequently abandoned, refiled and again abandoned before being refiled in 1990, which apparently resulted in a patent covering a fixed-bed process. Unlike the Fe-Co spinel cases, only high-surface-area Fe-Mn spinels were covered, since prior art appears to preclude coverage for Fe-Mn spinels prepared by sintering mixtures of iron oxide and manganese oxide.

The first patent in this series, issued to Fiato and Soled (X.11), claims compositions comprising an unsupported Group Ia or Group IIa metal and copper promoted Fe-Mn spinel having a BET surface area $>30 \text{ m}^2/\text{g}$, an Fe/Mn ratio >2 , and an empirical formula of $\text{Fe}_x\text{Mn}_{3-x}\text{O}_4$, where x is >2 . The second patent issued to Fiato and Soled (X.12) is identical to Fiato and Soled (X.11), except for the claims, and claims a slurry FT process using a catalyst comprising the composition of Fiato and Soled (X.11). The third patent issued to Iglesia et al. (X.13) claims a fixed-bed FT process using a catalyst comprising the composition of Fiato and Soled (X.11) in a pelletized form.

In the examples, a high-surface area Cu-K promoted $\text{Fe}_{2.25}\text{Mn}_{0.75}\text{O}_4$ spinel was prepared by combining Fe and Mn nitrate, in a molar ratio of 3/1, with a solution of ammonium glycolate having a pH of 6.5 in a ratio to give a total metal ion to glycolate ion ratio of 1/1. Water was removed at room temperature and the solid was air calcined at 175°C for 2 hours to produce the spinel having a surface area $>50 \text{ m}^2/\text{g}$. Promoter was added by impregnating the spinel with 2 atomic % K and 1 atomic % Cu. Interestingly, a paper that appeared in 1985 by Maiti et al., (X.20) at about the same time that the final application was filed, also reported preparing Fe-Mn spinels by base precipitation of Fe and Mn nitrate salt solutions. The reduced and carbided form of the resulting solids, none of which contained promoters, was active for FT synthesis gas conversion. Even though the Maiti paper disclosed materials related to the claimed compositions, it apparently did not preclude the issuing of a patent for these compositions.

Under slurry conditions, the high surface area K-Cu dual-promoted Fe-Mn spinel gave higher CO conversions than either the comparable K or Cu promoted spinels, as shown in X.Table 9. At half the catalyst loading, CO conversion for the Cu promoted

catalyst was higher at 69% than the 34% and 36% conversion for the K-promoted catalyst. The methane selectivity was also favorable in that it was lower for the dual promoted catalyst. The effect of Fe-Mn ratio is shown in Table X.10. CO conversions for Cu-K promoted spinels having Mn concentrations with x values >2, as claimed in this patent, were higher than for two spinels having x values of 0.25 and 1.5, which were below the Mn concentrations in the compositions claimed in this patent.

Unlike patent coverage for the Fe-Co spinels, which claimed both high and low-surface area compositions, none of the patents assigned to Exxon claimed compositions or processes comprising low-surface area Fe-Mn spinels as catalysts or precursors to catalysts for synthesis gas reactions. Such catalysts are apparently covered by a previous patent issued to McGrath and Rubin (X.14), and assigned to Kellogg, which claims a process for converting synthesis gas using a catalyst comprising elementary Fe with manganese oxide and alkali compound as promoters. Fiato and Soled (X.11) showed that a reduced low-surface area Fe-Mn composition reported by McGrath and Rubin (X.14) was inactive for CO conversion in the slurry process. This composition had an empirical formula of $\text{Fe}_{2.86}\text{Mn}_{0.14}\text{O}_4/0.7$ atomic % K and was prepared by sintering a paste of $\text{Mn}(\text{NO}_3)_2$ and Fe_3O_4 containing K_2CO_3 at 1400°C for 6 hrs and reducing with H_2 at 371°C for 48 hrs. For comparison, two low-surface area ($<5 \text{ m}^2/\text{g}$) K and K-Cu promoted Fe-Mn spinels were evaluated. They were prepared by fusing a mixture of Fe_2O_3 , Fe and Mn_3O_4 at $800\text{-}1000^\circ\text{C}$ for 48-72 hours and impregnating with K or with K and Cu to give spinels having a composition of $\text{Fe}_{2.25}\text{Mn}_{0.75}\text{O}_4$ and containing 2 atom % K or 2 atom % K/1 atom % Cu. Both of these materials were inactive for CO conversion in the slurry process (see Table X.9). However, based upon the fact that reduced and carbided low-surface area Fe-Co

spinels are quite active for CO conversion in the slurry process (see Table X.3), similarly pretreated Fe-Mn spinels may also be active; however, such information was not provided.

The use of glycolate in the production of the $\text{Fe}_x\text{Mn}_{3-x}\text{O}_4$ spinel is covered in an independent claim that specifies the use of α -hydroxy aliphatic carboxylic acid. The spinel prepared in the examples using glycolate, as the carboxylic acid, was more active than spinel prepared by precipitating a solution of the salts using ammonium hydroxide. The latter spinel was prepared by calcining at 500°C. The CO conversion for the glycolate spinel was 68.9% versus 20.5% for the ammonium hydroxide prepared spinel.

Another related patent issued to Soled et al. (X.15) claims a process for producing powdered metal-based iron alloys which are structurally the same as prepared by reducing $\text{Fe}_{2.25}\text{Mn}_{0.75}\text{O}_4$. This method comprises heating a mixture of powdered mixed metal oxide with a stoichiometric amount of calcium metal in an inert atmosphere at 850°C for 72 hours, leaching out the Ca and calcium products with an aqueous acid and recovering the metal-based alloy. The other method used by Fiato and Soled (X.11) involves sintering the metal oxides at 1000°C to form the alloy.

The patent issued to Iglesia et al. (X.13) claims a fixed-bed FT process using a catalyst comprising the Cu-K-promoted Fe-Mn spinel composition in a pelletized form. Comparison between a fixed bed and slurry operation for this catalyst indicates the slurry catalyst gives higher conversion, similar CO_2 selectivity, and lower methane and higher C_5+ olefin yields (see Table X.11).

Fe - Zn Spinels

A patent issued to Gates and Fiato (X.16) claims a sintered combination of metal oxides having the following components (preferred metals) from Group VIII (Fe), Group

IIB (Zn), Group IA (K), and the Lanthanum Group (Ce). Although there are no limits on the claimed composition, the only catalyst prepared in the examples had an empirical formula of $\text{Fe}_{2.81}\text{Zn}_{0.19}\text{O}_4\cdot\text{Ce}_{0.08}\text{K}_{0.08}$ (atom ratio of 1.0/0.065/0.03/0.03). This corresponds to an Fe_2O_3 concentration of 87 wt.%, which, surprisingly, falls outside the 5-80 wt.% range specified in the independent claim 7. The spinel catalyst was prepared by sintering a mixture of Fe_2O_3 , ZnO, and CeO_2 at $\sim 1050^\circ\text{C}$ in air for 24 hours. It had a BET surface area $< 2 \text{ m}^2/\text{g}$ and XRD indicated it was a highly crystalline mixture of mixed spinels and iron oxides in a CeO_2 phase. The composition is very similar to the Fe/Zn/Ti-Mn spinels that are discussed below. The spinels were reduced in H_2 at 500°C for 7 hours, after which they were passivated by exposure to oxygen at 25°C . The reduced form still contained unreduced metal oxides as shown by X-ray diffraction analysis. The passivated reduced catalysts, after preheating in H_2 in a fixed bed reactor at 500°C , gave the same level of CO conversion as a Zn and Ce-free 1% K/ Fe_2O_3 that was prepared in the same way. The Zn-Ce containing catalyst gave lower methane and higher C_7+ liquid selectivity in addition to producing a higher yield of CO_2 , as shown in Table X.12.

Another patent issued to Soled et al. (X.17) claims compositions comprising Fe, Zn, and Cu and one member chosen from the group of K, Rb, or Cs wherein the Fe/Zn atomic ratio is ≥ 5 and the alkali metal/Cu atomic ratio is ≥ 2 . The claim specifies spinel compositions having empirical formulas of $\text{Fe}_x\text{Zn}_{1-x}\text{O}_4$ with x values ≥ 2.5 . Although compositions having single phase spinel structures are preferred, the compositions claimed in the patent are not limited to a method of preparation, specific structures or any morphological feature. A corresponding patent, having an identical specification, issued to Soled et al. (X.21) claims a FT process utilizing these catalyst compositions.

Only methods that generate high surface area materials were used in the examples to demonstrate the preparation of three different spinel compositions, i.e. $\text{Fe}_{2.8}\text{Zn}_{0.2}\text{O}_4$, $\text{Fe}_{2.45}\text{Zn}_{0.55}\text{O}_4$ and $\text{Fe}_{2.3}\text{Zn}_{0.7}\text{O}_4$. Only the first catalyst, which was prepared by two different methods, fell within the range specified in the claims. All three catalysts were prepared by mixing a solution of iron nitrate and zinc nitrate with an ammonium glycolate solution having a pH of 6.5, forming a precipitate, and drying and heating in air at 350°C/1 hr. The resulting spinels were impregnated with K_2CO_3 and $\text{Cu}(\text{NO}_3)_2$ and dried in a similar fashion. The second $\text{Fe}_{2.8}\text{Zn}_{0.2}\text{O}_4$ spinel was prepared by adding ammonium hydroxide to a solution of iron nitrate and zinc nitrate to a final pH of 9. The washing, drying and impregnation steps were the same.

Although the catalysts were claimed to be useful in either fixed-bed or slurry FT reactors, the examples included only slurry reactor applications. The effect of promoter on synthesis gas conversion of Cu, K and Cu-K promoted $\text{Fe}_{2.8}\text{Zn}_{0.2}\text{O}_4$ showed that the K/Cu promoted catalyst gave higher CO conversion and methane selectivity, as shown in Table X.13. Surprisingly, the highest CO conversion was observed for a spinel having a Fe/Zn ratio less than 5 which falls outside the claimed composition range. It is not clear why this composition was not included in the claimed range of compositions.

Comparative performance tests of the zinc ferrite based catalysts were conducted with 2g samples of catalyst and 72g of octacosane in a 300 cc Parr CSTR. The synthesis gas ($\text{H}_2:\text{CO} = 2:1$) feed rate was 180 cc/min at 75 psig and 270°C. Activation was accomplished by heating up to and at 270°C in synthesis gas. Nitrogen (20 cc/min) was added as an internal standard. The superficial space-velocity (V/V/hr) based on an initial catalyst density of 1.8 g/cc was approximately 15,000 V/V/hr. CO conversions in excess of 60% were maintained during initial 80 hr test. Methane

selectivity of 4.5% (CO₂ free) was obtained. C₅₊ selectivities were >75% on a CO₂ free basis. On this basis, the space velocity (including 20% inert gas) was about 6 NL/hr-g catalyst (Table X.14); this compares favorably with the activity of cobalt catalysts discussed later. The Exxon workers report that the pressure useful in the process will range between 150 and 450 psig and preferably 250 and 400 psig. They state that higher pressures can be used but these can lead to high levels of condensed water which can retard activity. This statement implies that the catalyst either has low water-gas shift activity or is being operated under conditions where the fraction of CO converted to hydrocarbons, and not CO₂, is very high.

Fe-Zn-Ti and Fe-Zn-Mn Spinels

A patent issued to Fiato et al. (X.18) claims compositions comprising sintered combinations of metal oxides taken from Group VIII (Fe), Group IIb (Zn), Group IVb (Ti) and/or Group VIIb (Mn), Group Ia (K), and the Lanthanum Group (Ce) such that the sintered combinations comprise a series of spinels of Group VIII (Fe), Group IIb (Zn), Group IVb (Ti) and/or Group VIIb (Mn) and a Group Ia metal oxide in a lanthanum group oxide matrix. The preferred metals are shown in parenthesis. There were specific limits on concentration of the metal oxides in the mixture which are quite similar to the sintered combination in Gates and Fiato (X.16) which included Fe, Zn, Ce and K. In that case, the only limits on concentrations of the metals were in a subordinate claim. The sintered catalysts are red-brown or red-purple, have BET surface areas ≤ 2 m²/g and are highly crystalline. The crystalline phase comprise hematite, magnetite, ilmenite, a series of mixed spinels and CeO₂. A corresponding identical patent issued to Fiato et al. (X.22) claims a FT process utilizing this catalyst.

The catalysts are prepared, as in Gates and Fiato (X.16) by sintering a mixture of oxides having the correct atomic ratio and reducing in H_2 at $500^\circ C$ for 6 hrs. The K, Ce, and K/Ce catalysts in a fixed-bed reactor configuration had CO conversion activities that varied with the promoter following the order $K/Ce > Ce > K$, as shown in Table X.15. At a reasonable CO conversion level the C_2 - C_3 olefin selectivity was high and the methane selectivity was lower for the K/Ce spinel. Data were also given at higher reactor temperature, i.e. $305^\circ C$, as well as at lower space velocity, which resulted in excess of 80% CO conversion with high olefin concentrations in the C_2 - C_4 fraction plus a sizable yield of C_5+ product.

K, Ce and K/Ce catalysts having compositions in which Ti was replaced with Mn were also included. The atomic ratio of the metallic components in the catalyst containing both K and Ce was 1.0 Fe/1.0 Mn/0.07 Zn/0.05 K/0.04 Ce. On a weight basis, this composition (43.6% Fe_2O_3 /48.2% MnO_2 /3.1% ZnO/1.2% K/3.8% Ce) is excluded from being a covered composition since it fell outside the specified composition in the main claim. Specifically, the MnO_2 composition of 48.2 wt.% of the total oxides is excluded, unless there is an error in the composition as stated in Example 6, since the claims specify a range for MnO_2 of 10 to 40 wt.% of the combination. The performance of the K, Ce and K/Ce promoted Fe/Mn/Zn spinels in a fixed-bed reactor configuration are shown in Table X.16. The K/Ce dual promoted spinel provides high activity, low methane selectivity and high C_2 - C_3 olefin selectivity.

Thallium Impregnated Iron Supports

Two patents were issued regarding thallium and iron catalysts. One is a composition of matter case issued to Wright (X.23) and the second, a process patent issued to Wright et al. (X.24). Both cases involved several filings and abandonments;

there is also a difference in the inventors for the two cases. Overall, the texts in these two are very similar, though not identical. The main claims cover all Fe-Tl compositions wherein the thallium compound, being supported or unsupported, is substantially deposited on the surface of the iron compound, with the iron compound in the trivalent state. Included in a dependent claim is incorporation of promoters including Co, Zn, Cr, Mn, Ba and Group I metals.

The main claim appears confusing since it states that the thallium may be both supported and unsupported but is also substantially supported on the surface of the iron. The examples contain numerous examples in which the thallium was impregnated onto the surface of the iron, however one catalyst was prepared by impregnating a melt of ferric nitrate and thallium nitrate onto a magnesium-alumina spinel. This presumably is a supported example. Also, there is nothing in the claims regarding pretreatment of the catalyst to reduce the Tl and Fe to the metallic or carbided forms, although a number of different methods for preparing the catalysts are included in the examples.

Several techniques for preparing Fe/Tl catalysts were presented in the examples. Several Fe-Tl catalysts were produced having Fe/Tl ratios from 10/1 to 2.5/1 by precipitating solutions of ferric nitrate with ammonium carbonate and impregnating the washed and dried solids (110°C for 12 hrs in air) by an incipient wetness method with solutions of thallium nitrate or thallium chloride. Examples were also given for preparation of other Fe/Tl catalysts supported on alumina, cesium-doped and magnesia-doped aluminas, and commercially available iron oxide. Examples explaining the preparation of several fluoride impregnated catalysts were also provided. Test results were provided on only a limited number of these preparations.

All of the Fe-Tl catalysts that were prepared in the examples were run under FT conditions that gave CO conversions up to 97%. The product contained large concentrations of liquid hydrocarbons in the C₅-C₁₁ range that was rich in olefins and contained a lesser amount of aromatics. Data for a 10 Fe/1 Tl catalyst prepared by precipitating ferric nitrate and impregnating the resulting solid with thallium nitrate and reducing at 270°C/18 hrs are shown in Table X.17. Over a range of temperatures from 270 to 350°C, the maximum C₆+ yield at CO conversions >90% was ~20% with methane yields ranging between 6 and 15%. CO conversion is very dependent on space velocity, however, methane, C₅-C₁₁ liquid, C₁-C₄ gas, alpha-olefin and aromatic selectivities are only weakly dependent on space velocity. It was suggested that the aromatics yield is probably related to conversion of olefins. None of the examples provided any data on CO₂ yields.

The performance of two Fe-Tl catalysts in the FT reaction was compared with an Fe/K and a commercial ammonia synthesis catalyst. Two Fe-Tl catalysts, having Fe/Tl ratios of 10/1 and 5/1, were prepared by precipitating ferric nitrate and impregnating the resulting solid with thallium nitrate. The method for preparing the Fe/K catalyst that contained 4% K is not clear and no further description of the commercial ammonia synthesis catalyst was given. Selected results from runs presented in Example 9 in the patent are shown in Table X.18. In the patent, in several instances, differing sets of results are given for the same run condition without any explanation. For example, included in Table X.18 are two sets of data that were both taken at 350°C and 300 GHSV for the 10 Fe/1 Tl catalyst. Due to the lack of clarity in the presentation of the data, it is difficult to draw any conclusions regarding the CO conversion activities of these various catalysts. However, the product selectivities in these runs are quite

similar. The discussion in Example 9 of the patent states that CO conversions were initially in the 80-98% range. Whereas the Fe/0.4K catalyst appeared to lose activity after about 18 hours on stream, conversion for the Fe/Ti catalyst decreased to only 40-60% after several days on stream. The selectivity for the 10 Fe/1 Ti catalyst appears to be maximum at 270°C at a CO conversion of 46.8%.

Iron - Cobalt Impregnated Slurry Catalysts

A patent issued to Fiato et al. (X.25) claims a process for preparing a slurry FT catalyst system in which an Fe-Co catalyst is formed (in situ) in the absence of air. A corresponding identical patent, except for references and claims, issued to Fiato et al. (X.26), claims a FT process utilizing this catalyst system. The catalyst is prepared by adding Fe and Co carbonyl compounds, or Fe and Co compounds which are capable of forming carbonyl complexes, in a CO atmosphere, along with a powdered support, to a hydrocarbon liquid. The iron and cobalt compounds are present in a ratio of from 35:1 to 1:10. This combination is decomposed in the presence of CO such that the cobalt complex is decomposed to the metal at a lower temperature followed by decomposition of the Fe complex at a higher temperature. The slurry is heated in H₂ to reduce the metals and their decomposition products. Representative complexes are Fe₃(CO)₁₂, bis(dicarbonylcyclopentadienyliron), [CpFe(CO)₂]₂, and Co₂(CO)₈. Potassium carbonate, that promotes olefin formation in the reaction and decreases the formation of methane, may be added to the mixture in the first step.

In the examples in the patent, [CpFe(CO)₂]₂ and Co₂(CO)₈ were added to the reactor either alone or in the presence of a support. In each case shown in Table X.19, the absolute amount of Fe and Co in the reactor was the same except for the run in which Fe₂O₃/1% K was added as the support. In runs with a 1:1 H₂/CO synthesis gas

mixture, CO conversions were 20-30% with the C₂-C₄ fraction being predominantly olefinic. After 96 hours on stream, conversion had increased from ~21 to 27%. In a comparative run, an *ex situ* catalyst, Fe_{2.85}Co_{0.15}O₄/1%K, gave <5% CO conversion. For this run, the preparation of the catalyst nor its concentration in the reactor were not given.

TITANIA AND TRANSITION METAL OXIDE SUPPORTS

An extensive number of patents were obtained related to the use of titania containing catalysts in various applications, including the FT reaction. Early patents in this area disclosed the unique features of titania containing supports but did not refer to any FT type of application. However, these cases were fundamental to many of the subsequent patents that were issued for FT application. A patent issued to Tauster et al. (X.27) disclosed compositions comprising Group VIII metals supported on bulk oxides of titanium, vanadium, niobium, tantalum, zirconium titanate and barium titanate which were reduced in H₂ before use. A corresponding approach of coating a support with titania and adding a Group VIII metal is disclosed in a related patent issued shortly thereafter to Wheelock (X.28). Numerous patents have subsequently been issued using these approaches.

Tauster et al. (X.27) claimed that H₂ reduced Group VIII metals supported on Group IVb and Group Vb oxides are distinctly different from the same metals deposited on common carriers such as alumina, silica, carbon, magnesia, and silica alumina. These metals deposited on common carriers are found to retain their capacity for H₂ chemisorption, whereas the same metals when supported on various Group IVb and Group Vb oxides exhibit a marked suppression of this capacity. This change is attributed to the chemical nature of a strong metal-support interaction (SMSI) that

consists essentially of covalent bond formation between metal atoms of the supported phase and metal cations of the oxide support at the surface.

Such an interaction between the supported metal and the support is highly unusual. Typically, the role of the support is simply a geometrical one which exerts the major influence in the preparation of a well dispersed supported-metal catalyst. Thus chemically dissimilar materials, such as alumina and carbon, are able to efficiently disperse supported metals, provided that they are employed in their high surface area form, e.g. $>100 \text{ m}^2/\text{g}$. In these situations no strong chemical interaction between the support and the metallic phase is required to bring about good dispersion. If surface interaction occurred, the results observed for temperature-programmed-desorption of H_2 from Pt/alumina and Pt/silica catalysts, which are very similar, would be expected to be quite different.

The patent argues that although covalently-bonded species are observed in the hexagonal barium titanates and Lewis acid-base intermetallic compounds, which are representative of cation to cation and metal-atom to metal-atom types of bonding, respectively, the metal-atom to cation bonding in the SMSI are unique to the structures of this invention. In a Lewis acid-base intermetallic type of bonding structure, the titanium would be present as zero-valent. By photoelectron spectroscopy, or ESCA (electron spectroscopy for chemical analysis), zero valent titanium was not found in a composition of this invention, i.e. a 2% Rh/ TiO_2 catalyst that had been reduced in H_2 at 550°C .

In the broadest sense, the catalyst composition consists of a catalytic metal component selected from the group consisting of Group VIII metals, and mixtures thereof, supported on a transition metal oxide selected from the group Ti, V, Nb, Ta,

alkaline earth titanates, and mixtures thereof. These SMSI oxides can be used either in the pure state or, alternatively, in combination with additional oxides such as alumina, silica, magnesia, zirconia, hafnia, thoria, ceria, etc. They may be prepared by coprecipitation from solutions containing precursor salts of the respective oxides or by deposition of the precursor salt of the SMSI oxide on a carrier. The latter compositions, comprising titania deposited on the surface of an inorganic oxide support to which Group VIII metals are added, were disclosed by Wheelock (X.28) who anticipated a stabilizing interaction between Group VIII metals and Group IVb metal oxides.

The key characteristic of the SMSI oxides is that after the critical temperature for reduction is reached, the supported metal is no longer able to absorb H_2 and CO at room temperature. However, the supported metal particles are still in a high state of dispersion and retain their ability to chemisorb oxygen resulting in high ratios of adsorbed oxygen to metal atoms. Since the SMSI effect is a chemical interaction between the supported metal and the carrier, it is necessary for the metal to be well dispersed in order to provide sufficient interfacial contact between metal and support. Thus large metal crystallites are incapable of significantly affecting the properties of the surface metal atoms in contact with the gas phase. Therefore, the particle size of the supported metal should be preferably 50 Å or less. There also is a difference in the temperature of H_2 -activation needed to confer SMSI properties on the Group VIII metal, which varies primarily with the particular SMSI support. A SMSI state is achieved when a composition, e.g. Group VIII metal supported on the oxide of Ti, V, Nb, Ta, a mixture thereof, or a Zr or Ba titanate, is subjected, as a final preparative step, to reduction in a reducing atmosphere at a temperature sufficient to cause the composition to exhibit the suppression of H_2 and CO chemisorption.

Properties of Titania Supports. Tauster et al. (X.27) did not address the question of surface area and how it relates to the development of the SMSI state, although they used the argument that chemically dissimilar materials, such as alumina and carbon, are able to efficiently disperse supported metals, provided they are employed in their high surface area form, e.g. $>100 \text{ m}^2/\text{g}$. Based upon data contained in a subsequent patent issued to Arcuri et al. (X.29) the titania supported catalysts prepared by Tauster et al. (X.27) probably had only moderate surface areas. Arcuri et al. (X.29) showed that the rutile to anatase ratio increased with higher air calcination temperatures which caused a corresponding decrease in surface area (see Table X.20). They also found reduction of a calcined sample with H_2 at 450°C did not prevent further decrease in surface area upon further calcination in air at 500°C . These data suggest that the surface areas of the titania used by Tauster et al. (X.27) was initially about $60 \text{ m}^2/\text{g}$ and because of the thermal transformation of anatase to the rutile form, the final surface areas were probably somewhat less than the starting material and somewhat enriched in the rutile form. In a still later patent issued to Mauldin and Riley (X.30), additional data were reported showing increases in rutile concentration with calcination temperature (see Table X.21).

Vannice and Garten (X.31) described the titania that was probably used in many of these patents as being prepared by flame hydrolysis of TiCl_4 and having a surface area of $\sim 60 \text{ m}^2/\text{g}$ after thermal treatment at temperatures $\leq 500^\circ\text{C}$. A number of the cases referred to a material of this type that was designated as Degussa P-25 and was described as having a BET surface area of $50 \text{ m}^2/\text{g}$ and contained 65% anatase and 35% rutile titania in Wachs and Yang (X.32). Although a number of these patents contained claims that specified limits on the concentrations of the crystalline forms in

the titania phase, several actually contained these limits in either the main claim or another independent claim. This, of course, provides an unalterable requirement for the catalyst of the invention and was peculiar to a series of five patents, four of which claim titanias having high rutile contents while the fifth claims a stabilized titania having a high anatase content. Interestingly, the four high rutile cases, that originated from work presumably done at the Baton Rouge laboratories, were filed on the same day, June 29, 1984, and no subsequent patents had such a restriction in their main claim, although several continued to claim such materials in dependent claims. The level of rutile specified in the claims is >40%.

An alternative to using bulk titania is supports in which titania would be coated onto common, inorganic oxides. Such compositions were covered in a patent issued to Wheelock (X.28) which disclosed compositions comprising Group VIII noble metals and titania deposited onto inorganic oxides. Interestingly, that patent actually specified in its main claim that the titania existed on the surface as clusters. Whether such speculation regarding the morphological form of the catalyst, which was based upon ion scattering experiments, limits the compositions claimed by the invention is not clear. Assuming that it does not, Exxon then has rights to all compositions comprising Group VIII noble metals on titania coated inorganic oxides, of which platinum was specifically mentioned.

Ruthenium on Titania and Transition Metal Oxide Supports

The earliest Ru on titania Exxon patent that was found related to application in NO_x reduction. A composition of matter patent issued to DeLuca et al. (X.33) claimed a composition comprising ruthenium in combination with zirconium titanate or zirconium titanate in admixture with titanium dioxide, but not with TiO₂ alone. Ruthenium on titania compositions had been disclosed in previous patents, one of which was issued to

Kobylinski and Taylor (X.34), and assigned to Gulf, which claimed a process for reducing the content of nitrogen oxides in the exhaust gases from internal combustion engines. Such patents probably precluded claiming such compositions.

A problem with Ru/TiO₂ catalysts is the loss of Ru oxide upon treatment at temperatures around 840°C. DeLuca et al. (X.33) claimed decreased volatility of Ru oxide from compositions comprising Ru on zirconium titanate, either with or without additional titania being present. Tauster et al. (X.27) claimed the use of these materials in hydrocarbon conversion reactions but not in a FT type application. Various combinations of these supports, either alone or in combination with supported metals, are claimed in subsequent composition of matter patents or as catalysts in various FT process application patents. Several patents were issued regarding ruthenium on titania type supports. The claims in all these cases included not only titania but numerous combinations with silica, alumina, carbon, Group Vb metal oxides, and various alkali, alkaline earth and rare earth oxides. Exxon came close to claiming the composition Ru on TiO₂ in a patent issued to Arcuri et al. (X.29) which claimed catalyst compositions comprising ruthenium with rhenium on titania. A companion process patent that utilized this catalyst, which was essentially identical except for the claims, was issued to Arcuri (X.35). The titania support in these compositions were specified as having rutile concentrations >40%. The examples in these patents showed in extended runs with synthesis gas that Ru/TiO₂ that contained rhenium had a longer half-life at a level of 97% CO conversion than rhenium-free catalyst (see Table X.22). The interactive effects of these two metals on catalysts containing 0.5-1.0% Re with ruthenium concentrations from 0.1-1.0% indicate that the highest CO conversions were obtained for catalysts containing 0.5% Re and 1.0% Ru (Table X.23). The effect of the

ratio of rutile to anatase in the catalyst is shown in Table X.24 in which the catalyst containing 67% rutile in the titania had the slowest deactivation rate when operating at the 90% CO conversion level. Also, methane selectivities were much lower for the catalysts containing higher levels of rutile.

Several of the ruthenium-titania patents that were issued relate to processes that use Ru on titania. Vannice and Garten (X.31) claimed the use of a reduced Ru on titania, which they prepared by impregnating RuCl_3 onto titania and reducing in H_2 for 1 hr at 450°C . The Ru/TiO_2 catalyst gave higher olefin yields than a related Ru on $\eta\text{-Al}_2\text{O}_3$ (see Table X.25), albeit at a CO conversion level of 10% or less in both cases. Mauldin (X.36) claims a process for converting methanol in the presence of H_2 using a catalyst comprising ruthenium composited with titania. At a 4/1 methanol to H_2 ratio, conversion to hydrocarbon product was 76% after 35 hrs on stream (see Table X.26). Either in the absence of H_2 or the presence of added CO, conversions dropped significantly. CO was presumed to adsorb preferentially on the catalyst preventing reaction of the methanol.

Vannice and Tauster (X.37) claimed a FT process using a catalyst comprising Ru deposited on V, Nb and Ta oxides either alone or in combination with silica, alumina, or carbon type supports. Titania was not included in the claims. Preparation of the catalysts was by methods as presented in Tauster et al. (X.27) which was incorporated by reference. Higher olefin yields were obtained with the catalysts of the invention under conditions that the CO conversions were less than 18% (see Table X.27).

Madon (X.38) also claimed a FT process using a catalyst comprising Ru deposited on the same supports claimed by Tauster et al. (X.27), i.e., Ti, V, Nb and Ta oxides. In an improvement over Vannice and Tauster (X.37), this case claimed a

process which employed a reduced catalyst which was contacted with a mixture of H_2 and CO for at least 10 hours, after which continued contact with H_2/CO gave a C_5-C_{40} hydrocarbon product having a paraffin to olefin ratio in the C_5-C_{20} fraction of ≥ 1.5 . With a 0.76% Ru on TiO_2 catalyst, in excess of 80% CO from a 1.39 H_2/CO synthesis gas mixture was converted to liquid products under conditions shown in Table X.28. All of these catalysts were shown to be more active than Ru supported on conventional SiO_2 or Al_2O_3 (see Table X.29).

A patent issued to Wachs and Yang (X.39) claims a catalyst comprising Ru supported on a surface modified titania support wherein the support comprises an oxide of a metal selected from the group Nb, V, and Ta supported on the titania. In a corresponding patent, Wachs and Yang (X.32) claim a method for preparing this catalyst composition by depositing noncrystalline metal oxides of V, Nb, and/or Ta on a titania support having a $50\text{ m}^2/\text{g}$ surface area. In a related patent, Wachs and Chersich (X.40) claim a simple Ta_2O_3/TiO_2 composition prepared in this manner. No related patents claiming V and Nb oxide modified titania surface compositions were found. In Wachs and Yang (X.39) the modified support was impregnated with a solution of the Ru precursor which was reduced to the metal form. In the examples, all of the catalysts contained 1% Ru loadings. The activity of the catalysts containing various concentrations of the oxide promoters were compared with an impregnated physical mixture of TiO_2 and Ta_2O_5 in a fixed bed reactor (see Table X.30). Although the patent states that the data clearly show the difference between the catalysts of this invention and prior art Ru/TiO_2 catalysts, it is a challenge to recognize any differences.

A patent issued to Fiato and Miseo (X.41) claims slurry catalyst compositions consisting of titania, the decomposition product of $Ru_3(CO)_{12}$ formed in the presence of

H₂, and an inert alkane hydrocarbon. Fiato and Miseo (X.42) claim a process for preparing the *in situ* Ru/TiO₂ slurry catalyst. Preparation includes adding TiO₂, a Ru carbonyl complex, and an inert alkane hydrocarbon to a slurry reactor and increasing the temperature of the reactor to 230-270°C and pressure from 4 to 20 atm for 2-6 hr while adding a gas mixture of N₂:H₂ to cause the decomposition of the Ru carbonyl complex to form a slurry catalyst composition. In the example, a TiO₂ that had been pretreated with H₂ for several hours was added to the reactor with the Ru carbonyl complex and then subjected to the carbonyl decomposition step. The catalyst was highly active and selective for production of liquid hydrocarbons giving 40 to 60% CO conversion at 240°C with an alpha of 0.80. When TiO₂ was not present in the reactor, the Ru carbonyl complex was incompletely reduced and gave only 15% CO conversion (see Table X.31). The performance of the slurry catalyst was compared with a particulate Ru/TiO₂ and a Ru supported on ceria and alumina. The Ru - TiO₂ slurry catalyst had the highest CO conversion (55%) with a selectivity very similar to the particulate Ru/TiO₂ catalyst.

A patent issued to Mauldin (X.43) claims a process wherein the Ru on titania catalyst is pretreated with steam or steam and H₂ at 200 to 550°C to mildly agglomerate the ruthenium. By this procedure, Ru particles are generated having the same size as obtained after start-up with synthesis gas. The same effect occurs upon treating in air at 500°C where the crystallite size of the Ru grows from 12 to 30 Å. In the examples, a Ru/TiO₂ was prepared by impregnating a titania having a rutile content of 73% with ruthenium nitrate in acetone solution. One portion of this material was calcined in air at 500°C for 4 hours. Another was contacted with mixtures of steam with H₂ or N₂ at elevated temperature, as shown in Table X.32. The oxygen chemisorption decreased

while the Ru crystallite size increased. The performance of the Ru/TiO₂ that had been treated in air at 500°C for 3 hrs was compared with an untreated sample. Results after several times on stream, as shown in Table X.33, indicate that the selectivity to methane was higher and to C₂+ hydrocarbons was generally lower than for the untreated catalyst. The catalyst treatments that were presented in the patent, including air or steam with H₂ or a carrier gas, provide an advantage over a non-treated catalyst, as determined by Ru crystallite size, oxygen chemisorption or synthesis gas conversion and selectivity.

A patent issued to Pruett and Bradley (X.44) claims compositions comprising bimetallic cluster compounds containing Ru with Tl, In or Ga. A cluster having the formula [(C₂H₅)₄N][(Ru₆C(CO)_{16/2}Tl)] deposited onto an alumina surface was reduced in H₂ at 200°C and used for conversion of 1.5/1 H₂/CO mixture at 7 MPa and 275°C. The product contained a mixture of linear hydrocarbons and alcohols.

Rhodium on Titania

A patent issued to Vannice and Garten (X.45) claims a process in which synthesis gas is passed over a catalyst comprising Rh on a titanium-containing oxide support. The activity of this catalyst, reduced at 450°C and 100 kPa, though quite low, was higher than for a Rh on alumina catalyst (Table X.34). The product was largely methane.

Cobalt on Titania and Transition Metal Oxide Supports

There has been a considerable amount of activity by Exxon regarding cobalt on titania catalysts with a number of patents being issued that parallel the ruthenium cases discussed above. Included in the series were three filed on June 29, 1984 from the Baton Rouge laboratory that relate to titanias having rutile concentrations ≥40%. Very

broad coverage was obtained in a patent issued to Payne and Mauldin (X.46) which claims catalyst compositions comprising cobalt on high-rutile titania which are useful for both synthesis gas and methanol conversion. A subsequent patent issued to Behrmann et al. (X.47) claims catalyst compositions comprising cobalt dispersed and impregnated upon the surface of titania to an average depth of 0.02 to 0.20 mm with a cobalt loading, on a total bulk basis, from 0.04 to 0.15 g/cc, which is ~4-17 wt.%, depending on the packing density of the titania. A related patent issued to Iglesia et al. (X.48) claims a method for preparing supported cobalt catalyst on which the Co is deposited to a depth of less than about 200 μm on the rim of the catalyst particles. Other patents issued to Payne and Mauldin (X.49) and Behrmann et al. (X.50) claim processes that utilize these catalysts for conversion of synthesis gas. The addition of rhenium as a promoter to this family of catalysts, i.e. rhenium with cobalt on titania, was also covered. Catalysts in which the Co and Re were concentrated at the surface of the spherical particle was claimed by Behrmann et al. (X.47). Rhenium is claimed to improve activity for CO conversion for cobalt as it does for ruthenium. Bulk Co/TiO₂ catalysts, either with or without thoria, were claimed in a patent issued to Mauldin (X.51) with addition of thoria being claimed to be especially beneficial for conversion of methanol. Since the main claim in this case specified an inorganic oxide support, with titania being mentioned in a dependent claim, compositions that were covered were actually broader than titania itself, although titania supports were the only ones used in the examples.

Of the nine examples on Co/TiO₂ in the Payne and Mauldin (X.46) case, the first six relate to conversion of methanol and the last three to conversion of synthesis gas. The latter examples with synthesis gas are repeated in Payne and Mauldin (X.49) while the first six, which are related to methanol conversion, were probably included in

Application Number 626,026, which was filed on the same day, as noted in Payne and Mauldin (X.49), but apparently never resulted in an issued patent. A process patent issued to Mauldin (X.52) used the Mauldin (X.51) catalyst comprising rhenium and cobalt on titania.

The examples of bulk titania catalysts in Payne and Mauldin (X.46) were prepared from calcined Degussa TiO_2 , which was impregnated with Co nitrate and/or perrhenic acid. The addition of perrhenic acid to the substrate is a puzzle, since none of the catalysts contain Re, nor do any of the claims refer to catalysts containing Re. At any rate, the impregnated materials were then calcined in air at 250 or 500°C and reduced in H_2 at 450°C. Thoria containing catalysts were prepared by impregnating the support with a thorium compound or salt in a similar manner to give thorium concentration up to 10%. Actually, the specific thorium compounds or salts that were used to impregnate the substrate were not mentioned anywhere in the specification. Another set of cobalt-titania catalysts were also prepared having both high and low rutile concentrations. The low rutile concentration catalyst was prepared by impregnating cobalt carbonyl onto uncalcined Degussa P-25 titania that had a rutile concentration of 28% while the high-rutile catalyst was prepared from Degussa P-25 that had been calcined at 600°C. The impregnated cobalt carbonyl was decomposed either by heating at 257°C in vacuo for 1 hr, or by calcining at elevated temperatures. Catalysts were tested in a fixed bed reactor either with synthesis gas or with methanol after reducing in H_2 .

A subsequent patent issued to Behrmann et al. (X.47) claims catalyst compositions comprising cobalt dispersed and impregnated upon the surface of spherical titania with an average thickness of 0.02 to 0.20 mm. A corresponding patent

issued to Behrmann et al. (X.50) claims use of these compositions in a FT process. The cobalt loading in these catalysts, on a total bulk basis, was from 0.04 to 0.15 g/cc, which is ~4-17 wt.%, depending on the packing density of the titania. Special techniques for depositing the cobalt along with Re as a promoter were used wherein the metals were concentrated at the surface of the spherical titania particles having diameters of approximately 1 mm. The activity of rhenium promoted Co/TiO₂ catalysts, in which the metals are deposited on the surface of spherical titania substrate, is related to the thickness of the metal layer. With these catalysts that were prepared from spherical titania, the methane concentrations in the hydrocarbon product, relative to the converted CO, was lower than for Co-Re/TiO₂ in which the metals were uniformly distributed onto powdered substrate (see Figure X.1). The metals were deposited onto the surface of the spheres by either spraying a metal-containing solution onto the titania spheres and quickly removing the solvent or treating spheres that had been saturated with one solvent with a metal-containing immiscible solvent which would not penetrate into the particle.

Another method to prepare rim-type supported cobalt catalysts is covered in a patent issued to Iglesia et al. (X.48) who claim that contacting a support particle with a molten cobalt salt results in deposit of the cobalt to a depth of less than about 200 μm on the rim of the support. After reduction in H₂, these catalysts are more active than incipient wetness impregnated catalysts where the Co is evenly distributed throughout the particle, as shown in Table X.35, where a lower GHSV is necessary to achieve the same level of CO conversion. Each of the rim-impregnated silica based catalysts have a higher volume of CO conversion per volume of catalyst per hour. Crushing the 2.2 mm spheres provided a slight increase in CO conversion which denotes some additional

diffusional effect in the rim catalysts even though the Co is located primarily at the surface of the particle. There is also an advantage of having higher Co concentrations on higher surface area supports, as shown in Table X.35.

The advantage of incorporating a binder into titania was covered in patents issued to Mauldin and Riley (X.30) which claim support compositions comprising titania in which up to 20% alumina or zirconia is incorporated. A corresponding essentially identical patent issued to Mauldin and Riley (X.53) claims a FT process utilizing these catalysts. Their data show that incorporating a small amount of alumina increases the volume of CO converted per gram of cobalt/hr, as shown in Figure X.2. This increased activity is attributed to an increase in cobalt dispersion due to the increase in pore volume of the binder. Hydrocarbon synthesis activity suffers at higher alumina concentrations, however, because the Co oxide is only partially reduced on the alumina, as compared to titania where complete reduction occurs. This is reflected in the higher turnover numbers for the titania and the steady decline as incorporation of alumina increases (see Figure X.3). Thus, incorporation of small amounts of alumina results in an increase in activity. Higher dilutions, however, result in a decline in activity. An example is also presented that shows that catalysts prepared by spraying Co salts onto titania substrate containing 3.5% alumina binder using the method of Behrmann et al. (X.47) were more active than spherical titania without the binder.

A method for impregnating cobalt onto supports was covered in a patent issued to Mauldin and Riley (X.54) which claims a process for preparing a FT catalyst in which a catalytically effective amount of Co is impregnated and dispersed as a film or layer on the peripheral outer surface of a particulate porous inorganic oxide support, wherein the catalysts are prepared by spraying a bed of the fluidized particulate support particles

with a liquid containing a dispersed or dissolved Co metal compound. The operation is performed at specified operating conditions of 0.6 g liquid/ft³ fluidizing gas. Titania was one of the supports specified in a dependent claim. In the examples, solutions of cobalt nitrate and perrenic acid were sprayed onto particulate material and reduced at 450°C for 1 hr. Conversion of a 2/1 H₂/CO feed at 200°C, 280 psig and 1000 GHSV after 20 hrs on stream was 79% with product selectivities for CH₄ of 6.0%, CO₂ of 6.0% and C₂+ of 93.6%.

Synthesis Gas Reactions. Co/TiO₂ catalyst has a higher activity toward synthesis gas conversion, as shown in Table X.36, than conventional cobalt on silica or alumina or Co-Mg-thoria on kieselguhr, which was prepared following a published procedure (X.55). The 0.91 Schulz-Flory alpha value for the titania catalyst was higher than for conventional catalysts and was reflected in a C₁₀+ hydrocarbon yield that was >75%. Higher CO conversions in these Co/TiO₂ catalyst appear related to higher rutile concentrations and higher O₂ chemisorption values of the starting catalysts as shown in Table X.37. The pseudo first-order CO conversion rate constants calculated by Equation 1 correlate directly with the oxygen chemisorption values for these four catalysts, as shown in Figure X.4.

$$k = \frac{GHSV}{P} \ln \frac{1}{(1 - X)} \quad (15)$$

where:

x = fraction CO conversion,

P = reactor pressure in atm, and

GHSV = space velocity at ambient temperature and pressure in hr⁻¹.

Similar results were obtained with catalysts prepared by impregnating cobalt carbonyl onto 28% and 100% rutile titanias where the carbonyl was decomposed by heating in vacuum. Synthesis gas conversion over these catalysts shows that the high rutile catalyst gave much higher CO conversion (see Table X.38). Cobalt catalysts prepared either from the nitrate or the carbonyl gave essentially the same results.

Incorporation of 0.5 to 3% Re in the Co/TiO₂ catalyst further improved both oxygen chemisorption and CO conversion, as shown in Table X.37. The improvement resulting from addition of Re is probably through improving the reduction of the Co in the pretreatment step (X.56). Results from a 200 hr extended run, presented in (Figure X. show that CO conversion dropped from about ~98% to ~80%. Comparison with a Ru/TiO₂ catalyst with the Co-Re catalyst under the same conditions (Figure X.6) indicate the Co-Re catalyst was significantly more active than the Ru catalyst while both had similar selectivities for methane and CO₂ (Figure X.7).

Methanol Reaction. Examples of methanol conversions were given for a number of cobalt catalysts including Co/TiO₂, Co-Re/TiO₂, Co/ThO₂/TiO₂, and Co-Re/ThO₂/TiO₂. The effect of rutile concentration on methanol conversion was observed for catalysts containing 12% cobalt on titania. The 100% rutile catalyst completely converted the methanol while the 55% rutile titania support gave only 66% conversion (see Table X.39). The selectivities were also quite different with the catalyst having the lower rutile content being more selective for producing C₂+ hydrocarbon product and less CO₂.

Experimental data showing the effect of adding thorium on the conversion of methanol is provided in Payne and Mauldin (X.46). In these cases the rutile contents of the catalysts were not specified (see Table X.40). Assuming that the titania components in these catalysts had the same rutile concentration, the data show that

addition of thoria to the catalyst increases methanol conversion, decreases methane yield, and gives nearly the same Schulz-Flory alpha values. Comparisons with other state-of-the-art catalysts showed that conventional FT 100 Co/5 ThO₂/8 MgO/200 Kieselguhr catalyst gave higher methanol conversion but poorer C₂+ hydrocarbon selectivity under the run conditions. Compared to Co on silica or alumina, both Co-titania catalysts, with or without thoria, gave better C₂+ selectivity at comparable or higher methanol conversion levels. The liquid product was highly paraffinic as reflected in the 78.2% straight chain paraffinic content of the C₈ fraction from the thoria containing catalyst. Even over the Co/alumina catalyst, where methanol conversion was 64%, the yield of dimethyl ether was only 2.4%, indicating the non-acidic nature of the alumina support. At the low methanol conversion levels, dimethyl ether formation was quite small.

The presence of rhenium with cobalt in 56% rutile titania catalysts, either with and without added thoria, increased MeOH conversion (see Table X.41). Addition of 0.5 wt.% Re to Co/ThO₂/TiO₂ increased methanol conversion quite sharply from 49% to 100%. Conversion to CO₂ increased sharply while C₂+ yields decreased from 74% to 56%. The effect of Re/TiO₂ on methanol conversion was not provided.

Hydrogen partial pressure has a strong effect on methanol conversion and product selectivity. Payne and Mauldin (X.46) showed that increasing the H₂ partial pressure at constant methanol space velocity increased conversion from 38% to 83% (see Table X.42), decreased the yields of CO+CO₂, and sharply increased methane selectivity. The C₂+ yield appears to go through a maximum at a H₂ partial pressure of 17 psi. At low methanol pressures over a 12% Co/2% ThO₂/TiO₂ catalyst, the products are almost exclusively CO and H₂, except for a very small amount of methane.

A patent issued to Mauldin et al. (X.57) claims cobalt-titania catalyst to which is added small amounts of hafnium, zirconium, cerium or uranium to maintain the cobalt in a high state of dispersion and stabilize the catalyst during high temperature air treatment. The concentration of promoter to cobalt was specified as a weight ratio greater than 0.01 to 1 and typically between 0.04-0.25 to 1. Although there were no limits placed on the catalyst composition, the catalysts presented in the examples were prepared by impregnating high rutile titania either sequentially with Zr, Hf, Ce or U compounds followed by Co nitrate or simultaneously with the promoter metals and cobalt nitrate. In the preparation of these catalysts when the metals were added sequentially, the catalysts were calcined between metal additions. The final catalysts were then calcined at 400, 500 or 600°C to simulate catalyst regeneration and tested for synthesis gas reactions. CO conversions for the promoted catalysts were higher than for the non-promoted catalysts at all air treat temperatures >150°C, as shown in Figure X.8. The 500°C catalyst regeneration data plotted in Figure X.9 show that addition of approximately 0.5 wt.% promoter provides optimal thermal stabilization giving CO conversions of 70-80%. The examples also showed that addition of 0.06 wt.% Hf and 0.3 wt.% Zr, both of which fell within the limits of the claimed compositions, was not adequate to stabilize the Co/titania, although higher concentrations did stabilize the catalysts.

Synthesis gas conversion data were provided for a 2/1 H₂/CO mixture that was passed over a Co-Hf-TiO₂ catalyst at 1000 GHSV and 204°C at 280 psig to give 89% CO conversion with a 91% C₅+ hydrocarbon product selectivity. No other synthesis gas data were provided. Comparative runs with methanol, however, are reported for each of the metal promoters (see Table X.43). All of the promoted catalysts gave

higher MeOH conversion than the unpromoted catalysts with about the same selectivities for higher hydrocarbon product.

Silica Promoted Co/TiO₂

A patent issued to Iglesia et al. (X.58) claims compositions of cobalt on an inorganic refractory support comprised of a major portion of titania to which up to 15 wt.% silica has been added. This catalyst is utilized in another process related patent issued to Iglesia et al. (X.59). These two cases are identical except for the claims. The patent specifies that the Co may be incorporated onto the inorganic refractory titania support either before or after adding the silica or silica precursor. Incorporation of rhenium in the catalyst is covered in a subordinate claim. Although the main claim does not specify Re in the catalyst, the examples include only Re-containing catalysts.

In the examples, a series of catalysts, as described in Table X.44 were prepared starting with a CoRe/TiO₂ (Catalyst A) that was prepared by depositing Co and Re components from an acetone solution onto a 97% rutile titania and calcining at 250°C for 3 hrs. Two silica containing catalysts (Catalysts B and C) were prepared by impregnating Catalyst A with tetraethoxysilane (TEOS), treating with a stream of H₂O (40 Torr) in He while heating at 400°C for 13 hrs after which it was reduced at 250-400°C for 2-14 hrs. A catalyst that was free of silica but exposed to the same H₂O treatment (Catalyst D) was prepared by treating Catalyst A with H₂O (40 Torr)/He while heating at 400°C/13 hrs, after which it was reduced at 250-400°C for 2 to 14 hrs. The activities of the catalysts were determined at run times up to almost 200 hrs under conditions to give ~60% CO conversion. There was little difference in hydrocarbon selectivity observed by incorporating silica into the samples. Although the CO₂ yield was in every case quite small, it dropped to an almost imperceptible level with silica.

The increased stability of the silica containing catalysts was observed in reduced carbon buildup at low temperatures on the surface of the catalyst in the presence of CO. The "effect of SiO₂ during carburization suggests that it may prevent short term deactivation during the first few hours in H₂/CO environments; the effect is to increase the apparent site activity by maintaining surface cobalt atoms available during hydrocarbon synthesis."

Anatase Titania Supported Cobalt Catalysts

A patent issued to Soled et al. (X.60) claims both a composition of matter and a method for preparing a catalyst containing anatase titania. What appears to be the omnibus claim is claim 13 which claims a catalyst composition comprising Co composited with a ternary metal oxide support of titania having the general formula Co/Ti_{1-x}M_xO₂ where x is 0.01-0.14 and M is selected from the group consisting of silicon, zirconium, and tantalum and wherein the titania is an anatase polymorph stable under oxidative regeneration at temperatures of 400-750 °C. Claim 1, on the other hand, claims a method for preparing this catalyst which comprises contacting a titanium alkoxide or titanium chloride, such as TiCl₄, with a metal alkoxide or metal chloride, respectively, to form a solution; adding water to the mixture of alkoxides or an aqueous base to the mixture of chlorides to form a co-precipitate; separating the co-precipitate; calcining the dried co-precipitate to form a ternary metal oxide; depositing a cobalt metal compound solution onto the surface of the ternary metal oxide to form a composite; and activating the composite to form a catalyst. Activating the composite includes drying and calcining followed by reduction of the Co. Depending on the precedence of claims 1 and 13, the coverage may be broad as defined in claim 13 or it may be very narrow being confined to the composition prepared by the method disclosed in claim #1.

Neither the claims nor the specification in this case discuss the coexistence of mixtures of rutile and anatase forms in the titania. Likewise, the concentration of the anatase phase in the titania prepared by the method of this invention was also not revealed. If the composition of the claimed catalyst is limited to the material prepared according to the method in claim 1, then the question of anatase concentration is mute. However, if the patent covers all $\text{Co/Ti}_{1-x}\text{M}_x\text{O}_2$ compositions per claim 13 where M is silicon, zirconium, and tantalum and where titania is in an anatase form, the limits on anatase concentration covers only titania compositions that contain, at most, very small amounts of rutile. Regardless, this case is likely an improvement over Iglesia et al. (X.58) which claims cobalt on silica-modified titania wherein no limitation on the form of the titania is made. It also must be an improvement over Mauldin et al. (X.57) which claims catalysts comprising zirconium added to titania to maintain the cobalt in a high state of dispersion and stabilize the catalyst during high temperature air treatments. In the main claim, there are no limitations on the form of the titania. These three cases, however, provide Exxon with coverage for cobalt impregnated anatase to complement their many cases on rutile-rich titanias.

Apparently the reason why the anatase phase is stabilized at high temperatures is related to substitution of Si, Ta, and Zr cations into the anatase structure of the catalyst which apparently retards the formation of CoTiO_3 preventing the entrapment of the cobalt and preserving its specific surface area. Once cobalt titanates form, a higher temperature is required to reduce them to the metal. Through addition of Si, Ta, and Zr, the amount of the CoTiO_3 is decreased. For a Si incorporated polymorph, the concentration of the CoTiO_3 is decreased, as determined by XRD, and its concentration is a function of calcination temperature, as shown in Figure X.10. Silica incorporation

has no effect on the thermal properties of the catalyst but increases by approximately 100 centigrade degrees the temperature for onset of carburization in a synthesis gas stream, as shown in Figure X.11.

Catalysts incorporating each of the promoters were prepared and their stability to calcination was reported in the examples. Anatase titania was prepared by first hydrolyzing $\text{Ti}(\text{t-buO})_4$ and calcining at 430°C . Co as Co nitrate was then impregnated onto the substrate and calcined at $430\text{-}700^\circ\text{C}$. Calcining at 430°C gives anatase having a surface area of $120\text{ m}^2/\text{g}$ while calcining at 700°C transforms the anatase to rutile having a surface area of $2\text{ m}^2/\text{g}$. Silicon promoted titanate was prepared by adding the silicon alkoxide, tetramethylorthosilicate (TMOS), to $\text{Ti}(\text{t-BuO})_4$ following the above procedure. Surface areas containing various levels of silicon substitution were obtained upon calcination at 700°C :

<u>Si, %</u>	<u>m^2/g</u>
1%	52
3%	76
5%	119
14%	133

Zirconium promoted titanate was prepared by adding zirconium n-propoxide to $\text{Ti}(\text{t-BuO})_4$ following the above procedure. A catalyst containing 3% Zr had a surface area of $36\text{ m}^2/\text{g}$ while a 14% Zr catalyst had a surface area of $56\text{ m}^2/\text{g}$, both of which stabilized the anatase. A tantalum promoted titanate was prepared by adding tantalum ethoxide to $\text{Ti}(\text{t-BuO})_4$ following the above procedure. A catalyst containing 14% tantalum had a surface area of $71\text{ m}^2/\text{g}$. No FT data were provided in the patent.

Cobalt-Ruthenium on Titania

A patent issued to Iglesia et al. (X.61) claims a catalyst prepared by a process comprising impregnating titania with solutions of cobalt and ruthenium salts, drying, reducing the cobalt and ruthenium, treating the metals with an oxygen containing stream to form the oxides and reducing the oxides. A corresponding patent issued to Iglesia et al. (X.62) claims a process that utilizes this catalyst. The intimate contact of the Co and Ru in the catalyst lowers the temperature at which the cobalt is reduced to the metallic form. This results in a decrease in the amount of carbon deposited upon heating in synthesis gas at temperatures up to 500°C. Intimate contact is obtained by reducing the metals on the surface, calcining in air to reform the oxides and then reducing to the metal form. Unlike many of the other composition of matter patents, a corresponding process patent was not found.

TGA and DTA data provided in the patent showed that the carbon deposited more slowly on calcined Co-Ru/TiO₂ when subjected to a 1:1 H₂/CO synthesis gas mixture than on either Co/TiO₂ or uncalcined Co-Ru/TiO₂. The patent states that the advantage of the Co-Ru combination relative to other catalysts is that "a combination of increased cobalt oxide reducibility and inhibited catalyst poisoning by carbon are believed to account for the increased number of active sites observed on calcined CoRu/TiO₂ catalysts."

Energy dispersive X-ray (EDX) analysis of uncalcined versus calcined CoRu/TiO₂ catalysts that had been aged in process runs for 700 hrs showed that both aged catalysts were identical. Apparently Ru in fresh uncalcined CoRu/TiO₂ catalyst cannot be detected since its concentration over the surface is below detection limits. However, in calcined CoRu/TiO₂ catalyst that has been reduced, Ru can be detected in the cobalt

particles where it concentrates sufficiently to be detected by EDX. Apparently, Ru also concentrates in aged uncalcined CoRu/TiO₂ catalysts since the EDX analysis was the same as the calcined sample.

In the examples, three titania catalysts were prepared starting with a sample containing 70% rutile. The first catalyst, Co/TiO₂, was impregnated with cobalt, calcined at 400°C for 4 hrs in air and reduced in H₂ at 400°C for 16 hrs (Catalyst A). Ruthenium was then impregnated onto this catalyst and reduced to give reduced-Co-Ru/TiO₂ (Catalyst B). A portion of this material was calcined in air at 300°C/4 hrs and reduced in H₂ to give the calcined-reduced Co-Ru/TiO₂ composition of this invention (Catalyst C). A Co/SiO₂ catalyst was prepared for comparison by impregnating silica with a cobalt salt (Catalyst D). In synthesis gas runs in which the space velocity was adjusted to attain comparable conversion levels (see Table X.45), the cobalt time yields of the calcined-reduced Co/Ru/TiO₂ catalyst was higher than for the other three catalysts. This appears to be similar to Gulf patents where reduced-oxidized-reduced catalysts had a higher activity than the reduced catalyst (X.63). The methane and C₅+ selectivities of reduced-Co/Ru/TiO₂ and the oxidized-reduced Co/Ru/TiO₂ were very nearly the same, but slightly better than Co/TiO₂ or Co/SiO₂ catalysts.

Data were provided that showed that hydrogen regeneration of oxidized-reduced Co/Ru/TiO₂ catalysts that had been aged from 10-30 days, was more complete than for the untreated Co/Ru/TiO₂ catalyst (see Table X.46). CO conversions and methane and C₅+ selectivities were higher for both the fresh and regenerated oxidized-reduced Co/Ru/TiO₂ catalyst than for the untreated reduced Co/Ru/TiO₂ catalyst and the ruthenium free Co/TiO₂ catalyst.

Iron on Titania

A series of three patents were issued to Fiato and Kugler which are identical except for the claims. Fiato and Kugler (X.64) claim a composition consisting of a mixture of iron carbide and ilmenite, either with or without an alkali metal promoter, having an Fe_2O_3 concentration of 2-25 mg/cm², wherein the catalyst is formed by depositing an iron salt onto titania, calcining, treating with H_2 free of CO at 300-500°C until the composite is reduced and then contacting with CO at a temperature that is 100-200°C lower than the H_2 reduction temperature. In this preparation, the iron precursor deposited on the titania is calcined to form the iron oxide which is reduced in H_2 to form Fe metal which then reacts with CO to form carbide. X-ray diffraction showed that the calcined material contained anatase and rutile forms of TiO_2 , FeTiO_3 (ilmenite), and metallic Fe. X-ray diffraction of the sample after CO treatment showed that the TiO_2 and ilmenite were unchanged, metallic Fe disappeared, and Fe_5C_2 was formed.

In one of the other cases, Fiato and Kugler (X.65) claim a process for producing hydrocarbons from synthesis gas using this catalyst composition. In the other, Fiato and Kugler (X.66) claim a process for improving the activity of this catalyst in a FT reaction by cycling the temperature in the reaction zone, by increasing the temperature by 50-150°C above the FT reaction temperature in the absence of H_2 for from 1-6 hours and then returning to reaction temperature and reestablishing the H_2 content of the feed stream. None of the examples actually illustrated the effectiveness of this procedure.

The activity of a series of catalysts indicated that the Fe concentration in these catalysts must be ≥ 2 mg $\text{Fe}_2\text{O}_3/\text{m}^2$ of titania (see Figure X.12). The activity of an Fe supported titania catalyst of this invention that had been both reduced and subsequently carbided, with an Fe concentration of 0.002 g Fe/m² TiO_2 , was higher than a

corresponding material that had not been carbided, i.e. 27 versus 60% CO conversion, respectively. The hydrocarbon selectivities for the carbided catalyst was lower for methane and higher for C₅+

A patent issued to Wachs et al. (X.67) claims catalysts comprising an iron carbide on a modified titania support comprising at least 25% of an oxide of Nb, V, and Ta in a noncrystalline form and containing at least 2 mg Fe, as Fe₂O₃, per m² support surface. A corresponding process patent, which was essentially identical, issued to Wachs et al. (X.68) claims a process for producing hydrocarbons using this catalyst. These cases relate to an application by Wachs and Chersich (X.40), that was filed on the same day, that claims compositions of tantalum oxide on titania support that were used as catalyst supports. The background on this case was that the Fe/Group Vb oxide/TiO₂ combination was anticipated in the specification by Tauster et al. (X.27) but not actually claimed as compositions of that invention. The Wachs et al. patent (X.67) differs in that the titania surface was modified by addition of limited amounts of Nb, V, and Ta to modify the TiO₂.

The catalysts used in the example were prepared by slurring Degussa P-25 titania with an ethanol solution containing either Nb(C₂H₅O)₅ or VO(C₂H₅O)₃. The solvent was removed, the V or Nb ethoxides were oxidized, and the resulting powders calcined in pure O₂ at 575°C for 2 hours. The resulting supports contained 10% Nb₂O₅ or V₂O₅ on TiO₂. The Fe precursor was impregnated onto the support, reduced in H₂ at 500°C for 5 hrs, and carbided by exposure to synthesis gas. Results from runs with synthesis gas (see Table X.47) show that at similar CO conversions levels, i.e. 47-49% or 60-70%, the vanadia and niobia catalysts gave lower methane and higher olefin

selectivities than a Fe/TiO₂ catalyst. At the same run temperature, i.e. 270°C, the methane yields were lower for the catalysts of the invention.

Nickel on Titania

Two patents related to nickel-titania catalysts were issued; in one, Ni as a promoter of titania based catalysts was claimed while in the second, titania promoted bulk Ni catalysts were claimed. The first patent issued to Vannice and Garten (X.69) claims a FT process that uses a catalyst comprising nickel on a titanium-containing oxide support with a Ni concentration up to 75% by weight. The second patent issued to Kugler and Garten (X.70) claims a FT process using a catalyst comprising bulk nickel promoted with up to 10% titania. These two patents pretty well cover the use of all possible combinations of Ni and titania catalysts in the FT reaction.

In the first patent, Vannice and Garten (X.69) claim that nickel on titania exhibits higher activity, improved selectivity to higher hydrocarbons, improved life and tolerance to sulfur, and resistance to Ni carbonyl formation. The catalysts were prepared by impregnating nickel salts onto the titania support and reducing in H₂ at temperatures >400°C. Synthesis gas conversion at 1 atm over these Ni/TiO₂ catalysts was higher than with bulk nickel or Ni on silica, alumina, and graphite. C₂+ paraffin selectivity versus CO conversion is shown in Figure X.13. In these runs, the Ni/TiO₂ catalysts had higher CO conversions per gram Ni, and lower methane and higher C₂+ hydrocarbon selectivities. Still, the methanation reaction was quite high for the Ni/TiO₂ catalyst. An experiment was described in which the volatility of the Ni was shown to be lower over the TiO₂ catalyst than a Ni/SiO₂ catalyst (see Figure X.14).

In the second patent, Kugler and Garten (X.70) claim the addition of titania to bulk nickel shifts hydrocarbon selectivity from methane to C₂-C₆ hydrocarbons, along

with trace quantities of C₇ product. The influence of increasing titania concentration up to 8.4%, as shown in Table X.48, was to increase the CO conversion while the selectivity to higher hydrocarbons increased. Since the relative rates for CO conversion and CH₄ formation both increased, the changed product distribution reflected the much higher increase in the rate of CO conversion versus the smaller increase in methanation rate. The selectivity of the 8.4% TiO₂ on Ni catalyst is very similar to the selectivity of 10% Ni on TiO₂.

A physical mixture of 1/1 Ni powder and TiO₂ behaved very similarly to Ni powder indicating that for such a physical mixture a synergistic interaction did not occur upon activation in H₂. The effect that was observed with the catalysts prepared by addition of solutions of the Ti oxide precursor to bulk Ni indicates a chemical interaction between the titania and the Ni, since a change in activity and selectivity occurs. Evidence for a chemical interaction was observed in ESCA that showed that Ti exists on the catalyst surface before reduction as Ti⁺⁴. After reduction in H₂ at 250°C, some of the Ti is in a lower oxidation state but not reduced to the metallic form. The titanium promoter changes the surface area and chemisorption properties of the bulk nickel. Small quantities of Ti additive increases the surface area while creating an oxide layer, as observed by ESCA. Concomitantly, H₂ chemisorption was reduced due to physical blockage of the sites. The highest CO conversion level was observed at the lowest H₂ chemisorption level for the Ti promoted samples.

MANGANESE OXIDE SUPPORTS

Exxon has been assigned 2 patents which claim compositions, or use thereof, comprising the five Group VIII metal oxides of iron, cobalt, nickel, iridium and ruthenium on manganese oxide supports which are reduced at a temperature sufficient to

suppress hydrogen chemisorption. These cases parallel Tauster et al. (X.27) who claim catalyst compositions comprising Group VIII metals on Group IVb and Group Vb metal oxides that are reduced at a temperature to suppress hydrogen chemisorption. Since manganese falls in Group VIIb, it falls outside of Tauster et al. (X.27). There are other manganese patents assigned to Exxon which involve the use of manganese in spinels which are discussed elsewhere in this review.

Ruthenium

A patent issued to Kugler et al. (X.71) claims a FT process that provides improved yields of C_2 - C_4 olefins that uses a catalyst comprising ruthenium on a manganese containing support which has been reduced at a temperature sufficient to suppress hydrogen chemisorption. Manganese can be used in its pure form or combined with alumina, carbon, silica, or oxides of Groups IVb and Vb. A 1% Ru/MnO catalyst was prepared by impregnating MnO with $RuCl_3$ and reducing with H_2 at 450°C. Synthesis gas mixtures, having H_2/CO ratios from 1.6 to 3, were passed over the catalyst at 300°C and at 1 atm pressure to give CO conversions less than 10%. Under those conditions Ru/MnO catalyst gave higher yields of C_2 - C_3 olefins and lower yields of CH_4 relative to a Ru/Al_2O_3 catalyst.

Iron, Cobalt, Nickel, Iridium

A composition of matter patent issued to Tauster and Fung (X.72) claims compositions comprising iron, nickel, cobalt and iridium supported on a manganese containing oxide support, the improvement comprising contacting said composition with a reducing atmosphere at temperatures $\geq 300^\circ C$, except for iridium which requires a temperature $\geq 250^\circ C$, to produce a catalyst composition which exhibits suppressed hydrogen chemisorption. Under these conditions, the reduced materials would,

therefore, be in the SMSI state as defined by Tauster et al. (X.27). Two different 2% Ir/MnO catalysts were prepared by impregnating the metal onto two different MnO substrates. The two MnO substrates prepared by reducing battery grade MnO_2 in H_2 at 540 and 740°C had surface areas of 21.7 and 7.8 m^2/g , respectively. Less than 0.01 atoms of hydrogen were adsorbed per atom of Ir for each of these catalysts that had been reduced in H_2 at 500°C versus values of 0.46-1.08 for samples reduced at 200°C. A sample (prepared at 740°C) reduced at 350°C adsorbed less H_2 (0.041 atoms per atom Ir) indicating it was in the SMSI state.

Cobalt - Manganese Spinel

A patent issued to Soled et al. (X.73) claims compositions comprising a copper promoted Co-Mn spinel having a formula $\text{Co}_{3-x}\text{Mn}_x\text{O}_4$ where x is 0.5-1.2. Subordinate claims specify a Cu concentration from 0.1 to 5 g-atom percent based on the total amount of Co and Mn in the catalyst and a surface area $>5 \text{ m}^2/\text{g}$. A corresponding patent, having an identical specification, which was issued to Soled et al. (X.74), claims a Fischer-Tropsch process using this composition. The spinel was prepared using the alpha-hydroxy aliphatic carboxylic acid method that has been used for all these high surface area spinels. A Co_2MnO_4 spinel, having a surface area of 30-60 m^2/g that is isostructural with Fe_3O_4 , was prepared from a solution of $\text{Co}(\text{NO}_3)_2$ and $\text{Mn}(\text{NO}_3)_2$ in the presence of citric acid and ethylene glycol, which was evaporated and calcined in air at 350°C for 30 min. The resulting spinel was impregnated to give a 1 wt.% Cu concentration. The activity of the Cu-promoted spinel in a slurry reactor with synthesis gas was compared with the spinel without added Cu under conditions shown in Table X.49. The catalyst was first reduced in situ with synthesis gas. The Cu-promoted

Co_2MnO_4 spinel had higher activity and gave higher olefin selectivity than unpromoted Co_2MnO_4 spinel or a Co_3O_4 /1% Cu catalyst.

GROUP VIII METAL SUPPORTED CATALYSTS

Several patents were issued in which inorganic metal oxides were used as supports for Group VIII metals. A patent issued McVicker and Vannice (X.75) claims catalysts prepared by depositing K or Rb Group VIII metal carbonyl cluster complexes on a high surface area support material, drying in the absence of oxygen and reducing at elevated temperatures. A companion case, issued to McVicker and Vannice (X.76), which is identical both in title and text, excluding claims, covers a process application for these catalysts. The catalysts were prepared by depositing bimetallic carbonyl compounds onto high surface area supports from solutions in organic solvents. At least some, if not all, of the materials were highly sensitive to air. A whole laundry list of potential bimetallic carbonyls were presented, of which 6 were actually used in catalyst preparations. Of the Group VIII carbonyls, only Pd and Os were not specifically included in dependent claims. Re, Ru and Ir, which were actually used in preparing catalysts, were specifically covered in dependent claims. Supports that were specifically claimed were alumina, silica, silica-alumina, titania, zirconia, hafnia, tantalum, niobia, vanadia, and magnesia.

Several catalysts were tested by passing a 3/1 H_2 /CO synthesis gas mixture over the catalysts at 250 to 284°C and 1 atmosphere. Under these conditions, very low CO conversions were observed. More long chain olefins were formed over the cluster catalysts of this invention than with conventional catalysts prepared by impregnating alumina (eta) with aqueous solutions of Fe nitrate and KNO_3 .

Palladium on Alumina

A patent assigned to Vannice and Garten (X.77) claims a process for producing methane by passing synthesis gas over palladium supported on an acidic metal oxide selected from alumina and HY zeolite with the palladium metal particle being maintained at $<100\text{\AA}$. CO conversions of 3.5% were obtained when a 3/1 H_2/CO mixture at 1 atm was passed over these catalysts. Methane was essentially the only hydrocarbon product. The methane yield per Pd surface was higher for the catalysts of this invention than for Ni on a 5% $\text{Ni}/\text{Al}_2\text{O}_3$ catalyst, although the CO conversion over the nickel catalyst was 55% under these conditions.

Platinum on Alumina

A patent issued to Vannice and Garten (X.78) claims a process for producing dimethyl ether by passing CO and H_2 over platinum supported on alumina. Over a 1.16% $\text{Pt}/\text{Al}_2\text{O}_3$ catalyst at 274°C for a 1/1 H_2/CO gas mixture at 10 atm pressure, 2.5% CO was converted to hydrocarbons with a hydrocarbon selectivity of 70% methane, 8% ethane, and 23% dimethyl ether.

Nickel on Silica or Alumina

A patent issued to Yates and Murrell (X.79) claim Ni catalysts having Ni surface areas of $200\text{--}400\text{ m}^2/\text{g}$ prepared by slurring a Ni metal precursor in a nonaqueous solvent with a high surface area refractory oxide, removing the solvent and reducing with H_2 to form Ni metal. A use for these catalysts is in hydrocarbon synthesis as in the FT reaction. Ethane hydrogenolysis and benzene hydrogenation are included in the examples. However, no examples are provided that cover conversion of synthesis gas. The specification states that several co-metals, of which potassium is one, should be avoided since they act as catalyst poisons.

MOLYBDENUM CATALYSTS

A patent issued to McCandlish and Kugler (X.80) claims a FT process using a catalyst comprised of molybdenum oxycarbonitride. The catalyst, in which the oxygen, carbon and nitrogen are distributed throughout the bulk structure, is prepared by thermally decomposing an ethylenediammonium molybdate at 650°C in an inert atmosphere. The catalyst was pyrophoric and could be passivated with oxygen for handling in air. The active form was easily regenerated in H₂ at 450°C. CO conversions up to 20% were obtained over this catalyst at 254 to 315°C with a 1/1 H₂/CO synthesis gas mixture at 1 atm and 2400 GHSV. Methane was the dominant product under these conditions.

ALCOHOL SYNTHESIS

A patent issued to Apesteguia et al. (X.81) claims catalyst compositions consisting of a solid solution or coprecipitated mixture of a first oxide and a second oxide, wherein the first oxide is selected from yttria and rare earth oxides and a second oxide is a Group Ia oxide and Group Ib metal. These catalysts are useful for conversion of synthesis gas to alcohols, especially isobutanol and methanol. Several representative catalysts were prepared: Cu impregnated onto cerium oxide; coprecipitated Cu, MgO and ceria; K impregnated onto coprecipitated Cu, MgO and ceria; Cu supported on MgO and yttria. These catalysts provided very large yields of alcohols, primarily methanol along with lesser amounts of isobutanol (see Table X.50). Methane and CO₂ yields were also quite sizable.

PROCESS IMPROVEMENTS

Although the overwhelming number of FT related patents that have been assigned to Exxon are related to catalyst compositions or their use, several patents

related to improvements in the design or operation of the FT process have been issued. Many of the more recently issued patents have concentrated on process improvements.

The FT-type process improvements that are covered are:

- ! use of 2-stage process configuration to improve hydrocarbon selectivity,
- ! improved product selectivity through olefin addition to the feed,
- ! improved CO conversion and C₅+ selectivity through water addition to the feed,
- ! modified gas inlet system to improve axial distribution of particulate catalyst in a slurry reactor,
- ! use of downcomers to redistribute catalyst in a slurry reactor,
- ! use of pentane as heat transfer fluid,
- ! bundled tubular reactor with shell-side cooling,
- ! fixed-bed start-up protocol to prevent temperature runaway,
- ! method for defining operating conditions for a slurry reactor,
- ! method for activating ex situ reduced cobalt slurry catalyst,
- ! method for rejuvenating and redistributing catalyst in a slurry reactor,
- ! method for removing fines from particulate catalysts.

2-Stage Processes

Two different 2-stage process configurations are covered. In one, a patent issued to Kim and Fiato (X.82) claims a process in which synthesis gas contacts in a reaction zone in a first bed a first catalyst having a high olefin selectivity and contacting the resulting olefins in a second bed with a catalyst having a high selectivity for converting olefins to heavier paraffinic hydrocarbons. The claim specifies that the first bed catalyst is selected from a group consisting of Fe/Zn/Ce/K, Fe/Mn/K and Fe/Co/K

and the second bed catalyst is selected from the group consisting of Ru/TiO₂, Ru/SiO₂, and Ru/Al₂O₃. The process operates at 150-220 psig with the temperature of the first catalyst being about 260-280°C and the second catalyst being about 190-210°C. The range of the preferred H₂/CO ratio, as stated in the specification, was 1.5 to 2.5. An example is provided that shows that over a Fe/Zn/Ce/K catalyst at a CO conversion of 59%, the selectivity to CO₂ was 26% with the remaining product being hydrocarbons (see Table X.51). Hydrocarbon formation is split between the 1st and 2nd catalyst beds in a ratio of 45/55. Based upon approximately equal yields from the two beds and equal yields from each of the two catalysts operating alone, a linear combination predicts a decrease in methane selectivity and an increase in C₁₀+ selectivity when operating in this fashion. Experimentally, the observed methane and C₁₀+ selectivities were even better than predicted (see Table X.52).

A second configuration involves an interstage product separation step. A patent issued to Fiato (X.83) claims a two stage hydrocarbon synthesis process comprising reacting synthesis gas at reaction conditions in a first stage in the presence of a supported cobalt or ruthenium catalyst at a pressure ≥ 10 atmospheres, separating liquid from H₂ and CO, and reacting the remaining H₂ and CO at a pressure less than 10-12 atmospheres, but no greater than the first stage, in the presence of cobalt supported on alumina at reaction conditions. This process configuration takes advantage of the apparently higher activity of Co/Al₂O₃ catalysts at lower partial pressures of CO and H₂ relative to catalysts comprising Co or Re on other oxides supports, such as titania. 2-Stage processes having interstage separation of hydrocarbon product, in which the remaining H₂ and CO are recompressed, have the additional advantage of lower energy requirement.

Product Improvement through Feed Modification

Olefin Addition to Feed. Two patents were issued for processes that reduce methane formation in the FT process through injection of olefins. The first patent issued to Kim (X.84) claims a process with a catalyst comprising Group VIII (Fe, Co, Ru) metals supported on an inorganic oxide support wherein olefins are added to the feed to reduce methane formation. The second patent issued to Iglesia (X.85) claims further methane reduction by injecting the olefins at a point below the inlet of the reactor.

Kim (X.84) showed that injection of ethylene in the feed stream increased CO conversion and decreased methane selectivity. A 2/1 H₂/CO synthesis gas mixture gave a CO conversion of 8.4% and a methane selectivity of 6.4% when passed over a Ru/TiO₂ catalyst at 200°C at 70 psig at a flow rate of 55 standard cm³/3 g catalyst/min. When 8.2 mol % ethylene was injected into the feed stream, CO conversion increased slightly to 9.0% and methane selectivity dropped to 3.5%. When 20% ethylene was added, the methane selectivity dropped even further to 2.7%. In another case, when 4% 1-decene was substituted for ethylene, an approximate 20% decrease in methane selectivity occurred. Over a precipitated bulk Fe catalyst the introduction of 9.6% ethylene into the same synthesis gas mixture at the same temperature and pressure at a flow rate of 100 standard cm³/10 g catalyst/min caused a 30% decrease in methane selectivity.

In the 2nd case, methane was further reduced through adding the ethylene downstream of the inlet of the reactor. A patent issued to Iglesia (X.58) claims that for a FT process using an Fe, Co or Ru catalyst, the methane yields are further reduced when the olefins are added to the reactor bed below a point equivalent to 10% of the distance from the top to the bottom of the reactor bed and above a point in the reactor

bed equivalent to 10% of the distance from bottom to the top of the reactor bed. The addition level is stated as the amount sufficient to suppress methane formation. In the examples, for ruthenium and cobalt-ruthenium on titania catalysts, adding ethylene below the top 1/3rd of the catalyst bed decreased the amount of ethane produced relative to the amount of ethylene added to the feed. Likewise, the amount of C₃+ increased accompanied by a small decrease in methane yield, as shown in Table X.53.

Water Addition to Feed. A patent issued to Kim (X.86) claims enhanced CO conversion and C₅+ selectivity for a once-through, fixed or slurry bed FT process comprising contacting the synthesis gas containing 1-70 vol % water in a reaction zone with a catalyst consisting of cobalt, ruthenium and mixtures thereof on titania converting 90% of the CO to liquid hydrocarbons in the substantial absence of CO₂. This case involved numerous filings and abandonments over an eight year period from the time of the first filing on July 13, 1985. The long background discussion of numerous prior patents outlines the extensive number of related cases. Numerous examples were shown for a range of catalysts exhibiting increased CO conversion, decreased methane selectivity and increased C₁₀+ liquid yield in the presence of added water.

Reactor Design

Modified Gas Inlet System. Two patents were issued related to the design of FT reactors. One patent issued to Chang and Coulaloglou (X.87) claims a method for improving axial distribution and mixing of particulate catalyst in a slurry bubble column by introducing a secondary gas into the column at a location within the lower 20% of the vertical height of the column but above the gas distributor plate. This gas stream can be part of the synthesis gas feed, recycle gas, inert gas, condensed light hydrocarbons or light synthesis hydrocarbons which vaporize under conditions present in the column.

A figure is presented of experimental data taken in a 5 ft diameter by 30 foot high slurry bubble column that shows that the solids distribution in the reactor is more uniform when using this gas inlet configuration.

The basis of this design is that since solids distribution along the axis of a column is a function of gas velocity in the column, by increasing gas velocity, solids distribution will decrease in the lower part of the column and increase in the upper part. The key to the method disclosed in this patent is that introducing a disproportionate share of the gases at an inlet point source close to but above the distributor inlet will reduce the concentration of solids in that particular portion of the reactor and result in an increase in solids concentration in other portions of the reactor. The overall result is a more even distribution of solids in an axial direction.

Downcomers. A patent issued to Behrmann et al. (X.88) claims a method for redistributing catalyst in a slurry reactor by use of a downcomer. The downcomer is specified as a vertical conduit which is open at both ends, fully submerged in the slurry with the bottom near the bottom of the reactor and the top near the top surface of the slurry. The bottom is shielded by a baffle plate to divert gases from rising from the bottom and gas free slurry enters at the top and passes down the conduit and out at the bottom. The preferred cross sectional area of the downcomer should be no more than 2% of the total cross sectional area of the entire reactor. An example is provided using the same equipment described under Pedrick et al. (X.89) in which the bubble column was run both with and without a downcomer in operation. In both cases rejuvenation tubes were operated in an equivalent manner. The results showed that axial distribution of the catalyst was more uniform when the downcomer was in operation, as shown in Figure X.15.

A patent issued to Chang (X.90) claims a slurry bubble column reactor design incorporating a peripheral downcomer. The reactor comprises a double walled vessel wherein the inner vessel serves as the main reactor zone and the peripheral circumferential top rim of the inner vessel wall, having attached to it an inverted channel having an apex and two edges, being attached to the inner wall along the outer edge of the inverted channel. The second edge of the inverted channel extending over the main reaction zone creating a gas space within its inverted contour with a gas vent extending upward from the inverted channel. A liquid by-pass pipe extends from below the top of the liquid level interface through the inverted channel between the attachment of the inverted channel to the inner reactor wall and the apex of the channel providing a means through which slurry flows into the peripheral downcomer section. This design is shown in Figure X.16 wherein the outer edge 8A of the inverted channel is attached to the top of the inner vessel wall. The innermost edge is in contact with the slurry in the main reaction zone. Gas disengaging from the slurry trapped in the inverted channel exits into the gas disengagement space 5 through line 12 and slurry exits through line 13 onto the top of inverted channel outside the apex 10 through line 13 into the downcomer section 4. The higher density in the downcomer section promotes flow from the top of the vessel to the bottom. A more complete description of this invention can be obtained by referring to the patent specification.

Heat Transfer System. A patent issued to Stark (X.91) claims a method for removing heat from a FT reactor which comprises passing pentane through the tube-side of cooling tubes, vaporizing the pentane to a pressure greater than the pressure in the reaction zone and recovering the vaporized cooling medium. In a preferred embodiment of this invention the vaporized pentane is sent to an expander where the

high pressure energy is recovered. The low pressure vapor leaving the expander is fed to a condenser where it is liquified and then pumped up to pressure and fed back to the reactor. The recovered energy can be used to drive compressors for an air separation plant or turbogenerators to generate electricity.

Tube-in-Shell Reactor. A patent issued to Koros (X.92) claims a slurry FT reactor wherein the slurry catalyst is disposed in a plurality of vertically arranged tubes having a length/diameter ratio of at least 10 with each tube surrounded by a common heat transfer medium disposed within the shell of a shell and tube reactor, the heat transfer medium not in fluid communication with the slurry liquid. The description of the operation of a reactor comprising a 5.76 in ID x 50 ft long pipe mounted in a 12 inch pipe cooling jacket was provided. Liquid heights varied between 12 and 32 feet with linear gas velocities up to 7.9 cm/sec. For a 2.1/1 H₂/CO synthesis gas mixture at a superficial velocity of 5 cm/sec, 2200 GHSV, reactor pressure of 285 psig, and steam jacket pressure of 140 psig, CO conversions in excess of 50% were obtained. The temperature of this run was not given.

Reactor Operation

Reactor Start-up. A patent issued to Arcuri (X.35) claims a procedure for the start-up of a fixed-bed FT reactor that allows a flexible and more effective response to a potential temperature runaway. While elevating the temperature, pressure and feed flow rate to line-out levels, the composition of the H₂ and CO in the feed is maintained at a H₂/CO mole ratio not exceeding 90% of the mole ratio at lineout. After the temperature, pressure and feed flow rate reach normal operating levels, the H₂/CO ratio is gradually increased to the operating lineout mole ratio.

The patent illustrates the advantage of using this operating protocol relative to using temperature as the main control parameter. Comparative exotherms are provided for two different startup procedures used on a 1/2 inch ID, 6 foot long tubular pilot scale FT reactor that was submerged in a sand bath, as shown in Figure X.17. Following a conventional start-up procedure in which temperature is slowly increased to bring the reactor online, a very significant temperature runaway occurred. In this example, the final target operating conditions were 359°F with a 2.08/1 H₂/CO synthesis gas mixture at 1000 GHSV at 280 psig. The steps that were followed and the corresponding exotherms that resulted in each step were as follows:

1. Synthesis gas mixture and flow rate were established at lineout conditions at a pressure of 60 psig and a sand bath temperature of 337°F. The maximum exotherm in the bed during this period was 5°F.
2. Pressure was then increased to lineout pressure of 280 psig and held 3 days. A maximum exotherm of 12°F resulted.
3. Then temperature was increased slowly from 337 to 353°F and held 24 hours. During this period the maximum exotherm was 21°F.
4. Afterwards, the temperature was increased 2°F over a 40 min period to 355°F. The magnitude of the maximum exotherm remained the same at 22°F.
5. However, when the temperature was increased over a 2 hour period to 359°F, which was a 4°F change in temperature, the maximum exotherm increased to 242 F°, indicating a severe temperature runaway.

By contrast, the exotherms were much less when the procedure taught in the patent was followed, namely using a decreased H₂ content in the feed gas. In this

example, the target lineout reactor conditions were 380°F with a 2.1/1 H₂/CO synthesis gas mixture flowing at 1000 GHSV at 280 psig. The steps that were followed and the corresponding exotherms that resulted in each step, as shown in Figure X.18, were as follows:

1. The H₂ feed gas (1.8/1 H₂/CO) rate was brought to 910 GHSV at 60 psig and 337°F. The maximum exotherm was 7°F.
2. The pressure was increased to the lineout pressure of 280 psig over 0.5 hours. The maximum exotherm was 9°F.
3. The temperature was increased almost to the lineout temperature of 374°F in 1 hour during which the maximum exotherm was 17°F.
4. H₂ in feed gas was increased to a 2.0/1 H₂/CO ratio in 1 minute as flow rate increased to 970 GHSV. Maximum exotherm was 23°F.
5. The H₂ in feed gas was increased to a 2.1/1 H₂/CO ratio as flow rate increased to the final 1000 GHSV. The maximum exotherm was 25°F.

During this sequence the exotherm remained under control and space time yield data was higher with a higher CO conversion. Another example was also given that illustrates how rapidly an exotherm can occur in a FT synthesis reactor.

Setting Operating Conditions. A patent issued to Herbolzheimer and Iglesia (X.93) claims a method for operating a solid-liquid-gas bubble column having a diameter >15 cm for FT synthesis over a supported cobalt catalyst in which the solids are fluidized by the gas. The invention comprises:

- (a) injecting gas at an average gas velocity >2 cm/sec;

- (b) fluidizing the particulate catalyst having an average diameter $>5 \mu\text{m}$ in an expanded liquid column >3 meters in height and a particle settling velocity U_s and a dispersion coefficient D , such that

$$0.5 (U_s - U_L) \leq \frac{D}{H}, \text{ where } H > 3\text{m}$$

where

$$U_s = \frac{1}{18} d_p^2 \frac{\rho_s - \rho_l}{\mu} g f(C_p), \text{ where } d_p > 5 \mu\text{m}$$

- (c) operating at plug flow at a gas velocity U_g , expanded liquid height H , and dispersion coefficient D such that

$$U_g \geq 0.2 \frac{D}{H} \text{ where } H > 3 \text{ m}, U_g > 2 \text{ cm/sec.}$$

In one example using a Co-Re/TiO₂ catalyst having a density of 2.7 g/cm³, a liquid density of 0.7 g/cm³, and a wax viscosity of 0.01 g°cm/sec, the particle settling velocity is:

$$U_s (\text{cm/sec}) = 1.1 \times 10^{-4} [d_p (\mu\text{m})^2]$$

For a 60 μm average particle, $U_s = 0.39 \text{ cm/sec}$. For a liquid velocity of $0.5 U_s$, and a column height of 3 m, a gas velocity of 2 cm/sec provides a Peclet number of 10, which

is the minimum gas velocity allowed that would maintain suspension of the solids in the column and maintain a plugflow operation in the column.

Catalyst Pretreatment

Catalyst Activation and Rejuvenation. A patent issued to Mitchell (X.94) claims a method for activating a fresh, reduced cobalt containing FT catalyst by treating the catalyst with H_2 in hydrocarbon liquids for a period sufficient to increase catalyst productivity. A patent having an identical specification issued to Mitchell (X.95) claims a process using the method of catalyst activation that is run under FT conditions. The method applies specifically to treating catalysts that had been previously reduced ex situ and exposed to the atmosphere before introduction into a slurry system. Such catalysts are suspended in a slurry and treated with H_2 at hydrocarbon synthesis temperature and pressure with temperatures no lower than $40^\circ C$ below hydrocarbon synthesis temperature. Another patent issued to Mitchell (X.96) claims a method for rejuvenating partially deactivated catalysts which is essentially the same procedure described above. An example for activating a 12% Co-1% Re on a 94% TiO_2 -5% Al_2O_3 catalyst by reducing the catalyst with H_2 was given. Following reduction, catalyst was passivated with a CO/H_2 stream. This passivated catalyst was combined with wax in a slurry reactor and treated with H_2 . Synthesis gas productivity over the treated catalyst increased to 100% relative to 25-60% productivity for the non- H_2 treated catalyst. The effect of several periods of catalyst rejuvenation during a 50 day run on catalyst productivity following this method is shown in Figure X.19.

A patent issued to Pedrick et al. (X.89) claims a method by which reversibly deactivated particulate hydrocarbon synthesis catalyst in a gas-slurry reactor is rejuvenated and more uniformly distributed in the reactor. A hydrogen rich gas, injected

into the bottom of a vertical draft tube which is fully immersed in the slurry, forces the catalyst up the draft tube while concomitantly reactivating the catalyst, which is discharged from the top into the upper portion of the slurry phase. The examples contained results from a series of balances made during a run in a 4 ft diameter by 35 ft high reactor that show both activation and axial redistribution of the catalyst. During the run, various combinations of draft tubes fed with H_2 , which were commonly referred to as rejuvenation tubes, and draft tubes fed with tail gas, were employed. The maximum flue-gas fed draft tube plus rejuvenation tube cross-sectional area for any of the run conditions was 2.6% of the cross sectional area of the reactor. A feed gas mixture comprising 56% H_2 /26% CO/13% CO_2 /5% CH_4 , by volume, was fed to the reactor containing a 12% Co-1% Re on a 94% TiO_2 -5% Al_2O_3 slurry catalyst at 210-230°C and 20 atm. When operating the reactor with two-2 inch diameter and two-4 inch diameter flue-gas fed draft tubes and one-3 inch diameter rejuvenation tube, the superficial velocities in the respective locations were:

inlet,	12-14 cm/sec;
outlet,	10.5-12.1 cm/sec;
draft tubes,	58-60 cm/sec;
rejuvenation tubes,	40-70 cm/sec.

Under these conditions the axial dispersion of the catalyst in the reactor improved significantly (Figure X.20) and productivity increased from 41 to 69 (vol CO/hr/vol slurry). The overall reactor temperature differentials from the bottom to the top of the reactor for the individual balances using both lift and rejuvenation tubes was only a couple of degrees.

The effect of rejuvenation tubes on catalyst activity is shown in runs where both flue gas fed draft tubes as well as rejuvenation tubes were used. In a run sequence described in Figure X.21, the decline in activity of catalyst was followed for a period of 3 days after which one 3 inch rejuvenation tube was brought on line. Immediately upon addition of H₂ an exotherm was observed followed by an immediate increase in catalyst activity recovering its initial activity in 1-2 days, after which it remained constant. After lineout, adding another rejuvenation tube provided no additional benefit. The exotherm in the rejuvenation tube was also used as a method to determine the degree of aging of the catalyst.

The beneficial effect of heating the rejuvenation tube to a temperature higher than the surrounding slurry was also demonstrated. Although the temperature in the rejuvenation tube is typically a few degrees higher than the surrounding slurry, through insulation of the tube and heating with steam, even higher temperatures can be attained. During one period in which the rejuvenation tube was heated sufficiently to raise the temperature an additional 10°F, CO conversion in the reactor increased from 26 to 36% over a 24 hr period whereas in a prior balance period without external heating being applied to the rejuvenation tube, CO conversion had dropped from 32 to 26% over a 12 hr period, as shown in Table X.54.

A patent issued to Hsia (X.97) claims a FT process comprising a slurry reactor design coupled with a continuous rejuvenation reactor. Deactivated catalyst is reactivated and rejuvenated using an external rejuvenation reactor vessel to which catalyst from the synthesis reactor is continuously fed via a downcomer from the top of the slurry bed in the synthesis reactor to the bottom of a slurry bed in the external rejuvenation reactor vessel (see Figure X.22). Likewise, rejuvenated catalyst is fed to

the synthesis reactor via a downcomer from the top of the slurry bed in the rejuvenation reactor to the bottom of the slurry bed in the synthesis reactor. Slurry flow from synthesis reactor vessel to the rejuvenation vessel and the flow of rejuvenated catalyst back to the synthesis reactor vessel are driven by gravity since both vessels are under the same pressure. A drawing is included but no examples are given.

Removal of Catalyst Fines. A patent issued to Hsu and Robbins (X.98) claims a method for removing $<1\ \mu\text{m}$ particles adhering to catalyst particles containing a Group VIII metal supported on an inorganic refractory oxide. The method comprises dispersing the particles to which the $<1\ \mu\text{m}$ particles adhere in a liquid comprising a Fischer-Tropsch derived wax, agitating the dispersion and concentrating the $<1\ \mu\text{m}$ particles in the supernatant liquid and separating the $<1\ \mu\text{m}$ particles by decanting this layer from the larger particle containing phase. Although examples are given in which the liquid used in the particle classification step includes solvents other than Fischer-Tropsch derived wax, the claims only apply to the latter (see Table X.55). Catalysts stirred with FT wax at 130°C gave initially a filtration rate of $5.8\ \text{gal/ft}^2/\text{min}$ which decreased to $0.05\ \text{gal/ft}^2/\text{min}$ after stirring for 44 hours. Using the method of this invention of extended stirring and separating the decant after 3 cycles, the filtration rate improved to $14.5\ \text{gal/ft}^2/\text{min}$.

Apparatus for Substantially Plug-Flow, Slurry Phase Synthesis

Koros (X.92) has patented a slurry apparatus that permits a substantially plug-flow slurry-phase operation in an arrangement of multiple tube reactors in a shell. Thus, the concept of the mechanical part of the tube and shell reactor resembles a Sasol Arge reactor; however, numerous additional features are incorporated to permit slurry-phase operation.

In Figure X.23, the syngas is added through 12 and is dispersed through sparger 14 into the liquid slurry medium, held at a level so as to maintain a gas-liquid interface, with the gas held in the space between 15, the slurry-gas interface and 18, a distributor tray.

A series of reactor zones, 20, are arranged within the shell, such as the ones shown by the example in Figure X.24.

The reactor tubes are held in place by lower, 22, and upper, 28, tube sheets. The space between the distributor plate, 18, and the lower tube sheet, 22, may or may not contain catalyst in addition to the slurry liquid. A detail of the distribution zone is provided in Figure X.25. The bubbly liquid from area 9 enters the tube/bubble cap 19A/19B. The bubble cap is aligned vertically with the reaction zone tube 20. The bubble cap is sized to give a pressure drop and injection velocity sufficient to decrease the size of the bubbles and to suspend the catalyst in the reaction zone (injection velocity about 20 to 100 ft/sec.). The gas to liquid transfer rates are at least equal to the conversion rate of the syngas gas.

Preferred slurry materials are stated to be Fischer-Tropsch waxes and C_{16} - C_{18} hydrocarbons. The concentration of solids are usually about 10-50 wt.%, preferably 30-40 wt.% solids.

Catalyst/slurry addition/withdrawal may be effected through line 32. The region between tube sheets, 28 and 30, allows interconnection between the upper ends of the reaction zones for gas, liquid and catalyst. Tube sheet 30 holds filter cartridges, 31, which may be manufactured from sintered metal mesh, woven metal fibers, glass fibers, cloth or fibrous carbon, which can retain the catalyst particles while allowing the wax to pass. The filter cartridges are aligned vertically above each reaction zone. A gas-liquid

disengagement zone lies above the filter cartridge tube sheet, and liquid product, separated from catalyst, can be withdrawn through tube 40 and/or 33. A demister, 41, separates gas from liquid droplets; residual gases are withdrawn through tube 42.

During operation the catalyst, 21, is preferably located in the reaction zone although some catalyst may be found in the liquid zones above or below the upper and lower tube sheets.

The catalyst most preferred is cobalt on titania (primarily in the rutile form) with less than about 70 m²/g. Preferred promoters are stated to be rhenium and hafnium.

It is stated that "...catalyst particle size is not critical..." but is preferably in the 20-150 micron size range.

The example described the operation of a single reactor (6" o.d., 5.76 i.d.) about 50 ft. tall mounted inside a 12" pipe to serve as a cooling jacket. Feed gas to the reactor was preheated.

The catalyst was prepared by impregnation cobalt onto titania extrudates which were crushed and screened to give ca. 30 micron diameter particles (presumably the catalyst contained promoters). The catalyst was reduced in hydrogen in a fluidized bed, and then the slurry wax was introduced. Following a prescribed procedure of start-up, they attained a CO conversion in excess of 50% at GHSV = 2800. Following a brief reactor upset, the unit was restarted at a higher steam jacket pressure (140 psig) and higher reactor pressure (285 psig at the reactor gas outlet). The reactor maintained CO conversion of 60-70% (2800-3600 hr⁻¹) for nearly seven days of synthesis. This material was stated to be a "...very active HCS catalyst." Methane selectivities were in the range of 2.7 to 3.2%. Assuming the steam jacket pressure represents steam/water,

this corresponds to 354°F (178°C); presumably the reactor side would not be at a much higher temperature.

This summarizes the patents abstracted through October 19, 1994; Appendix will cover later period.

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Table X.1. Activity of laser generated iron carbide catalysts Reaction Conditions: 270°C, 2/1 H ₂ /CO, 200 sccm, 75 psig, in octacosane				
	Carbide from Fe ₃ O ₄	Laser derived carbide	Laser derived carbide + K	Laser derived carbide + Si
Preparation Method	Fe ₃ O ₄ reduced in H ₂ @ 450°C/5-7 hrs and treated with H ₂ /CO/350°C	Fe(CO) ₅ /C ₂ H ₄ laser feed	Fe(CO) ₅ /C ₂ H ₄ laser feed/ impregnated with 2% K as K ₂ CO ₃	Fe(CO) ₅ /C ₂ H ₄ / SiH ₂ (CH ₃) ₂ laser feed
V/V cat/hr	2000	4000	4000	500
% CO conversion	71.9	82.5	66.5	5.0
Selectivity, wt% CO ₂ free basis				
CH ₄	16.1	9.5	5.6	15.9
C ₂ -C ₄ Paraffins	17.3	7.8	0.8	27.0
C ₂ -C ₄ Olefins	18.9	27.0	11.5	19.0
% olefins in C ₂ -C ₄	50.7	77.6	93.5	41.0

Table X.2. Activity of high and low surface-area Fe-Co spinels for synthesis gas conversion. <i>In situ</i> catalyst reduced in slurry with H ₂ at 200°C and 1 atm for 1 hr. <i>Ex situ</i> catalyst reduced with H ₂ at 300°C+ and then H ₂ /CO at 350°C+. Run in slurry reactor at 250°C, 1200 v/v/hr, 2/1 H ₂ /CO, 70 psig, 600 rpm in octacosane; time on stream not specified.						
	Starting Spinel					
	Fe _{2.85} Co _{0.15} O ₄ /1 wt.% K high surface area		Fe ₃ O ₄ /1%K high surface area		Fe _{2.85} Co _{0.15} O ₄ /1 wt.% K low surface area	
	in situ	ex situ	in situ ^a	ex situ	in situ	ex situ
Spinel surface area, m ₂ /g	>100	>100	>100	>100	0.29	<0.3
CO Conv, mol %	60	64	8.0	65	<4.0	42
CO ₂	36	36	5.2	39	na	24
Hydrocarbons	24	28	2.8	26	na	18
HC Selectivity wt%						
CH ₄	4.5	8.2	11.4	12.8	na	9.3
C ₂ -C ₄ paraffins	2.5	3.6	8.6	8.0	na	5.5
C ₂ -C ₄ olefins	17.5	27.4	34.3	32.2	na	27.0
C ₅ +	75.5	60.8	31.4	47.0	na	58.2
Taken from Example 3, Table III and Example 5, Table IV U.S. Patent 4518707 (X.4). a. Taken from Table V of U.S. Patent 4518707 (X.4).						

Table X.3. Activity of *ex situ* reduced and carbided high and low surface-area Fe-Co spinels. High and low-surface-area spinels were reduced *ex situ* with H₂ at 300°C+ followed by carbiding with H₂/CO at 350°C+. Reactions run in slurry reactor at 250°C, 1200 v/v/hr, 1/1 H₂/CO, 70 psig, in octacosane.

	Starting Spinel x = 2.85	
	high >100 m ² /g	low < 5 m ² /g
CO conv, mol %	45	44
CO ₂ , mol %	26	29
HC yield, mol %	19	15
HC Selectivity wt%		
C ₁	4.4	5.9
C ₂ -C ₄	19.3	25
C ₂ -C ₄ olefins	90	90
C ₅ +	76.3	69.1
Data taken from Example 2, Table II in U.S. Patent 4544672 and Ex 4, Table III in U.S. Patent 4518707 (X.4).		

Table X.4. Activity of alloys in a slurry reactor prepared *ex situ* from high surface-area Fe-Co spinels. Spinels reduced *ex situ* with H₂ at 350°C /12 hrs followed by 400°C/24 hrs, but not carburized. Run in slurry reactor at 270°C, 70 psig, 1200 v/v/hr, 600 rpm in octacosane.

	Fe ₃ O ₄ /1%K high surface area		Fe _{2.85} Co _{0.15} O ₄ /1 wt.% K high surface area	
	1.0	2.0	1.0	2.0
H ₂ /CO	1.0	2.0	1.0	2.0
CO Conv, mol %	44	28	55	54
CO to CO ₂ , mol %	26	15	34	34
CO to HC, mol %	18	13	21	20
HC Selectivity Wt. %				
CH ₄	4.4	2.1	5.8	6.5
C ₂ -C ₄ paraffins	1.9	0.6	3.4	2.7
C ₂ -C ₄ olefins	25.2	10	25.2	27.3
C ₅ +	68.7	87.2	65.0	63.4
Data taken from Example 7, Table VI, U.S. Patent 4518707 (X.4).				

Table X.5. Activity of low-surface area spinel derived catalysts in a fixed-bed reactor. Catalysts treated with flowing 90% H₂/N₂ at 500°C at 100 psig for 5-7 hrs. Run in fixed bed reactor with 1/1 H₂/CO at 300 psig.

	Fe ₃ O ₄ /1%K		Fe _{2.85} Co _{0.15} O ₄ /1 wt.% K	
Time on stream, hrs	1	12	1	12
V/V/hr	570	1000	570	1000
Furnace Temp°C ^c	305	305	270	270
CO Conv, mol %	79	67	98	98
CO to CO ₂ , mol %	36	31	42	40
CO to HC, mol %	43	36	56	58
Wt% selectivity				
C ₁	8.5	5.8	9.1	7.4
C ₂ -C ₄ paraffins	5.2	4.7	6.2	6.2
C ₂ -C ₄ Olefins	26.6	30.6 ^b	39.4	50.3 ^b
C ₅ +	59.7	-	45.2	
C ₆ +	-	58.9	-	36.1

Data taken from Example 1 of U. S. Patent 4537867 (X.8). Catalysts prepared by sintering mixtures of metal oxides.

b. Applies to C₂-C₅ olefins.

c. Actual bed temperatures were not reported.

Table X.6. Effect of Co concentration on Fe-Co spinel catalyst performance after 12 hrs on stream. Catalysts treated with flowing 90% H₂/N₂ at 500°C at 100 psig for 5-7 hrs. Catalysts run in fixed bed reactor at furnace temperature of 295°C, 300 psig, 1000 v/v/hr, 1:1 H₂:CO.

x in Fe _x Co _{3-x} O ₄	2.97	2.85	2.625	2.20
Time on stream, hrs	12	12	12	12
CO Conv, mol %	97	98	97	98
CO ₂ , mol %	27	40	41	42
HC, mol %	70	58	56	56
Selectivity				
CH ₄	8.3	7.4	18.0	13.2
C ₂ -C ₆ olefins	46.5	53.1	41.4	53.0
C ₂ -C ₆ paraffins	6.9	7.2	13.3	10.6
C ₇ +	38.3	32.3	27.3	23.2

Data taken from Example 7, Table 7 of U. S. Patent 4537867 (X.8).

Table X.7. Effect of temperature on performance of Fe-Co spinels in fixed bed reactor
Samples for 1-12 hrs on stream at 300 psig, 1000 v/v/hr, 1/1 H₂/CO.

	Starting Spinel						
	Fe _{2.625} Co _{0.375} O ₄ /1 wt.% K					Fe _{2.85} Co _{0.15} O ₄ /1 wt.% K	
Furnace Temperature, °C	225	240	260	270	290	235	270
Bed Temperature, °C	230	248	304	325	340	na	na
CO Conv, mol %	30	31	97	98	98	29.4	98.0
CO ₂ , mol %	4	7	40	33	41	8.0	42.0
HC, mol %	26	24	57	55	57	21.4	56.0
Selectivity							
CH ₄	8.1	8.2	19.1	16.7	19.1	2.6	5.2
C ₂ -C ₅ olefins	42.3	55.3	37.1	31.9	24.8	18.1	33.6
C ₂ -C ₅ paraffins	14.4	22.0	17.7	10.6	14.8	2.7	4.4
C ₆ +	35.2	34.5	26.1	40.8	41.3	76.8	55.9
Taken from Examples 8 and 12 of U.S. Patent 4537867 (X.8). na = not available							

Table X.8. Cu promoted high-surface area Fe-Co spinels as slurry catalysts.
Slurry reactor runs at 270°C, 2000 v/v/hr, 2/1 H₂/CO, 75 psig, 600 rpm in octacosane.

	Fe ₃ O ₄ /2%K		Fe _{2.85} Co _{0.15} O ₄ /2 wt.% K	Fe _{2.85} Co _{0.15} O ₄ /2 wt.% K/1 wt% Cu	
	In-situ	Ex-situ	In-situ	In-situ	Ex-situ
CO Conv, mol %	67	49	77	86	54
Wt% Selectivity					
CH ₄	2.0	3.8	4.4	4.2	4.5
C ₂ -C ₄ Olefin %	47.5	77	91	87	85
C ₁₀ Distribution					
α-olefins		50	49	59	46
n-paraffins		8	14.9	15	18
n-alcohols		2	1.0	3	1
β-olefins		17	4.1	2	6.0
all else		23	31	21	29
Taken from Tables I and II, U.S. Patent 4607020 (X.6).					

Table X.9. Effect of promoters on both high and low surface area $\text{Fe}_{2.25}\text{Mn}_{0.75}\text{O}_4$ spinels. Runs made at 270°C, 75 psi, 120 H₂/60 CO/20 N₂ cc/min flows, 70-80 g octacosane solvent, 20+ hrs on feed, 2 gm cat.

atomic % K	-	2.0	2.0	2.0	2.0	2.0
atomic % Cu	1.0	-	1.0	1.0	-	1.0
Surface area, m ² /g	>50	>50	>50	>50	<5	<5
gm catalyst	2	2	1	2	2	2
% CO conv	34	36	69	83 ^a	nil	nil
wt Selectivity						
CH ₄	8.8	3.5	1.7	2.3		
olefins in C ₂ -C ₄	78	91	94	92		
olefins in C ₁₀ +	?	?	63	65		
Taken from Example 2, Table 2 of U.S. Patent 4618597 (X.11).						
a. 30+ hours on feed						

Table X.10. Effect of Fe-Mn ratio in $\text{Fe}_x\text{Mn}_{3-x}\text{O}_4$ /2% K/ 1% Cu (>50 m²/g) on synthesis gas conversion. Runs made at 270°C, 75 psi, 120 H₂/60 CO/20 N₂ cc/min flows, 72 g octacosane solvent, 30+ hrs on feed, 2 gm cat.

gm catalyst	2	2	2	8	8
x	0.25	1.5	2.25	2.25	2.85
CO Conv	nil	30	83	87	79
Selectivity					
CH ₄	na	2.6	2.3	4.1	4.2
olefins in C ₂ -C ₄	na	86	93	92	94
Taken from Tables 3-4 of U.S. Patent 4618597 (X.11).					

Table X.11. Activity of $\text{Fe}_{2.25}\text{Mn}_{0.75}\text{O}_4/2$ at % K/1 at % Cu as catalysts for FT fixed bed and slurry reactors with 2/1 H_2/CO synthesis gas.			
	Fixed-Bed		Slurry
Temperature, C	263	275	270
Pressure, psig	65	65	75
Cat mesh	40-100	40-100	>140
Fe-SV	2.0	9.0	11.2
CO Conv	50	43	69
Selectivity			
CH ₄	8.6	9.5	1.1
C ₂ -C ₄	26.4	25.0	1.8
C ₅ +	65	65.5	97
CO ₂	35	44.0	38
Olefin % Content			
C ₂ -C ₄ olefin fraction	82	84	93
C ₁₀ + olefin fraction	65	67	63
Taken from Tables 2 and 4 of U.S. Patent 5118715 (X.13).			

Table X.12. Activity of Fe-Zn Spinel. Catalysts pretreated to 500°C in a 9/1 H_2/N_2 mixture at 100 psi and 100 v/v/hr space velocity for 5-8 h. Runs made in 1.7/1 H_2/CO at 300 psi at 550 vol/vol/h, 270°C furnace temperature, 10.5 hrs on stream.		
	1.0 Fe/0.065 Zn/0.030 Ce/0.030 K	Fe/1% K
CO conversion	98	96
wt% selectivity		
CH ₄	3.0	9.4
C ₂ -C ₆	36.0	50.1
C ₇ +	21.4	14.5
CO ₂	39.6	26
Specific olefin/paraffin prodn. ratios were:		
C ₂	3.1	2.5
C ₃	7.5	8.0
C ₄	15.0	8.3
C ₅	7.5	3.7
C ₆	4.6	2.0
Taken from Example 3, Table V of U.S. Patent 4639431 (X.16).		

Table X.13. Activity of Fe-Zn spinels promoted with Cu and K prepared with glycolate. Runs made with 2 g catalysts in at 270°C in 2/1 H₂/CO, 75 psig at 180 cc/min in octacosane for 40-100+ hr periods.

	CO Conv	CH ₄ selectivity	% olefins in C ₄	% Olefins in C ₂ -C ₄	% α-Olefin in C ₁₀ +
Fe _{2.8} Zn _{0.2} O ₄ ·2 at% K	33	2	89		
Fe _{2.8} Zn _{0.2} O ₄ ·1 at%Cu	34	10.1	81		
Fe _{2.8} Zn _{0.2} O ₄ ·2 at%K+1 at%Cu	73	1.9	89		
Fe _{2.8} Zn _{0.2} O ₄ ·2 at% K, 1 at% Cu	80	1.7		93	63
Fe _{2.45} Zn _{0.55} O ₄ ·2 at% K, 1 at% Cu	84	1.7		92	61
Fe _{2.3} Zn _{0.7} O ₄ ·2 at% K, 1 at% Cu	32	2.3		85	nd
Taken from Example 2, 6 and 7 of U.S. Patent 5100856 (X.17). Spinels having Fe concentrations greater than Fe _{2.5} Zn _{0.5} O ₄ fall within claimed compositions.					

Table X.14

Conversion of Synthesis Gas with Fe_{3-x}Zn_xO₄ in 0.3 L CSTR at 270°C, C₂₈ Solvent, H₂/CO = 2, 75 psig (from U.S. Patent 5118715, (X.13))

Catalyst	Fe _{2.8} Zn _{0.2} O ₄ A	Fe _{2.55} Zn _{0.45} O ₄ B	Fe _{2.3} Zn _{0.7} O ₄ C	Fe _{2.79} Zn _{0.21} O ₄	Fe _{2.79} Zn _{0.21} O ₄	Fe _{2.79} Zn _{0.21} O ₄
% Fe	66.87	60.28	53.70	71.50	71.50	71.50
% g-atom K	---	---	---	2	2	0
% g-atom Cu	---	---	0	1	0	1
CO Conv., %	80	84	32	73	33	34
CH ₄ /% Carbon	1.7	1.7	2.3	1.9	2.0	10.1
Olefin, %						
C ₂ -C ₄	93	92	85			
% α- in C ₁₀	63	61	*			
% α- in C ₄	---	---	---	89	89	81
NL/gFe-hr**	8.97 (7.18)	9.95 (7.96)	11.17 (8.94)	8.89 (7.11)	8.89 (7.11)	8.89 (7.11)
NL/g cat-hr	6.00	6.00	6.00	6.36	6.36	6.36

* Insufficient yield of liquids.

** NL total flow; parentheses, flow based on CO + H₂.

Table X.15. Comparison of Ce,K and K/Ce promoters for 1.0 Fe/0.30 Ti/0.065 Zn/0.03 Ce and/or 0.03 K in fixed-bed reactor. Pretreated at 500°C with 9/1 H₂/N₂ at 800 v/v/hr for 5-6 hrs. Runs made at 270°C, 1/1 H₂/CO at 2.6 MPa at 870 v/v/hr space velocity for time on stream of 30-50 hrs

	K	Ce	K/Ce
CO Conv	2	17	24
wt HC selectivity			
CH ₄	42	24.5	14.8
C ₂ -C ₃ paraffins	6	14.6	12.2
C ₂ -C ₃ olefins	42	14.1	32.5
C ₄ +	10	46.8	40.5

Taken from Example 5, Table VII in U.S. Patent 4657885 (X.18).

Table X.16. Manganese Catalysts with Ce,K and K/Ce in fixed-bed reactor. Pretreated at 500°C with 9/1 H₂/N₂ at 800 v/v/hr for 5-6 hrs. Runs made with 1/1 H₂/CO, 870 v/v/hr, 305°C, 2.0 MPa

	K	Ce	K/Ce
CO Conv	18	62.5	54.9
HC selectivity, wt. %			
CH ₄	10.2	17.5	7.5
C ₂ -C ₃ paraffin	4.1	10.0	2.6
C ₂ -C ₃ olefin	29.2	20.6	24.4
C ₄ +	56.5	51.9	65.5

Taken from Example 6, Table VIII in U.S. Patent 4657885 (X.18).

Table 17. Activity of a 10/1 Fe/Ti catalyst in a fixed bed reactor for synthesis gas conversion. Pretreated with 49 H₂/50 CO/1 N₂ at 270°C at 1 atm and 500 v/v/hr for 18 hrs. Runs made at 270 to 350°C, 1/1 H₂/CO at 120 psia and 150-1200 v/v/hr.

Temp, °C	270	300	325	350
CO Conv, %	90-20	65-40	96-80	97-90
Selectivity				
CH ₄	6-4	6-3	6-10	9-15
C ₅ -C ₁₁	50-54	51-57	50-51	42-51
C ₄ - (Gas)	35-30	34-26	35-39	39-50
Olefins in C ₆ +	21-26	23-26	21-16	14-8
Aromatics	2-3	2-3	4-8	7-14

Taken from Example 5, Tables 1 to 6 in U.S. Patent 4513104 (X.24).

Table X.18. Performance of Fe/Ti Catalysts in a fixed-bed reactor.

Pretreated with 49 H₂/50 CO/1 N₂ at 270°C at 1 atm and 500 v/v/hr for 18 hrs. Runs made with 1/1 H₂/CO at 300 GHSV and 0.9 MPa (130 psi).

	Fe/0.1 Ti			Fe/0.2 Ti	Fe/.04 K		NH ₃ synthesis catalyst
Temp	350	350	270	350	350	270	350
GHSV	300	300	300	300	300	300	300
CO Conv	96.7	63.6	46.8	45.0	55.5	68.9	97.1
Selectivity to HC %	60.9	62.5	69.9	59.6	66.0	wax	69.5
C ₁	10.1	13.0	3.4	16.6	11.1	3.0	3.3
C ₁ -C ₅	38.4	44.7	30.4	46.6	31.8	-	42.2
C ₆ -C ₁₁	45.3	45.4	44.8	39.0	32.5	-	42.3
C ₁₂ -C ₂₃	16.0	9.7	23.8	13.6	24.9	-	14.8
C ₂₃ +	0.3	0.2	1.0	0.8	10.8	-	0.7
Aromatics	12.7	14.02	2.92	10.3	6.57	-	8.65
α-olefins	14.9	9.66	22.31	10.0	16.6 9	-	11.43

Taken from Example 9, Tables 10 and 11 in U.S. Patent 4513104 (X.24).

Table X.19. Activity of *in situ* prepared catalyst in a slurry reactor.

Runs made at 270°C, 1:1 H₂/CO at 70 psig at 1200 V/V/hr in C16 paraffin solvent, 600 rpm.

Support	wt% support ^a		CO Conv	CO ₂	CH ₄	C ₂ -C ₄ olefins	C ₂ -C ₄ paraffins	C ₅ +
	Fe	Co						
None (Complexes only)	-	-	25	35.4	15.4	17.8	5.3	26.1
Fe ₂ O ₃ /1% K	9.5	3.2	54	50	3.0	7.2	1.1	38.5
Al ₂ O ₃	4.8	1.6	21	25	20.0	18.3	9.0	27.7
Al ₂ O ₃ ^b	"	"	27	9.2	19.8	12.9	6.8	60.5
MgO	4.8	1.6	30	35	18.6	16.1	6.8	23.5
MgO/1% Cu	9.5	3.2	26	50	9.6	14.7	3.8	21.9

Taken from Example 1, Tables I and II, and Example 4, Table V, of U.S. Patent 4532229 (X.25).

a. Same weight of Fe and Co in reactor in all runs, except for Fe₂O₃/1% K run.

b. Product yield after 96 hours on stream.

Table X.20. Effect of air calcination on the crystalline form of titania		
	Rutile content, wt%	Surface Area, m ² /g
Degussa P-25	28 ^a -35 ^b	60 m ² /g
500°C in air/16 hrs	55	33-36
500°C in air/16 hrs and H ₂ at 450°C	67	22-26
560°C in air/ 4 hrs ^d	70	30
600°C in air/16 hrs	~100 (>30/1)	10-16
650°C in air/16 hrs ^c	97	14
a. From U.S. Patent 4711871 (X.32). b. From U.S. Patent 4595703 (X.49). c. From U.S. Patent 4663305 (X.57). d. From U.S. Patent 4738948 (X.61).		

Table X.21. Effect of calcination on rutile content of titanias							
Source	Description	Binder/%	Hg PV ^a , cc/g	Hg PD ^b , Å	BET SA, m ² /g	% Rutile in titania	Calcination, °C/hr
Company A	-	none	0.253	140	45	27	-
Company A	-	none	0.162	270	15	92	700/1
Company A	-	none	0.134	250	14	95	700/1
Company A	-	none	0.120	481	5	100	840/1
Company A	Extrudate	none	0.154	389	8	98	650/16
Ti(OC ₃ H ₇) ₄ hydrolysis	-	none	0.160	n.a.	10	94	650/50
Ti(OC ₃ H ₇) ₄ hydrolysis	Extrudate	none	0.299	n.a.	41	n.a.	500/16
Ti(OC ₃ H ₇) ₄ hydrolysis	Extrudate	none	0.180	n.a.	15	n.a.	600/16
Company A	Extrudate	M/3.5	0.387	454	27	82	750/3
Company A	Extrudate	M/3.5	0.326	590	22	96	800/1
Company A	Extrudate	M/3.5	0.354	678	15	98	800/3
Company A	Extrudate	M/3.5	0.301	697	15	100	800/16
Company A	Extrudate	M/3.5	0.276	590	12	100	850/3
Company A	Extrudate	M/3.5	0.254	1151	13	100	850/10
Company A	Extrudate	M/3.5	0.237	1706	10	100	850/72
Taken from Example 1, Table 1 of U.S. Patent 4992406 (X.30). M binder = 30 TiO ₂ /70 Al ₂ O ₃ a. PV = pore volume. b. PD = pore diameter.							

Table X.22. Effect of rhenium on stability of Re/TiO ₂ for synthesis gas conversion. Conditions of run: 230°C, 280 psig, 2/1 H ₂ /CO, 1000 GHSV		
	1% Ru and 0.5% Re/TiO ₂	1% Ru/TiO ₂
Half-life, days	231	26
CO Conv	97	97
HC Yield	90	94
Selectivities		
CH ₄	3.7	3.5
CO ₂	7.0	1.5
Taken from Example 1, Table I of U. S. Patent 4558030 (X.29).		

Table X.23. Effect of Re/Ru ratios on Re promoted Ru/TiO ₂ catalyst. Conditions: 280 psig, 2/1 H ₂ /CO, 1000 GHSV				
Wt.% Ru	Wt% Re	CO Conv	C ₁ select	CO ₂ select
0.1	1.0	11	4	20
0.5	0.5	33	7.5	5
0.75	0.5	43	9	6
1.0	0.5	82	5.6	6
Taken from Example 2, Table II of U. S. Patent 4558030 (X.29).				

Table X.24. Effect of rutile content on activity of 1% Ru-0.5% Re on TiO ₂ . Conditions: 230°C, 280 psig, 2/1 H ₂ /CO, 1000 GHSV at 90% CO conversion			
Rutile/Anatase ratio wt	1.2/1	2/1	>30/1
Rutile, wt% in TiO ₂	55	67	~100
C ₁ selectivity	7	4.5	2
Half-life days	4	231	87
Deactivation, Δ <i>ln</i> k/day	-0.18	-0.003	-0.008
Pore Vol ml/g	0.4	0.2	0.15
SA m ² /g	35	24	12
Taken from Example 3, Table III of U. S. Patent 4558030 (X.29).			

Table X.25. Selectivity of Ru Catalysts for synthesis gas conversion. Conditions: Catalysts reduced in H ₂ at 450°C for 1 hr before introducing 1/1 H ₂ /Co at 980 kPa (9.5 psig),						
	Temp	%CO Conv	Prod	Total wt%	Olefin, wt%	Paraffin wt%
2% Ru/TiO ₂	267	7	C1	14	-	-
			C ₂ -C ₄	47	32	15
			C ₅ -C ₇	39	23	16
			C8+	-	-	-
5% Ru/ηAl ₂ O ₃	274	10	C1	24	-	-
			C ₂ -C ₄	43	19	14
			C ₅ -C ₇	32	6	6
			C8+	12		
Taken from Example 1, Table II of U. S. Patent 4042614 (X.31).						

Table X.26. Methanol conversion over Ru/TiO ₂ . Conditions: 230°C, 500 v/v/hr, fixed bed reactor			
Methanol, psi	236	236	236 ^a
H ₂ , psi	0	59	59
CO, psi	0	0	31
Methanol conv at 35 hrs, %	13	76	<3
Reactor effluent composition			
CO	38	1	84
CO ₂	4	12	n.a.
CH ₄	1	24	n.a.
C ₂ +	55	63	n.a.
Taken Example 4, Table IV and Example 6, Table VI of U.S. Patent 4513161 (X.36). a. GHSV=560.			

Table X.27. Activity of Ru on V, Nb and Ta oxides versus prior art.
Conditions: 3/1 H₂/CO, 1 atm, no other data provided.

	Temp C	CO Conv %	Hydrocarbon selectivities		
			CH ₄	C ₂ -C ₅ Olefins	C ₂ +
1% Ru/Nb ₂ O ₅	234	7.8	48	22	52
1% Ru/Ta ₂ O ₅	228	17.7	46	17	54
1% Ru/V ₂ O ₅	243	4.1	45	28	55
1% Ru/SiO ₂	232	4.1	87	2	13
1% Ru/Al ₂ O ₃	244	14.1	71	10	29
Data taken from U. S. Patent 4171320 (X.37).					

Table X.28. Reaction of a 0.76% Ru on TiO₂ in a fixed bed reactor.
Conditions: reduced at 400-450°C for 2-4 hrs in H₂. Run in 1.39/1 H₂/CO

Run No	3	5	7	14
Pressure,atm	3.0	3.0	5.0	4.3
°C	206	224	218	213
GHSV	198	301	494	1240
H ₂ Conv	84	84	89	26
CO Conv	84	84	89	30
Selectivity on CO ₂ free basis				
CH ₄	4.8	6.1	5.4	6.9
C ₂ /C ₄	9.15	11.6	7.9	17.8
C ₅ -C ₂₀	76.5	74.4	72.7	64.1
C ₂₀ -C ₄₀	8.3	6.2	11.3	8.3
C ₄₁ +	0.15	0.13	1.5	0.2
Oxygenates	1.13	1.4	1.2	2.7
C ₂ = in C ₂				40
C ₃ = in C ₃				84
C ₄ = in C ₄				82
Total olefin in C ₇ -C ₁₂				39
Total olefin in C ₄ -C ₂₀				31
Taken from U. S. Patent 4477595 (X.38).				

Table X.29. Effect of support on activity of Ru catalysts
Fixed bed reactor with supported Ru, reduced at 400-450°C for 2-4 hrs in H₂

	0.76 Ru/ TiO ₂	0.56 Ru/ Nb ₂ O ₃	0.67 Ru/ Ta ₂ O ₃	1.57Ru/ SiO ₂	0.56Ru/ Nb ₂ O ₃	1.1 Ru/ TiO ₂	1.57Ru/ SiO ₂	1.1Ru/ TiO ₂	1.1Ru/ Al ₂ O ₃
H ₂ /CO	1.39	1.39	1.39	1.39	2	2	2	2	2
Pressure, atm	5.0	5.0	5.2	21	7	4.6	4.6	2.1	2.1
°C	203	196	200	251	229	209	209	214	214
GHSV	298	300	303	200	1225	300	300	303	303
H ₂ & CO Conv	86	88.3	79	88.7	81	82	5	87	32
Selectivity									
CH ₄	2.9	2.0	5.5	7.5		4.3	10.6	6.7	16.6
C ₂ /C ₄	6.2	2.5	18.5	17.4		12.5	34.0	12.8	19.5
C ₅ -C ₂₀	65.5	62.1	66.5	71.3		81.6	51.1	68.8	59.2
C ₂₁ +	25.4	33.4	9.5	3.8		-	-	9.2	2.1

Taken from U. S. Patent 4477595 (X.38).

Table X.30. Activity of Ru on oxide modified titania surfaces.
Conditions: 230-250°C, 300 v/v/hr, H₂/CO=2, 60 psig, fixed bed reactor

	1% Ru/TiO ₂	1% Ru/TiO ₂ +10%Nb	1% Ru/TiO ₂ +10%Ta	1% Ru/TiO ₂ +1%Ta	1% Ru/TiO ₂ +2%V	Physical Mixture 1% Ru/TiO ₂ +10%Ta
Temp	238	230	235	232	252	240
H ₂ +CO conv	37	43	19.5	31.5	71.3	47.4
CO ₂	3.8	1.9	3.7	3.2	3.5	5
CH ₄	14.5	10.9	10.9	15.3	12.5	8.4
C ₂	8.3	6.6	14.8	4.2	3.3	4.2
C ₃ +C ₄	23.0	17.3	13.8	24.0	10.0	16.9
C ₅ +	50.4	63.3	56.8	53.3	70.7	65.5
HC products						
Alcohols	5.1	0	0	1.4	3.8	3.0
olefins	39.1	67.7	6.3	44.2	15.6	46.4
paraffins	34.	32.3	93.7	54.4	80.6	50.3

Taken from U. S. Patent 4711871 (X.32).

Table X.31. Activity of Ru/TiO₂ slurry catalyst.
Conditions: 1 g catalyst, 50 g octacosane, 6/3/1 H₂/CO/N₂, 1200 v/v/hr, 6 atm, 1 std l /g catalyst/hr

Catalyst 1% Ru	°C	% CO Conv	Selectivity			
			CO ₂	CH ₄	C ₂ -C ₄	C ₅ +
Ru/TiO ₂ Particulate, reduced 450°C	250	49	3.2	14.4	8.9	73.5
Ru/TiO ₂ Particulate, not prereduced	260	10	2.0	20.0	30.0	48.0
Carbonyl based						
Ru	260	15	tr	4.7	19.5	75.8
Ru/CeO ₂	240	<5	nil	na	na	na
Ru/Al ₂ O ₃	240	25	3.0	19.3	9.4	68.3
Ru/TiO ₂	240	55	6.7	12.3	17.5	63.5
Taken from U.S. Patent 4752600 (X.41).						

Table X.32. Effect of steam treatment of Ru/TiO ₂		
Treatment of Ru/TiO ₂	O/Ru ratio from O ₂ chemisorption	Ru crystallite size Å
None	1.46	12
Air at 1 atm, 500°C/3 hrs	not reported	30
9/1 H ₂ O/H ₂ at 280 psig, 300°C/4 hrs	1.08	15
9/1 H ₂ O/H ₂ at 280 psig, 230°C/16 hrs	0.88	18
3% H ₂ O in N ₂ at 1 atm, 500°C/3 hrs	0.98	16
Taken from Table 1, U.S. Patent 4647592 (X.43).		

Table X.33. Effect of air treat on activity of Ru/TiO ₂ Run in 2/1 H ₂ /CO, 210°C, 280 psig, and 1000 v/v/hr					
Hrs	CO Conv	Selectivity to HC, %	wt.% selectivity		
			CH ₄	CO ₂	C ₂ +
No air treat					
0.7	84.8	80.3	7.3	5.3	87.4
1.4	94.8	90.8	4.9	4.2	90.9
2.4	94.7	88.2	3.6	6.9	89.5
3.0	98.3	89.6	3.6	8.8	87.6
3.7	97.7	89.5	3.8	8.4	87.8
Air treated sample					
0.7	78.6	72.1	3.0	8.3	88.7
1.3	91.9	85.0	2.3	7.5	90.2
2.2	94.5	88.5	2.3	6.4	91.3
3.0	93.7	88.6	2.5	5.4	92.1
3.7	93.1	88.9	2.5	4.5	93.0
Taken from Table II, U.S. Patent 4647592 (X.43).					

Table X.34. Activity of Rh Catalysts for synthesis gas conversion. Conditions: 1.6/1 H ₂ /CO, 100 kPa (1 atm), Catalyst reduced 450°C 1 hr,				
	Temp	%CO Conv	CH ₄ mol %	C ₂ -C ₅ yield, mol %
2% Rh/TiO ₂	248	1.3	74	26
2% Rh/Al ₂ O ₃	265	3.5	15	85
Taken from U. S. Patent 4116994 (X.45).				

Table X.35. Activity of rim-impregnated Co/TiO ₂ catalysts Conditions: 200°C, 2/1 H ₂ /CO, 2.1 MPa				
Particle size, mm	2.2	2.2	0.1-0.2	2.2
Co Conc, wt%	13.0	13	13	20.9
Co Distribution	even	rim	rim	rim
Rim thickness, μm	-	80±30	80±30	120±30
Surface area, m ² /g	80	80	80	350
Hrs on stream	193	318	175	315
GHSV	420	650	940	1750
CO Conv, %	64.5	66.0	48.0	64.0
CO Conv, vol/vol/hr	90	150	210	342
Selectivity				
CH ₄	12.0	8.3	4.7	12.7
C ₂ -C ₄	5.1	4.4	4.7	5.3
C ₅ +	82.0	87.0	90.5	81.3
CO ₂	0.9	0.4	0.1	0.7
Taken from Tables 1, 2, and 3 or U.S. Patent 5036032 (X.48).				

Table X.36. Activity of Co/TiO ₂ catalyst in a fixed-bed reactor. Runs at 230°C, 150 psig, 400 GHSV, 2/1 H ₂ /CO						
Cat		CO Conv	Selectivities			Schulz-Flory
			CO ₂	CH ₄	C ₂ +	
A	12 Co/TiO ₂ ^b (this invention)	88	1.1	8.6	90.3	0.91
B	100 Co/5 ThO ₂ /8 MgO/200 Kieselguhr ^a (known)	43	4.3	10.3	86.4	-
C	12 Co/SiO ₂ (known)	72	1.6	8.7	89.7	0.85
D	25 Co/1.8 Ti/100 SiO ₂ (known)	21	1.9	13.8	84.3	0.74
Taken from Example 7 in U. S. Patent 4542122 (X.46).						
a. Conventional FT catalyst						
b. Rutile/anatase ratio of 3.2. Reduced in H ₂ at 450°C for 1 hr						

Table X.37. Activities of Co and Co-Re on TiO₂ in a fixed-bed reactor. (Data shown in Figure 1 in Patent 4542122) Catalyst impregnated with nitrate/perrhenic acid and calcined in air at 500°C/3 hrs. Catalysts reduced in H₂ at 450°C for 1 hr. Runs made at 200°C, 2.15/1 H₂/CO, 280 psig, GHSV=1000.

Metals, wt% on TiO ₂	Rutile in TiO ₂ , wt%	Air treat°C for 3 hrs	O ₂ chemisorp. μ mol O ₂ / g cat	%CO Conversion	Surface area m ² /g	CH ₄	CO ₂	C ₂ +
12 Co	53	250	213	67	36	9.7	0.2	90.1
12 Co	100	250	265	79	10	11.5	0.7	87.8
12 Co	56	500	178	54	33	9.9	-	90.1
12 Co	100	500	202	67	10	11.7	0.3	88.0
12 Co-0.1 Re	100	500	145	67				
12 Co-0.5 Re	56	500	343	85				
12 Co-0.5 Re	100	500	285	82				
12 Co-3 Re	56	500	399	81				

Table I in U.S Patent 4568663 (X.51).

Table X.38. Effect of Anatase-Rutile Ratio on Co/TiO₂ catalyst.

Catalysts impregnated with cobalt carbonyl from pentane solution. Run conditions: 200°C, 280 psig, 1000 GHSV, H₂/CO=2.15/1

Co, wt%	10.1	9.2
Rutile in Titania, wt%	28	~100
Pretreatment Conditions:		
1st Stage	250°C/ air/3 hrs	250°C/ air/3 hrs
2nd Stage	450°C/ H ₂ /1 hr	450°C/ H ₂ /1 hr
CO Conv, mol %	5	97
CH ₄ Yield, mol %	15.1	5.4
O ₂ Chemisorption, μ mol/g cat	53	205
Example 9 in U.S. Patent 4542122 (X.46) and Example 3 in U.S. Patent 4595703 (X.49).		

Table X.39. Effect of rutile content on Co/TiO₂.
Run at 230°C, 40 MeOH:2 H₂:1 CO₂:7 Ar, 400 psig, GHSV=500.

Rutile content, %	55	100
MeOH Conv	66	100
Carbon Product Distribution		
CO	2.6	0.8
CO ₂	15.6	27.8
CH ₄	9.0	17.1
C ₂ +	72.8	54.3
Taken from Example 6 in U.S. Patent 4542122 (X.46).		

Table X.40. Activity and selectivity of Co on titania based catalysts for methanol conversion (rutile not specified).						
Run conditions: 230°C, 400 psig, GHSV=500, 40 %MeOH:2 H ₂ :1 CO ₂ :7 Ar						
	12% Co/TiO ₂	12% Co/2% ThO ₂ /TiO ₂		100 Co/5 ThO ₂ /8 MgO/200 Kieselguhr ^a	12% Co/SiO ₂	12% Co/Al ₂ O ₃
MeOH Conv, 35 hr	52	70 ^b		97	38	64
Carbon Product Distribution						
CO	5.5	3.1	2.9	1.0	4.3	2.8
CO ₂	12.9	17.0	12.6	38.4	22.3	21.8
CH ₃ OCH ₃	0.2	0.3	0.5	-	0.1	2.4
CH ₄	11.2	8.6	7.4	19.5	7.0	9.9
C ₂ +	70.2	71.0	76.6	41.1	66.3	63.1
Schulz-Flory Alpha	0.86	0.88	n.p.	n.p.	n.p.	n.p.
Example 5 of U.S. Patent 4542122 (X.46).						
a. Conventional FT catalyst						
b. Two sets of data provided for the same conditions having the same MeOH conversion that was not otherwise specified.						
n.p. = not provided						

Table X.41. Effect of Re on MeOH conversion over Co/TiO ₂ with or without ThO ₂ . Run conditions: 230°C, 400 psig, GHSV=500, MeOH/Argon=4. Catalysts calcined 500°C			
	12 Co/ 2 ThO ₂ /TiO ₂	12 Co/2 ThO ₂ / 0.5 Re/TiO ₂	12 Co/ 0.5 Re/TiO ₂
Rutile Conc, %	56	56	56
MeOH Conv	49	100	87
Product Distribution			
CO	6	2	2
CO ₂	14	28	22
CH ₄	6	14	9
C ₂ +	74	56	67
Table III in U.S. Patent 4568663 (X.51).			

Table X.42. Effect of H ₂ partial pressure on MeOH conversion. Co/ThO ₂ /TiO ₂ (rutile and catalyst composition not specified) at 230°C, 500 GHSV, 400 psig			
Partial Pressures, psig			
MeOH	332	332	332
Ar	83	66	0
H ₂	0	17	83
MeOH Conv, wt%	38	52	83
Carbon Product Distribution			
CO	8.5	3.9	0.9
CO ₂	11.3	8.9	12.2
CH ₃ OCH ₃	1.0	0.4	0.1
CH ₄	4.6	5.7	15.9
C ₂ +	74.6	81.1	70.9
CH ₄ in hydrocarbon, wt%	5.8	6.6	18.3
Table IV in U. S. Patent 4542122 (X.46).			

Table X.43. Effect of promoter on MeOH Conversion on Co/TiO ₂ . Conditions: 230°C, 400 psig, LHSV=0.67, 20 MeOH/1 H ₂ /4 Argon					
Catalyst composition					
Wt% Co	5.0	4.34	4.65	4.55	4.73
Promoter @ 1 wt%	none	Zr ^a	Hf	Ce	U
MeOH Conv	31	37	34	49	46
Rate MeOH Conv, g/hr/g Co	1.6	2.3	1.9	2.8	2.6
Carbon Prod Distribution					
CO	16	13	16	10	9
CO ₂	8	9	7	9	13
CH ₄	8	8	8	7	9
C ₂ +	68	70	69	74	69
Table IV, Example 2 in U.S. Patent 4663305 (X.57). a. The Zr salt was ZrO(O ₂ CCH ₃) ₂ .					

Table X.44. Effect of silica promotion on CoRe/TiO ₂ in a fixed-bed reactor. Conditions: 200°C, 2.1 MPa, H ₂ /CO=2, run at space velocity to give ~60% CO conversion.								
	(A) CoRe/TiO ₂		(D) CoRe/TiO ₂		(B) CoRe/TiO ₂ +SiO ₂		(C) CoRe/TiO ₂ +SiO ₂	
% SiO ₂	0		0		4		5.2	
Steam treat H ₂ O (40 Torr)/He at 400°C/13 hrs	No		Yes		Yes		Yes	
reduction in H ₂	250°C for 13 hrs		250-400°C for 2-14 hrs		250-400°C for 2-14 hrs		250-400°C for 2-14 hrs	
Hrs on stream	50	139	49	190	47	120	49	119
CO Conv	61.5	64	67	58	69	61	60	55
mol CO conv/g atom Co-hr	5.7	5.5	5.1	4.4	7.5	6.8	8.3	7.5
CH ₄	5.3	5.1	4.6	5.0	5.2	5.6	5.4	5.8
C ₂ (O/P)	0.6 (0.12)	0.6 (0.14)	0.6 (0.17)	0.6 (0.19)	0.7 (0.11)	0.7 (0.13)	0.6 (0.13)	0.6 (0.14)
C ₃ (O/P)	2.1 (1.9)	1.9 (2.1)	2.2 (2.6)	2.1 (2.8)	2.4 (2.0)	2.5 (2.1)	2.3 (2.0)	2.3 (2.1)
C ₄ (O/P)	2.3 (0.70)	2.16 (0.63)	2.0 (1.6)	1.9 (1.6)	2.4 (1.1)	2.6 (1.3)	2.6 (1.2)	2.5 (1.3)
C ₅ +	89.5	89.9	90.3	90.1	89.3	88.5	89.1	89.1
CO ₂	0.2	0.2	0.3	0.3	0.07	0.06	0.05	0.04
Combined Table 1 and Table 2 of U.S. Patent 4794099 (X.58). (O/P) = olefin/paraffin ratio								

Table X.45. Effect of Precalcination on FT activity of Co-Ru/TiO ₂ catalyst in fixed-bed reactor. Runs made at 200°C, 60H ₂ /30CO/7N ₂ , 75 psia, space velocity adjusted; catalysts 70% rutile titania,				
	D	A	B	C
	20% Co/ SiO ₂	11.6% Co/ TiO ₂	Reduced 11.6% Co/ 0.14% Ru/TiO ₂	Calcined-reduced 11.6% Co/ 0.14% Ru/TiO ₂
1st Calcination	none	400°C/16 hrs	400°C/16 hrs ^a	400°C/16 hrs ^b
Reduction/oxidation /reduction step ^c	No	No	No	Yes
CO Conv	65	50	64	68
CH ₄ select	7.4	9.3	6.8	6.5
C ₅ + select	82	80.2	87.3	87.8
Co time yield ^d	1	0.6	2.0	2.9
Taken from Table III in U. S. Patent 4738948 (X.61). a. Ru impregnated to catalyst A after 1st calcination. b. Started with catalyst B. c. Calcined in air at 300°C/4 hrs and then reduced in H ₂ d. moles CO converted per hr g-atom Co in catalyst.				

Table X.46. H ₂ Regeneration of Air-calcined-reduced Co-Ru/TiO ₂ Catalysts Aged 10-30 days				
	CO Conv, %	Co time yield, hr ⁻¹	CH ₄	C ₅ +
Cat A. Co/TiO ₂	At 560 kPa, 200°C, H ₂ /CO=1			
Initial	20	0.6	8.9	80.1
Aged	20	0.5	9.5	81
H ₂ Treated	20	0.5	9.5	80.5
Cat. B CoRu/TiO ₂	At 2060 kPa, 200°C, H ₂ /CO=1			
Initial	50-60	2.6	7.0	86
Aged	50-60	2.0	8.2	84
H ₂ Treated	50-60	2.6	6.5	87
Cat. C. CoRu/TiO ₂ Calc	At 2060 kPa, 200°C, H ₂ /CO=1			
Initial	50-60	4.5	5.5	91.0
Aged	50-60	3.9	6.4	88.8
H ₂ Treated	50-60	4.8	4.9	91.5
Taken from Example 5, Table IV in U. S. Patent 4738948 (X.61).				

Table X.47. Synthesis gas conversion activity of Fe-coated, vanadia and niobia modified titanias in a fixed-bed reactor. Runs made with 1:1 H ₂ /CO, 500 v/v/hr, 300 psig							
	4% Fe/TiO ₂			4% Fe/TiO ₂ +V			4%Fe/TiO ₂ +Nb
Temp	305	315	270	290	305	270	270
CO Conv	47	60	27.0	49	70	34.3	20.1
Selectivity (CO ₂ free)							
CH ₄	21.0	24.4	21.0	16.1	17.8	13.0	14.6
C ₂ -C ₄ olefins	14.6	13.3		42.7	23.4		
C ₂ -C ₄ paraffins	35.9	36.3	55.0	21.2	44.2	41.5	32.9
C ₅ +	27.5	26.0	24.0	20.0	14.6	45.5	52.5
Taken from Tables 1 and 2 in U. S. Patent 4559365 (X.68).							

Table X.48. Selectivity of TiO₂ Promoted Nickel Catalysts for Synthesis gas conversion in a fixed-bed reactor.
Run conditions: 250°C, 3/1 H₂/CO, 1 atm., catalyst reduced in H₂ at 250°C/1 hr.

	CO Conv %	HC Selectivity, wt%			umol/min/g of Ni ^a		H ₂ chemisorption umol/g	BET SA m ² /g	H/M
		CH ₄	C ₂ -C ₃	C ₄ -C ₆	CH ₄ formation rate	CO Conv rate			
Ni Powder	4.9	88	12	-	9.7(.0115)	11.0 (.0131)	7.0	0.41	0.0131
0.007% TiO ₂ on Ni	11.6	74	16	9	19.1(.0295)	26.3 (.0406)	5.4	0.48	0.0006 3
0.07% TiO ₂ on Ni	27.2	38	42	19	21.9(.0468)	60.2 (.129)	3.9	0.60	0.0004 6
0.20% TiO ₂ on Ni	25.4	39	44	17	21.2 (.0281)	56.6 (.0748)	6.4	1.15	0.0007 5
1.66% TiO ₂ on Ni	15.9	36	44	21	11.7 (.0244)	34.7 (.0723)	4.0	7.69	0.0004 7
8.40% TiO ₂ on Ni	18.8	33	42	24	14.3	46.0			
10% Ni on TiO ₂	49.0	37	34	28	14.6 (0.0194)	41.6 (0.0550)			
1/1 Ni powder + TiO ₂	2.1	92	8	-	7.6 (0.0101)	8.3 (0.0110)			

Taken from U.S. Patent 4273724 (X.70).

a. ( ) numbers in parenthesis are reactions/site/sec or turnover number.

Table X.49. Activity of Cu-promoted Co-Mo spinel catalysts in a slurry reactor. Conditions: CSTR: 2/1 H ₂ -CO feed, 270°C, 75 psig, and 2000 h ⁻¹ gas space velocity in octacosane. Catalyst first reduced <i>in situ</i> at 100-270°C with H ₂ /CO at 1000-2000 v/v/hr flow rate at 75 psig.			
	Co ₂ MnO ₄ /1% Cu	Co ₃ O ₄ /1% Cu	Co ₂ MnO ₄
CO Conv	45	23	nil
wt% Prod Select			
CO ₂	16	54	-
CH ₄	7	40	-
C ₂ -C ₄	26	6	-
C ₅ +	51	nil	-
%olefins in C ₂ -C ₄	83	52	-
Taken from U. S. Patent 5162284 (X.73).			

Table X.50. Synthesis gas conversion for making alcohols Conditions: 1/1 H ₂ /CO, 50 atm.. GHSV 1832			
	Cu _{0.5} Mg ₅ CeO _x	0.9%K on Cu _{0.5} Mg ₅ CeO _x	Cu _{0.45} NdCeMgO _x
Temp, °C	290	320	290
CO conv, %	25.5	15.5	20.6
CO ₂	22.5	31.0	17.1
Selectivity, % C exclusive of CO ₂			
Methanol	70.7	57.2	82.6
Isobutanol	8.2	10.4	8.2
Other alcohols	4.9	6.9	2.4
Methane	8.4	11.5	3.7
Higher Hydrocarbons	4.1	12.8	2.7
DME	3.3	1.2	1.6
Taken from U. S. Patent 5387570 (X.81).			

Process Tables

Table X.51. Synthesis gas reaction in dual fixed-bed reactors with different catalysts . First stage bed: 20g Fe/Zn/Ce/K Second stage bed: 1.5 g Ru/TiO ₂ + quartz	
Temp, °C	220
Pressure, atm	6.47
H ₂ /CO mole ratio	1.64
Flow rate, sccm/min	36.5
CO Conv	59.0
CO ₂ Selectivity in upper bed	26
CH ₄ Selectivity	2.5
HC Selectivity in upper bed	33
HC Selectivity in lower bed	41
Taken from U. S. Patent 4624968 (X.82).	

Table X.52. Hydrocarbon selectivity from one and two-stage beds				
	First stage Fe/Zn/Ce/K	Second stage Ru/TiO ₂	2-Stage Beds	
			Predicted	Observed
CH ₄	3.5	6.1	4.9	3.9
C ₂ -C ₄	18.5	11.0	15.4	13.8
C ₅ -C ₉	22.9	24.7	23.9	22.6
C ₁₀ +	55.1	58.2	56.8	60.3
Taken from U. S. Patent 4624968 (X.82).				

Table X.53. Effect of adding ethylene to the feed						
	Catalyst					
	Ru-Co/TiO ₂			Ru/TiO ₂		
C ₂ H ₄ in feed, %	0	2.5	2.5	0	6.2	6.2
Location of C ₂ H ₄ Addition ^a	-	inlet	below top one-third	-	inlet	below top one-third
CO Conv %	25-27	25-27	25-27	35-45	35-45	35-45
C ₂ H ₄ Conv		99.5	89.5		97	45.3
C ₂ H ₄ Selectivity	-			-		
to C ₂ H ₆	-	86.5	69.5	-	82	44
to C ₃ +	-	13.5	30.5	-	18	56
Added C ₂ H ₄ that appears as C ₃ + %		13.5	27.3	-	17	26
% Selectivity ^b						
CH ₄	9.4	8.3	7.2	5.5	4.3	3.9
C ₂	1.3	-	-	0.7	-	-
C ₃	2.7	3.3	3.7	2.1	2.6	3.4
C ₄	2.4	2.9	3.7	3.5	4.0	5.1
CO ₂	0.4	0.5	0.4	0.7	0.7	0.7
C ₅ +	83.8	92.9	99.3	87.5	105.6	117.0
Example 3 in U.S. Patent 4754092 (X.85). a. Downflow reactor. b. Selectivity defined as percent CO converted. When ethylene is added, the sum of selectivities is >100%.						

Table X.54. Effect of heating rejuvenation tubes on catalyst activation.		
Heat addition	no	Yes
Gas rate in tube, scfh	5100	4800
Avg reactor temp, °F	427	427
Avg rejuvenation temp, °F	430	440
CO conv, start to end of run, %	32 to 26 (over 12 hrs)	26 to 36 (over 24 hrs)
Conv, change/day	-12.4	+10.4
Example 4 in U.S. Patent 4754092 (X.85).		

Table X.55. Improvement in catalyst/wax separation in slurry FT processes by removal of catalyst fines.							
Classification Solvent	Catalyst/solvent t wt/wt	Other	Cycle s	Acetone cycles	Filter time	Filter rate	
						(gm/min)	gal/ft ² /min
0.45 µm Millipore filter paper							
Blank	-	-	-	-	95.0	0.5	
Water	15/85	-	6	2	0.9	55.0	
i-C ₃ H ₆ OH/n-C ₇ H ₁₆ (1/9)	10/150	1% Oleic acid added	7	2	1.0	50.0	
i-C ₃ H ₆ OH/n-C ₇ H ₁₆ (1/9)	10/150	1% Aerosol OT-100 added	7	2	1.0	50.0	
0.3 µm glass fiber filter							
FT wax @ 130°C	2/98	Stirred 5 min	none	none	-	-	5.8 @ 14 psig
		Stirred 44 hrs	none	none	-	-	0.05 @ 14 psig
FT wax @ 120°C	2/98	Stirring per cycle19/48/2 4	3	none	-	-	14.5 @ 14 psig
Taken from U.S. Patent 5070064 (X.98).							

LEGEND :
 ● UNIFORMLY IMPREGNATED SPHERES, INSCRIPTION INDICATES CATALYST NUMBERS
 ○ RIM IMPREGNATED SPHERES, INSCRIPTION INDICATES CATALYST N° & RIM THICKNESS (MICRONS)

Figure X.1. Plot of methane production for various catalysts (from ref. X.50).

Figure X.2. Plot of cobalt productivity versus binder content in the titania support (from ref. X.30).

Figure X.3. Plot of wt.% of binder versus turnover number (TON) (from ref. X.30).

Figure X.4. Effect of dispersion on cobalt catalyst activity (from ref. X.51).

Figure X.5. Dependence of CH_4 and CO_2 production on presence of ruthenium or rhenium in the cobalt catalyst (from ref. X.51).

Figure X.6. Dependence of CO conversion on presence of ruthenium or rhenium in the cobalt catalyst (from ref. X.51).

Figure X.7. The CO conversion and the methane and CO₂ production at increasing conversion time using a Co-Ru-TiO₂ catalyst (from ref. X.51).

Figure X.8. Comparison of activity for Zr, Hf, Ce and U promoted Co-TiO₂ catalysts and unpromoted catalysts after simulated catalyst regeneration (from ref. X.57).

Figure X.9. Effect of promoter loading on Co-TiO₂ catalyst after simulated regeneration at 500°C (from ref. X.57).

Figure X.10. Relationship between wt.% Co-TiO₃ and total TiO₂ versus temperature (from ref. X.60).

Figure X.11. Effect on catalysts A and B (see text) of carburization showing that silica suppresses carbon growth (from ref. X.58).

Figure X.12. Plot of CO conversion rate as a function of the iron loading on titania (from ref. X.64).

Figure X.13. C_{2+} selectivity for increasing conversion with nickel catalysts (from ref. X.69).

Figure X.14. Impact of support on the rate of nickel carbonyl fraction (from ref. X.69).

Figure X.15. Catalyst concentration versus reactor height for (!) no downcomer and for one 3" downcomer (Q).

Figure X.16. Schematic of reactor for enhanced gas separation for bubble column draft tubes (from ref. X.90).

Figure X.17. Temperature exotherm within bed position for different start-up procedure (see text) (from ref. X.35).

Figure X.18. Temperature exotherm within bed position for low $H_2:CO$ ratio start-up (from ref. X.35).

Figure X.19. Relative volumetric productivity represented by activity with days on stream with intervals of hydrogen rejuvenation (12 wt.% Co on titania with 6 wt.% Al_2O_3 as binder (from ref. X.96).

Figure X.20. Catalyst concentration versus elevation in the reactor with (Q) and without (F) use of draft tubes (from ref. X.89).

Figure X.21. Conversion using hydrogenation rejuvenation (to day 3 no rejuvenation; rejuvenation after day 3) (from ref. X.89).

Figure X.22. Schematic of multiple vessels for catalyst rejuvenation (from ref. X.97).

Figure X.23. Elevation of a shell and tube reactor arrangement showing the gas, liquid, catalyst interconnection both above and below the upper and lower tube sheets.

Figure X.24. Horizontal Section A - A through the elevation of Figure 23 showing a possible arrangement of tubes, that is, reaction zones.

Figure X.25. Detail of a possible distribution zone for one reaction tube/zone.

APPENDIX - EXXON PATENTS

The following provides a listing of the primary claim from the patents reviewed during the preparation of this document. It is intended to provide a scope of the coverage of the initial report and the first addendum.

1. Gates, William, R. Fiato; Catalysts in FT process for producing olefins; Patent 4,639,431 (1987). **Claim 1:** A hydrocarbon synthesis catalyst comprising a sintered combination of metal oxides having the following components: (a) an oxide of a Group VIII metal; (b) an oxide of a Group IIB metal; (c) an oxide of a Group IA alkali metal; and (d) an oxide of a lanthanide metal, such that said sintered combination comprises a series of the Group VIII metal and the Group IIB metal spinels and the alkali metal oxide dispersed in a lanthanide metal oxide matrix.
2. Kim, Chang; R. Fiato; Multi-state FT process, patent 4,624,968, (1986). **Claim 1:** A process for producing paraffinic hydrocarbons from carbon monoxide and hydrogen comprising: (a) introducing carbon monoxide and hydrogen into a reaction zone wherein the carbon monoxide and hydrogen contact in a first bed a first catalyst having a high olefin selectivity selected from the group consisting of Fe/Ce/Zn/K, Fe/Mn/K and Fe/Co/K; and (b) contacting the resulting olefin in a second bed with a second catalyst having a high selectivity for converting olefins to heavier paraffinic hydrocarbons selected from the group consisting of Ru/TiO₂, Ru/SiO₂ and Ru/Al₂O₃.
3. Fiato, Rocco; S. Soled; FT hydrocarbon synthesis with high surface area Cu and K-promoted reduced-carbided iron/manganese spinels; Patent 4,621,102, (1986). **Claim 1:** A process for synthesizing a hydrocarbon mixture containing C₂-C₂₀ olefins comprising contacting a catalyst composition, comprising at least one unsupported, single phase, iron-manganese spinal dual promoted with both copper and a Group IA and IIA metal, said spinel exhibiting a single phase being isostructural with Fe₃O₄ as determined by powder X-ray diffractometry, and possessing a BET surface area greater than 30 m²/G and an Fe:Mn atomic ratio of at least 2/1, with a mixture of CO and hydrogen under conditions of pressure, space velocity, and elevated temperature for a time sufficient to produce said C₂-C₂₀ olefins.
4. Soled, Stuart, R. Fiato; Copper promoted iron/cobalt spinels and their preparation; patent 4,607,020 (1986). **Claim 1:** A composition of matter comprising a reduced and carbided, copper promoted iron-cobalt alloy, said composition being substantially isostructural with chi-Fe₅C₂, as determined by X-ray diffractometry and possessing a BET surface area of greater than 5 m²/g, said composition produced by contacting, with a carbiding atmosphere for a time sufficient to produce said composition, said copper-promoted iron cobalt alloy, being isostructural with metallic alpha iron as determined by powder X-ray diffractometry, possessing a BET surface area of greater than 5 m²/g, wherein said alloy was produced by contacting, with a reducing atmosphere, an

unsupported Group IA or IIA metal salt promoted iron-cobalt spinel, or mixture thereof, said spinel exhibiting a single phase powder X-ray diffraction pattern substantially isostructural with Fe_3O_4 , and possessing a BET surface area greater than $5 \text{ m}^2/\text{g}$ and an iron-cobalt atomic ratio of 4 to 1 or above.

5. Iglesia, Enrique, S. Soled, R. Fiato, J. Baumgartner; Selective fixed-bed FT synthesis with high surface area Cu and K promoted, iron/manganese spinels; Patent 5,118,715 (June 1992). **Claim 1:** A hydrocarbon synthesis process for preparing a product containing C_5+ hydrocarbons and less than about 30% CO_2 comprising contacting in a fixed-bed a pelletized catalyst composition wherein the particle size is greater than about 200 microns average diameter, at a temperature of $200\text{-}400^\circ\text{C}$, the catalyst comprising at least one unsupported, single phase, iron-manganese spinel dual promoted with both copper and a Group IA or IIA metal, said spinel exhibiting a single phase being isostructural with Fe_3O_4 as determined by powder X-ray diffractometry, and possessing a BET surface area greater than $30 \text{ m}^2/\text{g}$ and an Fe:Mn atomic ratio of at least 2/1, with a mixture of CO and hydrogen under conditions of pressure, space velocity, and elevated temperature for a time sufficient to produce said C_5+ hydrocarbons.
6. Soled, Stuart, S. Miseo, E. Iglesia, R. Fiato; Iron-zinc based catalysts for the conversions of synthesis gas to alpha-olefins; patent 5,100,856 (Mar. 1992). **Claim 1:** A composition comprising of iron, zinc, copper, an alkali metal selected from the group consisting of potassium, rubidium, cesium, or mixtures thereof, wherein the iron:zinc atomic ratio is at least about 5:1, and the alkali metal:copper atomic ratio is at least about 2:1.
7. Fiato, Rocco; G.McVicker, A. Montagna; Process for preparing a Fe-CO catalyst slurry system for alpha olefin production; Patent 4,532,229 (Jul 1985). **Claim 1:** A process for preparing a slurry Fischer-Tropsch catalyst system comprising the steps of: (a) heating a slurry mixture comprised of a Fischer-Tropsch slurry liquid, an iron carbonyl compound, a cobalt carbonyl compound, or iron and cobalt compounds capable of forming carbonyl complexes in an atmosphere of CO, and mixtures thereof, and a powdered support, wherein said iron and cobalt compounds are present in a total iron:cobalt atomic ratio of about 35:1 to 1:10, taken as free metals, and wherein the cobalt carbonyl compound has a lower melting point/decomposition temperature than the iron carbonyl compound; in a carbon monoxide atmosphere under pressure, at a temperature above the melting point/decomposition temperature of the cobalt compound for a time sufficient to substantially decompose the cobalt compound; and (b) heating said slurry mixture from step (a) at a temperature above the melting point/decomposition of the iron compound in said CO atmosphere under pressure, to substantially decompose the iron compound; and (c) heating and slurry mixture from step (b) in an atmosphere of hydrogen gas to substantially reduce said iron and cobalt carbonyl compounds and their decomposition products.

8. Cody, Ian; D. Brown; Wax isomerization using small particle low fluoride content catalysts; patent 4,923,588 (May 1990). **Claim 1:** A method for the isomerization of waxes into liquid hydrocarbons comprising passing the wax to be isomerized in the presence of hydrogen and under isomerization conditions over an isomerization catalyst comprising a noble Group VIII metal on small particle size, fluorided, refractory metal oxide wherein the catalyst possesses a fluoride content in the range of 0.1 to up to but less than 2.0 wt.% and the small particle size refractory metal oxide has a particle diameter of less than 1/16 inch.

9. Pedrick, Larry; C. Mauldin, W. Behrmann; Draft tube for catalyst rejuvenation and distribution; Patent 5,268,344 (Dec. 1993); **Claim 1:** A method for rejuvenating reversibly deactivated particulate hydrocarbon synthesis catalyst in a slurry phase reactor, said method comprising the use of substantially vertical draft tube means, open at both ends, fully immersed in the slurry containing the catalyst and injecting a hydrogen containing gas at or substantially near the bottom of said draft tube means thereby lifting catalyst in slurry from the bottom of the slurry phase reactor into and through the open bottom end of the draft tube means, rejuvenating catalyst in the presence of said hydrogen containing gas in the vertical draft tube means and ejecting the rejuvenated catalyst into the top of the slurry phase in the slurry phase reactor through the open top of the draft tube means.

10. Kugler, Edwin, S. Tauster, S. Fung; Ruthenium supported on manganese oxide as hydrocarbon synthesis catalysts in Co/H₂ reactions; patent 4,206,134 (June 1980). **Claim 1:** A process for the enhanced synthesis of C₂-C₄ olefins with reduced production of methane comprising the steps of passing H₂ and CO in an H₂/CO ratio of from about 10 to about 0.1 over a catalyst reduced at a temperature greater than about 300°C comprising ruthenium on a manganese-containing oxide support, wherein said manganese-containing oxide support is selected from the group consisting of MnO, Al₂O₃-MnO, SiO₂-MnO, MnO-carbon, Group IVB-manganese oxide, Group VB-manganese oxides, Group IA-manganese oxides, Group IIA-manganese oxides, rare earth-manganese oxides and mixtures thereof, at a space velocity of from about 100 hr⁻¹ to about 50,000 hr⁻¹, at a temperature of from about 100°C to about 500°C at a pressure of from about 103 to about 1.03 x 10⁵ kPa for a time sufficient to effect the generation of the desired olefinic product, wherein the concentration of said ruthenium in said catalyst is from about 0.01 to about 15% by weight.

- II. Madon, Rostam; Liquid hydrocarbon synthesis using supported ruthenium catalysts; patent 4,477,595 (Oct. 1984). **Claim 1:** A process for selectively producing paraffins comprising (a) first contacting a mixture of H₂ and CO for at least 10 hours with a reduced and supported ruthenium catalyst, said ruthenium catalyst comprising ruthenium on a support selected from the group consisting of TiO₂, ZrTiO₄, TiO₂-carbon, TiO₂-Al₂O₃, TiO₂-SiO₂, alkaline earth titanates, alkali titanates, rare earth titanates, V₂O₃, Nb₂O₅, Ta₂O₅, Al₂O₃-V₂O₃, Al₂O₃-Nb₂O₅, Al₂O₃-Ta₂O₅, SiO₂-V₂O₃, SiO₂-NbO₅, SiO₂-Ta₂O₅, V₂O₃-carbon,

Nb₂O₅-carbon, Ta₂O₅-carbon, alkaline earth Group VB oxides, alkali-group VB oxides, rare earth-Group VB oxides, Group IVB-Group VB oxides, and mixtures thereof, at Fischer-Tropsch conditions such that the temperature ranges from about 100 to 400°C, the pressure ranges from about 0.2 to 10 MPaA, the gas hourly space velocity, GHSV, ranges from about 100 to 50,000 v/v/hr, and wherein the ratio of GHSV/pressure is below about 24,000 v/v/hr/MPaA, and at least about a 20% CO conversion is effected; and (b) continuing said contacting as in step (a) at a H₂/CO molar ratio from about 0.1 to 4 and thereafter recovering a hydrocarbon mixture comprising C₅-C₄₀ hydrocarbons, containing C₅-C₂₀ paraffins and olefins in a paraffins to olefins weight ratio of at least about 1.5.

12. Wachs, Israel, C. Chersich; Catalysts comprising tantalum supported on titania; patent 4,544,649 (Oct. 1985). **Claim 1:** A catalyst composition comprising an oxide of tantalum supported on titania wherein at least a portion of the supported tantalum metal oxide is in a non-crystalline form.
13. Kim, Chang; Reducing methane productions in FT reactions; patent 4,547,525 (Oct. 1985). **Claim 1:** A process for reducing methane formation in a Fischer-Tropsch process for synthesizing hydrocarbons which comprises contacting, at an elevated temperature of 100-500°C and a pressure of from about 100-10,000 kPa, a H₂/CO feed mixture with a heterogeneous catalyst comprising one or more Group VIII metals supported on an inorganic refractory oxide support for a time sufficient to produce hydrocarbons, including methane, wherein one or more olefins is added to the H₂/CO feed mixture in an amount sufficient to reduce said methane formation to a level lower than it would be without adding said olefin to said feed.
14. Mauldin, Charles; Cobalt catalysts for the conversion of methanol to hydrocarbons and for FT synthesis; patent 4,568,663 (Feb. 1986). **Claim 1:** A catalyst useful for the conversion at reaction conditions of methanol or synthesis gas to hydrocarbons by contact with a catalyst which comprises cobalt and thorium in catalytically active amounts and ruthenium, composited with an inorganic oxide support in weight ratio of ruthenium:cobalt ranging from about 0.025:1 to about 0.10:1.
15. Arcuri, Kym; C. Mauldin, D. Shaw; Ruthenium rhenium catalyst on titania support for FT synthesis; patent 4,558,030 (Dec. 1985). **Claim 1:** A catalyst composition useful for the synthesis of hydrocarbons from admixtures of carbon monoxide and hydrogen at reaction conditions which comprises: ruthenium in catalytically active amount composited with titania, or titania-containing support, having a rutile:anatase ratio of at least about 2:3 and rhenium in amount sufficient to provide a weight ratio of rhenium:ruthenium which ranges from about 2:1 to about 1:4, sufficient at corresponding reaction conditions to obtain improved activity maintenance vis-a-vis a ruthenium catalyst otherwise similar except that it does not contain rhenium.

16. Payne, Virgil; C. Mauldin; Preparation of hydrocarbons from synthesis gas; patent 4,959,703 (June 1986). **Claim 1:** A process useful for the conversion of synthesis gas to hydrocarbons which comprises contacting at reaction conditions a feed comprised of an admixture of carbon monoxide and hydrogen, in $H_2:CO$ molar ratio equal to or greater than about 0.5:1 at total pressure equal to or greater than about 80 psig, over a catalyst which comprises cobalt, or cobalt and thoria in catalytically active amount composited with titania or titania-containing support, wherein the titania support is one having a rutile:anatase ratio of at least about 2:3.
17. McVicker, Gary; M. Albert Vannice; Preparation and use of supported potassium (or rubidium)-group VIII metal cluster catalyst in CO/H_2 FT synthesis reactions; Patent 4,154,751 (May 1979). **Claim 1:** In a Fischer-Tropsch process reaction for the production of hydrocarbons from CO and H_2 wherein CO and H_2 are passed over a catalyst the improvement comprising using as the catalyst a supported potassium or rubidium-Group VIII metal cluster catalyst which catalyst is prepared by depositing a known, well-characterized potassium or rubidium-Group VIII metal carbonyl cluster complex on a high surface area support, drying the carbonyl cluster complex impregnated support in the absence of oxygen and reducing the supported complex at elevated temperatures, wherein using this catalyst in Fischer-Tropsch processes results in the selective formation of higher molecular weight paraffinic and olefinic hydrocarbons.
18. Fiato, Rocco; S. Soled; Cobalt promoted catalyst for use in FT slurry process; patent 4,544,672 (Oct. 1985). **Claim 1:** A slurry process for synthesizing a hydrocarbon mixture containing C_2-C_4 olefins comprising the step of contacting a liquid slurry catalyst system, comprised of a slurry liquid and a carbided and reduced, unsupported iron-cobalt single phase spinel catalyst containing a Group IA or IIA metal salt promoter agent, and said spinel having the initial empirical formula: $Fe_xCo_yO_4$, wherein x and y are integer or decimal values, other than zero, with the provisos that the sum of $x+y$ is 3 and the ratio of x/y is 7:1 or above, said spinel exhibiting a single phase X-ray diffraction pattern substantially isostructural with that of Fe_3O_4 and said spinel having a measured BET surface area of up to $5\text{ m}^2/\text{g}$, said process being conducted with a mixture of CO and hydrogen under conditions of pressure, space velocity, and elevated temperature, for a time sufficient to produce said product C_2-C_4 olefins.
19. Fiato, Rocco, S. Soled, A. Montagna; Cobalt promoted FT catalysts patent 4,544,674 (Oct. 1985). **Claim 1:** A fixed bed process for synthesizing a hydrocarbon mixture containing C_2-C_6 olefins comprising the step of contacting a fixed bed of a catalyst composition comprised of an unsupported Group IA or IIA metal salt promoted iron-cobalt spinel: said spinel exhibiting a single spinel phase, being isostructural with Fe_3O_4 as determined by X-ray diffractometry and possessing a BET nitrogen surface area of up to $5\text{ m}^2/\text{g}$, and an iron-cobalt atomic ratio of 7:1 or above; with a mixture of CO /hydrogen under process

conditions of pressure, space velocity (SHSV) and elevated temperature for a time sufficient to produce said C₂-C₆ olefins.

20. Vaughan, David; K. Strobmaier; Synthesis of ECR-26(C-2646); patent 5,283,047 (Feb. 1994). **Claim 1:** A synthetic transition metal aluminosilicate crystalline zeolite having the gmelinite structure and a chemical composition in the dehydrated form: 0.8 to 1.3 M_{2/n}O:(Al,Fe,Cr)₂O₃:4 to 8 SiO₂, where n is the valence of metal M; the atoms of Al $\geq$ atoms of

$$(Cr + Fe), \frac{Cr}{Cr + Al + Fe} \geq 0.05$$

and characterized by an X-ray diffraction pattern having the following essential lines:

dD	I/I ₀
11.9	VS
6.8	S
5.0	VS
5.59	M
4.11	MS
3.44	MS
2.97	MS
2.85	M
2.59	M

21. Iglesia, Enrique, S. Soled, R. Fiato; SiO₂ promoted cobalt catalyst on a support of TiO₂ for converting synthesis gas to heavy hydrocarbons; patent 4,794,099 (Dec. 1988). **Claim 1:** A hydrocarbon synthesis catalyst comprising cobalt in a catalytically active amount composited with an inorganic refractory support comprised of a major portion of titania to which a lesser portion up to about 15 wt.% of silica in the form of silica or a silica precursor has been added.
22. Iglesia, Enrique, R. Madon; Reducing methane production and increasing liquid yields in FT reactions; patent 4,754,092 June (1988); **Claim 1:** A process for reducing methane formation and increasing liquid (C₅+) yields in a Fischer-Tropsch hydrocarbon synthesis process comprising adding an olefin to a gas feed and contacting said gas feed comprising a mixture of H₂ and CO with a catalyst at an elevated temperature of at least about 100°C, said addition of said olefin and said contacting with said gas feed occurring within the reactor bed in the area of the reactor bed below 10% of the distance from the top to the bottom

of the reactor bed and above 10% of the distance from the bottom to the top of the reactor bed in an amount sufficient to reduce said methane formation, wherein said catalyst comprises a catalytic metal selected from the group consisting of iron, cobalt and ruthenium supported on an inorganic refractory oxide support.

23. Fiato, Rocco, S. Miseo; Process for the preparation of slurried CO hydrogenation catalysts; patent 4,749,677 (June 1988) **Claim 1:** A process for forming a slurry catalyst composition produced by the steps of: (a) adding to a stirred slurry reactor TiO_2 , ruthenium carbonyl complex and an inert alkane hydrocarbon; (b) sealing said stirred slurry reactor and adding a gas mixture of $\text{N}_2:\text{CO}$ at room temperature and one atmospheric pressure to said stirred slurry reactor to purge said stirred slurry reactor; (c) heating said stirred slurry reactor to about 100°C and raising the pressure of said stirred slurry reactor to about 4 to about 10 atmospheres and adding a gas mixture of $\text{N}_2:\text{H}_2$ to said stirred slurry reactor; and (d) increasing the temperature of said stirred slurry reactor to about 230°F to about 270° and the pressure of said stirred slurry reactor from about 4 to about 20 atmospheres for about 2 to about 6 hours to cause the decomposition of said ruthenium carbonyl complex to form said slurry catalyst composition.
24. Iglesia, Enrique, S. Soled, R. Fiato; Cobalt-ruthenium catalysts for FT synthesis and process for their preparation; patent 4,738,948 (Apr. 1988). **Claim 1:** A hydrocarbon synthesis catalyst prepared by a process comprising impregnating a refractory support comprising titania with solutions of catalytically active amounts of cobalt and ruthenium salts, drying the impregnated support, reducing the cobalt and ruthenium, treating the reduced metals with an oxygen containing stream at conditions sufficient to form oxides of cobalt and oxides of ruthenium and reducing the cobalt and ruthenium oxides.
25. Wachs, Israel, D. Yang; Catalysts comprising ruthenium on titania surface modified with group VA oxide of vanadium, niobium or tantalum; patent 4,711,871 (Dec.1987). **Claim 1:** A process for preparing a catalyst comprising ruthenium supported on a surface-modified titania support wherein said support comprises an oxide of a metal selected from the group consisting of niobium, vanadium, tantalum or mixture thereof, in a non-crystalline form, supported on said titania wherein said process comprises the sequential steps of: (a) forming said support comprising titania whose surface has been modified with and supports an oxide of a metal selected from the group consisting of niobium, tantalum, vanadium or mixture thereof wherein said supported, modifying oxide is a non-crystalline form; (b) impregnating said so-formed surface modified titania support with a solution of a ruthenium precursor compound; and (c) converting said ruthenium precursor compound to ruthenium to form said catalyst.
26. Mauldin, Charles, S. Davis, K. Arcuri; Cobalt catalysts for the conversion of methanol and for FT synthesis to produce hydrocarbons; patent 4,663,305 (May 1987). **Claim 1:** A regeneration stable catalyst for the conversion at reaction conditions of methanol or synthesis gas to liquid hydrocarbons which consists

essentially of from about 2% to about 25% cobalt, based on the weight of the catalyst composition, composited with titania, or a titania-containing support, to which is added sufficient of a zirconium, hafnium, cerium, or uranium promoter to provide a weight ratio of the zirconium, hafnium, cerium, or uranium metal:cobalt greater than about 0.101:1.

27. Fiato, Rocco, R. Bar-Gadda, S. Miseo; Cerium promoted FT catalysts; patent 4,657,885 (Apr. 1987). **Claim 1:** A hydrocarbon synthesis catalyst composition comprising sintered combination metal oxides having the following components in the stated weight percentage of the catalyst composition: (a) about 5 to about 80 wt.% of a Group VIII metal oxide; (b) about 4 to about 40 wt.% of a Group IIB metal oxide; (c) about 10 to about 40 wt.% of a Group IVB and/or VIIB metal oxide; (d) about 1 to about 5 wt.% of a Group IA metal oxide; and (e) about 1 to about 10 wt.% of a Lanthanum Group metal oxide, such that where the catalyst contains a Group VIII metal, said sintered combination comprises a series of spinels of a Group VIII metal, a Group IIB metal, and/or a Group IVB metal, and/or a Group VIIB metal, and a Group IA metal oxide in a lanthanum Group metal oxide matrix.
28. Mauldin, Charles; Start-up with ruthenium catalysts; patent 4,647,592 (MAR. 1987). **Claim 1:** In a process for the conversion of synthesis gas to hydrocarbons by contacting at reaction conditions a feed characterized as an admixture of carbon monoxide and hydrogen with a bed of particulate ruthenium catalyst constituted of a catalytically active amount of ruthenium composited with titania, or a titania-containing support, the improvement comprising contacting and pretreating the catalyst, prior to initiating the conversion reaction, with an admixture of steam and hydrogen at temperatures ranging from about 200°C to about 550°C sufficient to mildly agglomerate and ruthenium and form on the particles of catalyst larger agglomerates of ruthenium of average crystallize size from about 15 D to about 25 D approximating that obtained on completion of the startup portion of a synthesis gas operating run.
29. Arcuri, Kym; Process for the start-up of a FT reactor; patent 4,626,552 (Dec. 1986). **Claim 1:** In a process for the startup of a reactor wherein a feed comprised of hydrogen and carbon monoxide is contacted with a bed of hydrocarbon synthesis catalyst in which perturbations of the temperature profile across the bed can develop, and which, at line-out conditions defined by feed flow rate, pressure, temperature, and the molar ratio of hydrogen:carbon monoxide of the feed is sufficient to synthesize hydrocarbons from the hydrogen and carbon monoxide, the improvement which comprises: elevating, while maintaining the molar feed ratio of hydrogen:carbon monoxide at below about 90% of its line-out value, the feed flow rate, pressure and temperature to values approaching line-out feed flow rate, line-out pressure and line-out temperature and then gradually increasing the molar feed ratio of hydrogen:carbon monoxide to essentially that employed at line-out.

30. Davis, Stephen M.; Silica modified hydroisomerization catalyst; U.S. patent 5,187,138 (Feb. 1993). **Claim 1:** A catalyst composition comprising: a Group VIII metal; a support therefore of alumina or silica-alumina wherein the silica content is less than about 35 wt.%; at least about 0.5 wt.% silica other than the support silica; and a surface area of about 180-400 m²/gm.
31. Hamner, Glen P.; Process for the isomerization and hydrocracking of FT waxes to protect a syncrude and upgraded hydrocarbon products; patent 4,832,819 (May 1989). **Claim 1:** A process for producing a pumpable syncrude from a Fischer-Tropsch wax containing oxygenate compounds, which comprises: (1) separating the FT wax into (a) a low-boiling fraction which contains most of the oxygenate compounds and (b) a high-boiling fraction which is substantially free of water and oxygenate compounds, (2) reacting the high-boiling fraction from step (1) with hydrogen at hydroisomerization and mild hydrocracking conditions in the presence of a fluorided Group VIII metal-on-alumina catalyst to produce a C₅+ hydrocarbon product, and (3) combining the C₅+ hydrocarbon product from step (2) with the low-boiling fraction from step (1) to produce a pumpable, refinery processable syncrude that can be transported at atmospheric conditions.
32. Hsia, Stephen J.; External catalyst rejuvenation system for the hydrocarbon synthesis process; patent 5,260,239 (Nov. 1993). **Claim 1:** A process for practicing catalytic hydrocarbon synthesis and reactivation rejuvenation of deactivated hydrocarbon synthesis catalyst on a continuous basis, said process comprising combining catalyst and synthesis feed and hydrocarbon liquid in a hydrocarbon synthesis first vessel means to produce a reactor slurry comprising catalyst, synthesis feed and synthesis product, collecting deactivated catalyst from the top of the reactor slurry by means of a first downcomer C conduit means the top of which is fitted with gas disentrainment means and which is located just below the top surface of the reactor slurry, passing the deactivated catalyst down this first downcomer C conduit means from the top of the first vessel means to the bottom of a reactivation C rejuvenation second vessel means, said second vessel means having rejuvenating gas introduction means located at its bottom, forming a reactivating slurry of catalyst in reaction product and rejuvenating gas, wherein the deactivated catalyst is reactivated C rejuvenated in said second vessel means, collecting reactivated C rejuvenated catalyst from the top of the reactivating slurry by means of a second downcomer C conduit means the top of which is fitted with gas disentrainment means and which is located just below the top surface of the reactivation slurry and passing the reactivated C rejuvenated catalyst down the second downcomer C conduit means from the top of the second vessel means to the bottom of the first vessel means, all catalyst downward flows on both the first and second downcomer means occurring solely under the influence of gravity.
33. Mitchell, Willard N.; Activation of hydrocarbon synthesis catalyst; patent 5,292,705 (Mar. 1994). **Claim 1:** A method for activating an essentially fresh, reduced cobalt containing FT catalyst which comprises treating the catalyst with

hydrogen or a hydrogen containing gas in the presence of hydrocarbon liquids for a period sufficient to increase substantially the initial catalyst productivity.

Examples. In a hydrocarbon synthesis process demonstration unit, hydrogen treatment of the catalyst to enhance initial activity for slurry phase operations was demonstrated. In the unit, fresh catalyst 12 st% Co, 1 wt% Re on a titania support with 6 wt% Al_2O_3 as a binder material, was activated by first reducing the catalyst in hydrogen to reduce the cobalt oxide to the cobalt metal. This was accomplished in a **fluid bed reactor** at temperatures up to about 375°C. The H_2 treat gas rate was 8-18 SCFH H_2 /lb catalyst with a H_2 concentration of 18-25% in N_2 . Following the reduction the catalyst was passivated with 0.25-1.3 SCFH of CO in N_2+H_2 for 1-2 hours.

The dry reduced catalyst [presumably they mean the dry reduced and passivated catalyst] was combined with a wax to form a slurry in a slurry mix vessel. The slurry was transferred to the hydrocarbon synthesis reactor and synthesis was initiated. Following a short test to measure initial catalyst productivity, a hydrogen treat was conducted in the slurry reactor ("super" activation). The following table shows two samples of this "super" activation:

	Relative Productivity	
	Before	After
Example 1	60	100
Example 2	25	100

In the first example the relative productivity increased from 40% to 100% and the second case from 25% to 100%. The conditions for the H_2 treat of the slurry were typical of conditions described earlier.

In order to determine the real increase in initial activity, the catalyst had to be run at synthesis conditions for a period sufficient to obtain an initial activity or productivity. However, this minimal operation at synthesis conditions is not believed to change or effect the catalyst in any substantive way and the catalyst may be considered as essentially fresh catalyst.

34. Chang, Min; C. Coulaloglou; Enhanced catalyst mixing in slurry bubble columns (OP-3723); patent 5,252,613 (Oct. 1993). **Claim 1:** A method for improving the axial distribution of catalyst in a hydrocarbon synthesis slurry bubble column which uses rising synthesis gas introduced by means of synthesis gas distribution means located at the bottom of said column to provide the majority of the energy used in distributing catalyst in said column, the improvement in axial distribution of catalyst being achieved by using a secondary fluid introduction means in said slurry bubble column at a location above the synthesis gas

distribution means located at the bottom of said column to introduce a secondary fluid stream into said column.

35. Kim, Chang J.; Water addition for increased Co/N₂ hydro-carbon synthesis activity over catalysts comprising cobalt, ruthenium and mixtures thereof which may include a promoter metal; patent 5,227,407 (Jul 1993). **Claim 1:** A once-through, fixed or slurry bed FT process with CO conversion activity and C₅+ liquid hydrocarbon selectivity comprising contacting a feed mixture of carbon monoxide and hydrogen in a reaction zone with about 1 vol.% to about 70 vol.% water based on the total volume of feed mixture, at a pressure above one atmosphere and a temperature ranging from about 150°C to about 300°C, with a catalyst selected from the group consisting of cobalt, ruthenium, and mixtures thereof on a titania support, wherein said titania support is less than 40 m²/g, converting at least 90 vol.% of the carbon monoxide to liquid hydrocarbons, and in the substantial absence of CO₂ formation.
36. Soled, Stuart, E. Iglesia, R. Fiato, G. Ansell; Method for stabilizing titania supported cobalt catalyst and the catalyst for use in FT process; patent 5,169,821 (Dec. 1992). **Claim 1:** A method of preparing a 400-750°C regeneration stable catalyst composition comprising: (a) coprecipitating a titanium metal complex from a solution of a titanium alkoxide and a metal alkoxide or a solution of titanium chloride and a metal chloride wherein said metal is selected from the group consisting of silicon, zirconium and tantalum; (b) recovering the coprecipitate and calcining at temperatures of 400-750°C, to form a ternary metal oxide support; (c) depositing a cobalt compound onto said calcined ternary metal oxide support; (d) activating said cobalt calcined support to form a catalyst comprised of cobalt on a substituted ternary metal oxide support of titania having the general formula Co/Ti_xM_{1-x}O₂ wherein x is from 0.01 to 0.14 and M is selected from the group consisting of silicon, zirconium, and tantalum, wherein the titania is an anatase polymorph.
37. Soled, Stuart, E. Iglesia, R. Fiato; Copper promoted cobalt-manganese spinel catalyst and method for making the catalyst for FT synthesis; patent 5,162,284 (Nov. 1992). **Claim 1:** A composition of matter comprising a copper promoted cobalt-manganese spinel, the spinel having the formula: Co_{3-x}Mn_xO₄, where x is from about 0.5 to about 1.2.
38. Mauldin, Charles, K. Riley; Process for the preparation of surface impregnated dispersed cobalt metal catalysts; patent 4,977,126 (Dec. 1990). **Claim 1:** In a process for the production of catalysts wherein a catalytically effective amount of cobalt is impregnated and dispersed on the outer surface of a particulate porous inorganic oxide support to form a catalyst useful for the conversion of synthesis gas to hydrocarbons, and the support particles are contacted with a spray containing a decomposable compound of cobalt, the improvement comprising: maintaining a bed of the support particles in a fluidized state at temperature ranging from about 50°C to about 100°C by contact with a gas at temperature ranging from about 50°C to about 100°C; spraying the bed of the heated support

particles with a liquid in which a cobalt compound is dispersed at flow rate sufficient to provide a ratio between the flow rate of the liquid: flow rate of the fluidizing gas below about 0.6 grams liquid/ft³ of fluidizing gas to form on the particles a surface layer of cobalt compound in average thickness ranging from about 20 microns to about 250 microns, with the loading of cobalt compound ranging from about 0.01 g/cc to about 0.15 g/cc, calculated as metallic cobalt per packed bulk volume of catalyst.

39. Iglesia, Enrique; S. Soled, R. Fiato; Synthesis gas to heavy hydrocarbons on SiO₂ promoted Co/TiO₂; patent 4,960,801 (Oct. 1992). **Claim 1:** A process for preparing C₅+ hydrocarbons which comprises reacting hydrogen and carbon monoxide at hydrocarbon synthesis reaction conditions in the presence of a catalyst comprising cobalt in a catalytically active amount composited with an inorganic refractory support comprising a major portion of titania to which a lesser portion up to about 15 wt.% silica in the form of silica or a silica precursor has been added.
40. Pedrick, Larry E.; C. Mauldin, W. Behrmann; Draft tube for catalyst rejuvenation and distribution; patent 5,268,344, (Dec. 1993). **Claim 1:** A method for rejuvenating reversibly deactivated particulate hydrocarbon synthesis catalyst in a slurry phase reactor, said method comprising the use of substantially vertical draft tube means, open at both ends, fully immersed in the slurry containing the catalyst and injecting a hydrogen containing gas at or substantially near the bottom of said draft tube means thereby lifting catalyst in slurry from the bottom of the slurry phase reactor into and through the open bottom end of the draft tube means, rejuvenating catalyst in the presence of said hydrogen containing gas in the vertical draft tube means and ejecting the rejuvenated catalyst into the top of the slurry phase in the slurry phase reactor through the open top of the draft tube means.
45. McVicker, Gary; M. Albert Vannice; Preparation and use of supported potassium (or rubidium)-group VIII metal cluster catalysts in CO/H₂ FT synthesis reactions; patent 4,192,777 (Mar. 1980). **Claim 1:** Supported, highly dispersed, high activity potassium or rubidium-Group VIII metal cluster catalysts demonstrating improved selectivity olefinic and paraffinic hydrocarbons in CO/H₂ reactions prepared by the process which comprises depositing known, well-characterized potassium or rubidium-Group VIII metal carbonyl cluster complexes and mixtures thereof on a high surface area support material, drying the carbonyl cluster complex impregnated support in the absence of oxygen, and reducing the supported complex at elevated temperatures to effect the essentially complete reduction of the supported potassium or rubidium-Group VIII metal carbonyl cluster complexes to discrete potassium or rubidium-Group VIII clusters of metals on the support surface.
46. Wright, Franklin; M. Richard, J. Pirkle; Process using iron-thallium catalysts in CO hydrogenation; patent 4,513,104 (Apr. 1985). **Claim 1:** A process for producing liquid hydrocarbons, including those in the C₆-C₁₁ hydrocarbon range,

comprising the steps of: (a) first depositing thallium on the surface of a supported or unsupported iron catalyst wherein the weight ratio of iron-thallium, taken as the free metals, is from about 100:1 to 1:100, and wherein said iron compounds contain iron value substantially in the trivalent state; (b) contacting said iron-thallium catalyst with a mixture of CO and H₂ in a volume ratio of about 1:4 to 4:1, respectively, at a temperature ranging from 270 to 550°C, a pressure ranging from 0.1 to 10 MPa and a space velocity ranging from 10 to 10,000 v/v/hr, or equivalent conditions, for a sufficient time to substantially convert said thallium compounds to metallic thallium and said iron compounds to reduced and carbided iron; and (c) continuing said contacting as described in step (b) at a pressure above 0.1 MPa, a temperature ranging from 230 to 550°C, to produce liquid hydrocarbons comprising about 40 wt.% and greater C₆-C₁₁ liquid hydrocarbons and below about 5 wt.% C₂₃+ hydrocarbons.

47. Wright, Franklin; Iron-thallium catalysts for use in CO hydrogenation and process of preparing the catalysts, Patent 4,436,834 (Mar. 1984). **Claim 1:** A catalyst composition consisting essentially of a mixture of an iron compound and a thallium compound, being supported or unsupported, said compound of iron and thallium being selected from the group consisting of an oxide, hydroxide, carbonate, sulfate, carbide, halide, nitrate, or mixtures thereof, wherein the weight ratio of iron-thallium, taken as the free metals, is from about 100:1 to 1:100, and wherein said iron compound contains iron value substantially in the trivalent state, and wherein said thallium compound is substantially deposited on the surface of said iron compound.

48. Soled, Stuart, R. Fiato; Process for preparing high surface area iron/cobalt FT slurry catalysts; patent 4,518,707 (May 1985). **Claim 1:** A composition of matter comprising an unsupported, Group IA or IIA metal salt promoted iron-cobalt spinel, or mixture thereof, said spinel exhibiting a single phase powder X-ray diffraction pattern substantially isostructural with Fe₃O₄, and possessing a BET surface area greater than 5 m²/g and an iron-cobalt atomic ratio of 4 to 1 or above.

49. Soled, S. L. and R. A. Fiato; Process for preparing high surface area iron/cobalt Fischer-Tropsch slurry catalysts; U.S. Patent 4,544,671, Oct. 1, 1985. **Claim 1:** A slurry process for synthesizing a hydrocarbon mixture containing C₂-C₂₀ olefins comprising the step of contacting a catalyst composition, comprised of an unsupported iron-cobalt spinel, said spinel exhibiting a single phase being isostructural with Fe₃O₄ as determined by powder X-ray diffractometry, and possessing an initial BET surface area greater than 5 m²/g and an Fe:Co atomic ratio of 7:1 and above, with a mixture of CO and hydrogen under conditions of pressure, space velocity, and elevated temperature, for a time sufficient to produce said C₂-C₂₀ olefins.

50. Fiato, Rocco; S. Soled, A. Montagna; Promoted iron-cobalt spinel catalyst for FT process; patent 4,537,867 (Aug. 1985). **Claim 1:** A hydrocarbon synthesis catalyst composition comprising an unsupported, Group IA or IIA metal salt

promoted iron-cobalt single phase spinel, said spinel having the initial empirical formula: $\text{Fe}_x\text{Co}_y\text{O}_4$, wherein x and y are integer or decimal values, other than zero, with the proviso that the sum of x+y is 3 and the ratio of x/y is 7:1 or above, said spinel exhibiting a powder X-ray diffraction pattern substantially isostructural with Fe_3O_4 and said spinel having an initial BET surface area of up to about 5 m^2/g .

51. Vannice, M. A. and R. L. Garten; Hydrocarbon synthesis from CO and H_2 using Ni supported on a titanium oxide; U. S. Patent 4,042,615, Aug. 16, 1977. **Claim 1:** A process for the synthesis of higher molecular weight paraffins comprising the steps of passing CO and H_2 in a CO/ H_2 ratio of 10 to 0.1 over a catalyst comprising nickel on a titanium-containing oxide support, wherein said titanium-containing oxide support is selected from the group consisting of TiO_2 , ZrTiO_4 , TiO_2 -carbon, TiO_2 - Al_2O_3 , TiO_2 - SiO_2 , alkaline earth titanates, alkali titanates, rare earth titanates and mixtures thereof, at a space velocity of from 100 to 50,000 v/v/hr and a temperature of from 100 to 500 $^\circ\text{C}$ at pressure of from 103 to 1.03×10^5 kPa for a time sufficient to effect the generation of the desired paraffinic products in the desired ratio, wherein the concentration of said nickel in said catalyst is from 0.01 to 75% by weight.
52. Tauster, S. J. and S. C. Fung; Group VIII metals on manganese-containing oxide supports which exhibit strong metal support interactions; U.S. Patent 4,402,869, Sept. 6., 1983. **Claim 1:** Improved catalytic compositions comprising catalytic metal selected from the group consisting of iron, nickel, cobalt and mixtures thereof supported on a manganese-containing oxide support, the improvement comprising as a final step before use, contacting said catalyst composition with a reducing atmosphere at a temperature of at least about 300 $^\circ\text{C}$ to produce a catalyst composition which exhibits suppressed hydrogen chemisorption.
53. Wachs, Israel; R. Fiato, C. Chersich; Iron carbide on titania surface modified with group VA oxides as FT catalysts; patent 4,559,365 (Dec. 1985). **Claim 1:** A process for producing hydrocarbons, including alkane hydrocarbons, from gaseous feed mixtures of CO and H_2 comprising contacting said feed, at a temperature ranging from about 200 to 350 $^\circ\text{C}$ and for a time sufficient to convert at least a portion of said feed to alkane hydrocarbons, with a catalyst comprising iron carbide supported on a surface modified titania support wherein said support comprises an oxide of a metal selected from the group consisting of niobium, vanadium, tantalum and mixture thereof supported on titania wherein at least a portion of said supported oxide is in a non-crystalline form.
54. Soled, Stuart, R. Fiato; FT hydrocarbon synthesis with copper promoted iron/cobalt spinel catalyst; patent 4,584,323 (Apr. 1986). **Claim 1:** A process for synthesizing a hydrocarbon mixture containing C_2 - C_{20} olefins comprising contacting a catalyst composition, comprising an unsupported, copper promoted iron-cobalt spinel, said spinel exhibiting a single phase being isostructural with Fe_3O_4 as determined by powder X-ray diffractometry, and possessing an initial

BET surface area greater than 5 m²/g and an Fe:Co atomic ratio of 4:1 and above, with a mixture of CO and hydrogen in a slurry liquid under conditions of pressure, space velocity and elevated temperature, for a time sufficient to produce said C₂-C₂₀ olefins.

56. Kugler, E. L. and R. L. Garten; Hydrocarbon synthesis from CO and H₂ using titanium promoted bulk nickel catalysts; U.S. Patent 4,273,724, June 16, 1981. **Claim 1:** A process for the synthesis of higher molecular weight paraffinic hydrocarbons of from C₂ to C₇ carbon number comprising the steps of passing CO and H₂ at a CO/H₂ ratio of from 10 to 0.1 at a space velocity of from 100 hr⁻¹ to 50,000 hr⁻¹, at a temperature of from 100 to 500°C and at pressures of from 103 to 1.03 x 10⁵ kPa over a catalyst comprising bulk nickel promoted with from 0.07 to 10 wt.% titanium containing oxide (calculated as TiO₂) for a time sufficient to effect the generation of the desired paraffinic products.

57. Vannice, M. A. and S. J. Tauster; Hydrocarbon synthesis from CO and H₂ using Ru supported on group VB metal oxides; U.S. Patent 4,171,320, Oct. 16, 1979. **Claim 1:** A process for the synthesis of olefins of from C₂ to C₅ chain length inclusive, said process comprising the steps of passing H₂ and CO at a H₂/CO ratio of 0.1 to about 10 over a catalyst comprising ruthenium on a support selected from the group consisting of V₂O₃, Nb₂O₅, Ta₂O₅, Al₂O₃-V₂O₃, Al₂O₃-Nb₂O₅, Al₂O₃-Ta₂O₅, SiO₂-V₂O₃, SiO₂-Nb₂O₅, SiO₂-Ta₂O₅, V₂O₃-carbon, Nb₂O₅-carbon, Ta₂O₅-carbon, alkaline earth group VB oxides, alkali Group VB oxides, rare earth Group VB oxides, Group IVB-Group VB oxides and mixtures thereof, at a space velocity of from 100 to 50,000 hr⁻¹, at a temperature of from 100 to 500°C, at a pressure of from 100 to 10⁵ kPa for a time sufficient to effect the generation of the desired olefinic products wherein the concentration of said ruthenium in said catalyst is from 0.01 to 15 wt.% based on total catalyst weight.

58. Fiato, Rocco; S. Soled; High surface area dual promoted iron/manganese spinel compositions; patent 4,618,597 (Oct. 1986). **Claim 1:** A composition of matter comprising an unsupported, Group IA or IIA metal and copper promoted, single phase, iron-manganese spinel, said spinel exhibiting a powder X-ray diffraction pattern substantially isostructural with Fe₃O₄ and possessing a BET surface area greater than 30 m²/g and an iron-manganese atomic ratio greater than about 2:1.

59. DeLuca, J. P., L. L. Murrell, R. P. Rhodes and S. J. Tauster; Stabilized ruthenium catalysts for selective reduction of oxides of nitrogen; U.S. Patent 3,922,235, Nov. 25, 1975. **Claim 1:** A stabilized supported ruthenium catalyst, said catalyst comprising ruthenium metal in combination with an oxide support, said support being one selected from the group consisting of zirconium titanate, and zirconium titanate mixed with titania, the ruthenium being present in an amount which does not exceed 0.003 grams of ruthenium per gram of oxide support.

71. Kugler, E. L. and S. J. Tauster; Catalyst comparison nickel supported on tantalum oxide or niobium oxide and their use as hydrocarbon synthesis catalysts in CO/H₂ reactions; U.S. Patent 4,206,135, June 3, 1980. **Claim 1:** A process

for the enhanced synthesis of paraffinic hydrocarbons of from 2 to 6 carbon atoms inclusive with reduced production of methane comprising the steps of passing H_2 and CO in an H_2/CO mole ratio of from about 0.1 to about 10 over a catalyst reduced at a temperature of at least $375^\circ C$ comprising nickel on a tantalum or niobium-containing oxide support wherein said tantalum or niobium-containing oxide support is selected from the group consisting of tantalum oxides, niobium oxides, $Al_2O_3-Ta_2O_5$, $Al_2O_3-Nb_2O_5$, $SiO_2-Ta_2O_5$, $SiO_2-Nb_2O_5$, Ta_2O_5 -carbon, Nb_2O_5 -carbon, alkaline earth-tantalum oxides, alkaline earth-niobium oxides, alkali-tantalum oxides, alkali-niobium oxides, rare earth-tantalum oxides, rare earth-niobium oxides, Group IVb-tantalum oxides, Group IVb-niobium oxides, and mixtures thereof, at a space velocity of from 100 hr^{-1} to about $50,000\text{ hr}^{-1}$, at a temperature of from about $100^\circ C$ to about $500^\circ C$, at a pressure of from about 100 to about $1 \times 10^5\text{ kPa}$, for a time sufficient to effect the generation of the desired paraffinic product, wherein the concentration of said nickel in said catalyst is from about 0.01 to about 75 wt.%.

72. Murrell, L. I. and S. J. Tauster; Catalytic process for NO_x reduction under lean conditions; U.S. Patent 4,039,622, Aug. 2, 1977. **Claim 1:** A process for effecting the selective reduction of NO_x in lean effluent waste streams containing NO_x , CO, O_2 , H_2 , CO_2 and water, wherein the concentration of CO is at least equivalent to the concentration of NO_x present in the waste stream, a lean effluent waste stream being defined as one in which the concentration of oxygen is in excess over the concentration of reductants to a level as high as 8%, i.e., about 800% excess oxygen, over the total of reductants present, said reductants being selected from the group comprising CO and H_2 so that when such a waste stream is reacted to completion, the residuum is oxidizing in character, said process comprising the steps of contacting said lean exhaust stream in a reaction zone with an iridium catalyst, said contacting occurring at a temperature between $300^\circ C$ to $750^\circ C$ thereby effecting the selective reduction by CO of the oxides of nitrogen to molecular nitrogen.
73. Vannice, M. A. and R. L. Garten; Hydrocarbon synthesis from CO and H_2 using Rh supported on titanium oxides; U.S. Patent 4,116,994, Sept. 26, 1978. **Claim 1:** A process for the enhanced synthesis of olefins and paraffins, wherein said paraffins are other than methane, comprising the steps of passing H_2 and CO in a H_2/CO ratio of 0.1 to 10 over a catalyst comprising rhodium on a titanium-containing oxide support, wherein said titanium-containing oxide support is selected from the group consisting of TiO_2 , $ZrTiO_4$, TiO_2 -carbon, $TiO_2-Al_2O_3$, TiO_2-SiO_2 , alkaline earth titanates, alkali titanates, rare earth titanates and mixtures thereof, at a space velocity of from 100 to $50,000\text{ v/v/hr}$ and at a temperature of from 100 to $500^\circ C$, at a pressure of from 100 to 10^5 kPa for a time sufficient to effect the generation of the desired olefinic and paraffinic products in the desired ratio, wherein the concentration of said rhodium in said catalyst is from 0.01 to 10% by weight.
74. Vannice, M. A. and R. L. Garten; Catalytic formation of hydrocarbons from CO, H_2 mixtures and process for maintaining catalytic activity; U.S. Patent 4,093,643,

June 6, 1978. **Claim 1:** A process to produce low molecular weight organic compounds comprising substantially methane, said process consisting of the steps of passing a mixture of CO and H₂ over palladium supported on an acidic metal oxide selected from the group consisting of alumina and hydrogen-y-zeolite wherein the palladium metal particle size is maintained at less than 100 Å by running at a reactor bed temperature of less than 350°C, at a pressure ranging from 1 to 500 atm. and a GHSV of from 1200-4600 hr⁻¹.

75. Voorhies, Alexis, Jr., Hydrocarbon synthesis process, U.S. Patent 2,479,439, Aug. 16, 1949. **Claim 1:** An improved hydrocarbon synthesis process which comprises reacting together, under synthesis conditions, hydrogen and carbon monoxide initially in the presence of an unpromoted powdered iron catalyst in the form of a fluidized bed contained in a reaction zone, adding an alkali metal compound to the reaction zone at a slow rate during such a period of time as to cause a slow and homogeneous impregnation of said alkali metal compound within said catalyst, and to the extent that the desired yields or normally liquid hydrocarbons are obtained from the reaction zone, whereupon the feeding of the alkali metal compound is discontinued, the amount of said promoter with respect to the catalyst and contained thereon lying within the limits of from about 0.1 to 5 wt.% after the initial period, and adding water to the reaction zone to repress carbon formation in an amount such that the feed to the reaction zone contains 5 to 25 mols of hydrogen per mol of water.
76. Aldridge, C. L. and T. Kalina; Shift process for new catalysts; U.S. Patent 3,850,841, Nov. 26, 1974. **Claim 1:** A process for the preparation of hydrogen and carbon dioxide which comprises introducing a gas mixture containing monoxide and steam at a temperature varying from about 300 to 700°F, and introducing at least a portion of said cooled reaction mixture to at least one additional shift reaction stage and contacting the same therein with a catalyst, the temperature within each said reaction stage being maintained above the dew point temperature of the reaction mixture and the pressure within each said reaction stage being maintained below the dew point pressure of said reaction mixture and ranging from about atmospheric to about 3000 psig, the catalyst in each reaction stage comprising (i) an alkali metal compound derived from an acid having an ionization constant of less than about 1×10^{-3} and (ii) a hydrogenation-dehydrogenation component selected from the group consisting of (a) a metal composition comprising vanadium, molybdenum, tungsten, cobalt, tantalum or niobium materials or mixtures thereof or (b) mixtures of materials comprising vanadium, molybdenum, tungsten, cobalt, tantalum or niobium materials or mixtures thereof with a nickel, iron or chromium material or mixtures thereof, the weight ratio of said hydrogenation-dehydrogenation component to said alkali metal compound, each calculated on the basis of the oxides thereof, being less than 5:1.
77. Vannice, M. A. and R. L. Garten; Catalytic formation of hydrocarbons from CO hydrogen mixtures; U.S. Patent 3,941,819, March 2, 1976. **Claim 1:** A process for producing substantial amounts of dimethyl ether, said process comprising the

step of passing CO and H₂ over platinum supported on alumina, wherein the amount of platinum ranges from 0.3 to 2 wt.% based on total weight of the support including platinum at a temperature ranging from 200 to 300°C and a pressure ranging from 10.10 to 40 atm. and wherein the mol ratio of hydrogen to CO ranges from 0.1 to 2.

78. Kwang, K. K., R. E. Pennington, L. W. Vernon and N. C. Hahas; Methane production, U. S. Patent 3,958,957, May 25, 1976. **Claim 1:** A method for the production of a methane-rich gas which comprises introducing a gaseous mixture of hydrogen and at least one carbon oxide into a reaction zone containing a carbon-alkali metal catalyst at a temperature between about 800°F and about 1500°F and at a pressure between about atmospheric and about 2000 psig, said catalyst being prepared by heating an intimate mixture consisting essentially of a carbonaceous solid and an alkali metal constituent to an elevated temperature sufficient to produce a reaction between the carbon and alkali metal in said mixture and form a carbon-alkali metal reaction product, and recovering a methane-rich gas from said reaction zone.
79. Vannice, M. A.; Method for the direct preparation of halogenated hydrocarbons by the reaction of CO, H₂ and halogen in the presence of a catalyst; U.S. Patent 4,041,087, Aug. 9., 1977. **Claim 1:** method for the preparation of halogenated hydrocarbons of the formula C_AH_{2A+2-B}X_B wherein x is a halogen selected from the group consisting of fluorine, chlorine, bromine and iodine, A is an integer ranging from 1 to 4 inclusive and B is an integer ranging from 1 to 10 inclusive, except that 2A+2-B may not be less than zero, which method comprises the steps of: (1) preparing a system comprising CO, H₂ and a source of halogen wherein the source of halogen is selected from the group consisting of molecular halogen and hydrogen halides; (2) passing said system over a catalyst metal selected from the group consisting of Group VIII metals, rhenium, and platinum-iridium and platinum-rhenium alloys, which catalyst metal is in combination with an acidic inorganic oxide material; (3) heating the system containing the CO, H₂ and halogen source over the catalyst to a temperature in the range of 200-1000°C; and (4) pressurizing the system to a level in the range of 0.1 atm to 500 atm.
80. Vannice, M. A. and R. L. Garten; Hydrocarbon synthesis from CO and H₂ using Ru supported on a titanium oxide; U.S. Patent 4,042,614, Aug. 16, 1977. **Claim 1:** A process for the selective synthesis of olefins from C₂ to C₁₀ chain length inclusive, said process comprising the steps of passing H₂ and CO at a H₂/CO ratio of 0.1 to 10 over a catalyst comprising ruthenium on a titanium-containing oxide support, wherein said titanium-containing oxide support is selected from the group consisting of TiO₂, ZrTiO₄, TiO₂-carbon, TiO₂-Al₂O₃, TiO₂-SiO₂, alkaline earth titanates, alkali titanates, rare earth titanates and mixtures thereof, at a space velocity of from 100 to 50,000 v/v/hr at a temperature of from 100 to 500°C at a pressure of from 100 to 10⁵ kPa for a time sufficient to effect the generation of the desired olefinic products in the desired ratio wherein the concentration of said ruthenium in said catalyst is from 0.01 to 15% by weight.

81. Yates, D. J. C. and L. L. Murrell; Method for preparing a highly dispersed supported nickel catalyst; U.S. Patent 4,073,750, Feb. 14, 1978. **Claim 1:** A highly dispersed nickel catalyst having a nickel surface area of from 200 to 400 m²/g nickel prepared by the method which comprises slurring a nickel metal precursor dissolved in a nonaqueous organic liquid solvent with a high surface area refractory oxide support, removing the solvent to obtain a composite of said nickel metal precursor and said support, and activating said composite by reducing in hydrogen or hydrogen dilutes with an inert gas at conditions sufficient to convert substantially all of the nickel metal precursor to nickel metal.
82. Tauster, S. J., L. L. Murrell and S. C. Fung; Supported metal interaction catalysts; U. S. Patent 4,149,998, April 17, 1979. **Claim 1:** Improved catalytic composition consisting of a metal selected from the group consisting of iridium, osmium, rhodium, and mixtures thereof and an oxide of titanium support prepared by depositing said iridium, osmium, rhodium and mixtures thereof on the oxide of titanium and pretreating the composition prior to use, the improvement comprising, as a final step before use, reducing the composition in a hydrogen atmosphere at a temperature of at least 200°C, thereby producing a composition which exhibits suppressed hydrogen chemisorption.
83. Wheelock, K. S., Catalyst and a process for its preparation; U.S. Patent 4,219,447, Aug. 26, 1980. **Claim 1:** A catalyst useful for the conversion of a hydrocarbon feed by contact thereof at hydrocarbon conversion conditions which comprises a cluster of titanium metal oxide and a Group VIII noble metal deposited on the surface of an inorganic oxide support.
84. Murrell, L. L., C. J. Kim, and D. C. Grenoble; Acid catalyzed hydrocarbon conversion process utilizing a catalyst comprising a group IVB, VB or VIB metal oxide on an inorganic refractory oxide support; U.S. Patent 4,233,139, Nov. 11, 1980. **Claim 1:** In a hydrocarbon conversion process wherein hydrocarbon fractions are cracked over acid catalysts at elevated temperatures, the improvement comprising using as the catalyst a material comprising a catalytic metal oxide selected from the group consisting of the oxides of tungsten, niobium and mixtures thereof and tungsten or niobium oxides in combination with one or more additional metal oxides selected from the group consisting of tantalum oxide, hafnium oxide, chromium oxide, titanium oxide and zirconium oxide supported on an inorganic refractory metal oxide base selected from the group consisting of alumina, zirconia, boria, thoria, magnesia, zirconium-titanate, titania, chromia, kieselguhr and mixtures thereof, said catalyst being steamed prior to use.
85. McCandlish, L. E. and E. L. Kugler; CO hydrogenation process using molybdenum oxycarbonitride catalyst; U.S. Patent 4,418,154, Nov. 29, 1983. **Claim 1:** A process for preparing paraffinic hydrocarbons including linear and branched C₁-C₁₀ carbon chain numbers comprising contacting a gaseous mixture of CO and H₂ in a CO/H₂ volume ratio of 10:1 to 1:10, respectively, with a catalyst comprised of face-centered cubic molybdenum oxycarbonitride, in which the

interstitial oxygen, carbon and nitrogen atoms are distributed throughout the bulk structure, at a temperature of about 100 to 600°C, a pressure of about 0.1 to 50,000 v/v/hr and recovering product paraffinic hydrocarbons.

86. Hallulin, A. P. and A. E. Burnett; Coprecipitated Si-Al-metal-particle catalyst; U. S. Patent 4,497,907, Feb. 5, 1985. **Claim 1:** A calcined support catalyst comprised of: (a) one or more metals which are catalytically active for the hydrogenation of organic compounds, (b) alumina and silica at a weight ratio of 0.45:1 to 1:0.45, respectively, and (c) solid porous particles, the catalyst being characterized as having a BET total surface area ranging from about 150 to about 350 m²/g wherein the total amount of catalytically active metal in the catalyst ranges from about 10 wt.% to about 70 wt.% and wherein the catalyst has been prepared by: (aa) coprecipitating ions of one or more catalytically active metals, aluminum ions and silicate ions, with the solid porous particles, (bb) drying the coprecipitated catalyst and (cc) calcining the dried coprecipitated catalyst at a temperature from about 300 to 450°C.
87. Mauldin, C. H.; Conversion of methanol to hydrocarbons; U.S. Patent 4,513,161, Apr. 23, 1985. **Claim 1:** A process useful for the conversion of methanol to hydrocarbons which comprises contacting at reaction conditions a feed comprised of an admixture of methanol and hydrogen, in methanol:hydrogen molar ratio equal to or greater than about 2:1 at total pressure equal to or greater than about 160 psig, over a catalyst which comprises ruthenium in catalytically active amount composited with titania or titania-containing support.
88. Soled, S. L., A. Wold and R. Kershaw; Reduction process for forming powdered alloys from mixed metal iron oxides; U.S. Patent 4,525,206. **Claim 1:** A process for producing a powdered metal-based iron alloy comprising the steps of: (a) heating a mixture comprised of a powdered mixed metal iron oxide, being difficulty reducible in hydrogen gas, with at least a stoichiometric amount of calcium metal, in a non-oxidizing atmosphere, at a temperature below the melting point of the mixed metal iron oxide for a time sufficient to substantially reduce all the metal oxide present, and form said product metal-based iron alloy, as determined by X-ray diffractometry, (b) contacting said reduced mixed metal iron oxide with aqueous acid to remove calcium impurities and by-products; and (c) recovering said product metal-based iron alloy.
89. Payne, V. L. and C. H. Mauldin; Cobalt catalysts for the preparation of hydrocarbons from synthesis gas and from methanol; U.S. Patent 4,542,122, Sept. 17, 1985. **Claim 1:** A catalyst composition useful for the conversion of methanol or synthesis gas to hydrocarbons which consists essentially of cobalt, or cobalt and thoria in catalytically active amount composited with titania or a titania-containing support, wherein the titania support is one having a rutile:anatase ratio of at least about 2:3.
90. Wachs, I and C. C. Chersich; Catalysts comprising tantalum supported on titania; U.S. Patent 4,544,649, Oct. 1, 1985. **Claim 1:** A catalyst composition comprising

an oxide of tantalum support on titania wherein at least a portion of the supported tantalum metal oxide is in a non-crystalline form.

91. Madon, R. J.; Liquid hydrocarbon synthesis using supported ruthenium catalysts; U.S. 4,477,595, Oct. 16, 1984. **Claim 1:** A process for selectively producing paraffins comprising: (a) first contacting a mixture of H_2 and CO for at least 10 hours with a reduced and supported ruthenium catalyst, said ruthenium catalyst comprising ruthenium on a support selected from the group consisting of TiO_2 , $ZrTiO_4$, TiO_2 -carbon, $TiO_2-Al_2O_3$, TiO_2-SiO_2 , alkaline earth titanates, alkali titanates, rare earth titanates, V_2O_3 , Nb_2O_5 , Ta_2O_5 , $Al_2O_3-V_2O_3$, $Al_2O_3-Nb_2O_5$, $Al_2O_3-Ta_2O_5$, $SiO_2-V_2O_3$, $SiO_2-Nb_2O_5$, $SiO_2-Ta_2O_5$, V_2O_3 -carbon, Nb_2O_5 -carbon, Ta_2O_5 -carbon, alkaline earth Group VB oxides, alkali-Group VB oxides, rare earth-Group VB oxides, Group IVB-Group VB oxides, and mixtures thereof, at FT conditions such that the temperature ranges from about 100 to 400°C, the pressure ranges from about 0.2 to 10 mPaA, the gas hourly space velocity, GHSV, ranges from about 100 to 50,000 v/v/hr and wherein the ratio of GHSV/pressure is below about 24,000 v/v/hr/mPaA, and at least about a 20% CO conversion is effected; and (b) continuing said contacting as in step (a) at a H_2 /CO molar ratio from about 0.1 to 4 and thereafter recovering a hydrocarbon mixture comprising C_5 - C_{40} hydrocarbons, containing C_5 - C_{20} paraffins and olefins in a paraffins to olefins weight ratio of at least 1.5
92. Fiato, R. A. and E. L. Kugler; Production of alkanes from mixtures of CO and H_2 ; U.S. Patent 4,548,953, Oct. 22, 1985. **Claim 1:** A process for producing hydrocarbons, including alkane hydrocarbons, from gaseous mixtures of CO and H_2 comprising contacting said mixture, at a temperature ranging from about 200 to 350°C and for a time sufficient to convert at least a portion of said feed to alkane hydrocarbons, with a catalyst comprising a mixture of iron carbide and ilmenite supported on titania wherein the amount of said supported iron present in said supported iron carbide and ilmenite, calculated as Fe_2O_3 , is at least about 2×10^{-3} grams per square meter of titania support surface.
93. Arcuri, K. B., C. H. Mauldin and D. H. Shaw; Ruthenium catalysts, and use thereof for Fischer-Tropsch synthesis; U.S. Patent 4,567,205, Jan. 28, 1986. **Claim 1:** A process useful for the synthesis of hydrocarbons at reaction conditions from a feed constituting an admixture of carbon monoxide and hydrogen, which comprises contacting said feed with a catalyst which comprises ruthenium in catalytically active amount composited with titania, or titania-containing support, having a rutile:anatase ratio of at least about 2:3 and rhenium in amount sufficient to provide a weight ratio of rhenium:ruthenium which ranges from about 2:1 to about 1:4, sufficient at corresponding reaction conditions to obtain improved activity maintenance vis-a-vis a ruthenium catalyst otherwise similar except that it does not contain rhenium.
94. Halluin, A. P. and A. E. Barnett; Catalyst support compositions; U.S. Patent 4,593,014, June 3, 1986. **Claim 1:** A catalyst support composition consisting essentially of alumina and titania at a weight ratio of about 0.3:1 to 1:0.3

respectively, and solid porous particles selected from the group of kieselguhr, infusorial earth, diatomaceous earth and siliceous earth.

95. Fiato, R. A. and E. L. Kugler; Improving activity of iron carbide and ilmenite on titania Fischer-Tropsch catalyst; U.S. Patent 4,594,331, June 10, 1986. **Claim 1:** A process for improving the activity of a FT catalyst present in a FT reaction zone wherein said catalyst comprises a mixture of iron carbide and ilmenite supported on a titania support wherein the amount of iron present in said supported iron carbide and ilmenite mixture, calculated as Fe_2O_3 , is at least about 2×10^{-3} grams per square meter of titania support surface and wherein said reaction zone contains a FT feedstream comprising a mixture of H_2 and CO, said process comprising reducing or eliminating the hydrogen content of the FT feedstream, raising the temperature in said reactor between about 50 to about 150°C above the FT reaction temperature for from about 1 to 6 hrs. and then lowering the temperature back to the reaction temperature and reestablishing the hydrogen content of the feedstream.
96. Payne, V. L. and C. H. Mauldin; Preparation of hydrocarbons from synthesis gas; U.S. Patent 4,595,703, June 17, 1986. **Claim 1:** A process useful for the conversion of synthesis gas to hydrocarbons which comprises contacting at reaction conditions a feed comprised of an admixture of carbon monoxide and hydrogen, in H_2 :CO molar ratio equal to or greater than about 0.5:1 at total pressure equal to or greater than about 80 psig, over a catalyst which comprises cobalt, or cobalt and thoria in catalytically active amount composited with titania or titania-containing support, wherein the titania support is one having a rutile:anatase ratio of at least about 2:3.
97. Wachs, I. E., R. A. Fiato and C. C. Chersich; Iron carbide on titania surface modified with Group VA oxides as Fischer-Tropsch catalysts; U.S. Patent 4,608,359, Aug. 26, 1986. **Claim 1:** A catalyst comprising iron carbide supported on a surface modified titania support wherein said support comprises an oxide of a metal selected from the group consisting of niobium, vanadium, tantalum or mixture thereof supported on said titania wherein at least a portion of said supported oxide of niobium, vanadium, tantalum or mixture thereof is in a non-crystalline form, wherein the amount of said supported oxide ranges from about 0.5 to 25 wt.% metal oxide on the titania support based on the total support composition and wherein the catalyst contains at least about 2 milligrams of iron, calculated as Fe_2O_3 per square meter of support surface.
98. Fiato, R. A., G. B. McVicker and A. A. Montagna; Fe-Co catalyst slurry system for use in alpha olefin production; U.S. Patent 4,624,967, Nov. 25, 1986. **Claim 1:** A process for synthesizing hydrocarbons containing alpha olefins comprising contacting a gaseous feed mixture of H_2 and CO, in a reaction zone, with a slurry catalyst system at elevated temperature for a time sufficient to convert at least a portion of said gaseous feed to said alpha olefins, wherein said catalysts slurry system is prepared by a process comprising the steps of: (a) heating a slurry mixture comprised of: a FT slurry liquid, an iron carbonyl compound, a cobalt

carbonyl compound, or iron and cobalt compounds capable of forming carbonyl complexes in a atmosphere of CO, and mixtures thereof, and a powdered support, wherein said iron and cobalt compounds are present in a total iron:cobalt atomic ratio of about 35:1 to 1:10, taken as free metals, and wherein the cobalt carbonyl compound has a lower melting point/decomposition temperature than the iron carbonyl compound; in a carbon monoxide atmosphere under pressure, at a temperature above the melting point/decomposition temperature of the cobalt compound for a time sufficient to substantially decompose the cobalt compound, (b) heating said slurry mixture from step (a) at a temperature above the melting point/decomposition temperature of the iron compound in said CO atmosphere under pressure, to substantially decompose the iron compound; and (c) heating said slurry mixture from step (b) in an atmosphere of hydrogen gas to substantially reduce said iron and cobalt carbonyl compounds and their decomposition products to form said catalyst.

99. Rice, G. W., R. A. Fiato and S. L. Soled; Promoted iron-carbon-based catalysts produced in the presence laser radiation; U.S. Patent 4,659,681, April 21, 1987. **Claim 1:** A composition of matter comprising finely divided non-pyrophoric iron-carbide catalytic particles comprising iron and carbon in the substantial absence of silicon, a substantial portion of which is cementite, produced in a reaction zone in the presence of laser radiation under such conditions of laser flux density, power adsorption, concentration of iron compound reactants selected from the group consisting of iron carbonyls, iron acetyl-acetonate, and ferrocene and pressure sufficient to produce non-pyrophoric iron-carbon particles having average diameters between 1 and 100 nm, and which particles are subsequently impregnated with at least 2% of a promoter selected from the group of the salts and oxides of alkali and alkaline earth metals.
100. Rice, G. W., R. A. Fiato and S. L. Soled; Iron carbide-based catalyst produced in the presence of laser radiation; U.S. Patent 4,668,647, May 26, 1987. **Claim 1:** A composition of matter comprising finely divided non-pyrophoric iron-carbide catalytic particles comprising iron and carbon in the substantial absence of silicon, a substantial portion of which is cementite, produced in a reaction zone in the presence of laser radiation under such conditions of laser flux density, power adsorption, concentration of iron compound reactants selected from the group consisting of iron carbonyls, iron acetyl-acetonate, and ferrocene, and pressure sufficient to produce non-pyrophoric iron-carbon particles having average diameters between 1 and 100 nm.
101. Mauldin, C. H.; Improved cobalt catalysts, and use thereof for Fischer-Tropsch synthesis; U.S. Patent 4,670,475, June 2, 1987. **Claim 1:** A process useful for the conversion or synthesis gas feed comprised of hydrogen and carbon monoxide to hydrocarbons which comprises contacting said feed at reaction conditions with a catalyst which comprises cobalt, or cobalt and thoria in catalytically active amount composited with a titania or titania-containing support, to which is added sufficient rhenium to obtain, with a similar feed at

corresponding process conditions, improved activity, as contrasted with a catalyst composition otherwise similar except that it does not contain rhenium.

102. Fiato, R. A. and E. L. Kugler; Iron on titania Fischer-Tropsch catalyst; U.S. Patent 4,689,313, Aug. 25, 1987. **Claim 1:** A catalyst composition consisting essentially of catalytic components being selected from the group consisting of a mixture of iron carbide and ilmenite and a mixture of iron carbide and ilmenite containing at least one alkali metal promoter wherein the ratio of supported iron present in said supported iron carbide and ilmenite, calculated as Fe_2O_3 , to the surface area of said titania support ranges between about 2 to 25 milligrams per square centimeter, and wherein said catalyst has been formed by depositing an iron precursor salt of said catalytic component on said titania support, calcining said deposited salt and support to form a calcined composite and sequentially contacting said composite with a hydrogen containing reducing gas free of CO at elevated temperatures of from about 300 to about 500°C for a time sufficient to reduce the calcined composite followed by contacting said reduced composite with CO at a temperature from about 100 to about 200°C lower than the temperature used for said hydrogen contacting.
103. Fiato, R. A., R. Bar-Gadda and S. Miseo; Cerium promoted Fischer-Tropsch catalysts; U.S. Patent 4,719,240, Jan. 12, 1988. **Claim 1:** A hydrocarbon synthesis process comprising contacting a feed stream of CO and H_2 in a molar ratio of about 0.5 to about 4:1 with a catalyst at a temperature in the range of about 200 to 350°C, a pressure in the range of about 1 to 50 atm, a space velocity in the range of about 10 to 10,000 v/v/hr to produce a hydrocarbon product containing ethylene and ethane in which the ethylene/ethane mole ratio is greater than one, and recovering the product; the catalyst being comprised of a sintered composition containing: (a) about 5-80 wt.% Fe oxide; (b) about 4-20 wt.% Zn oxide, (c) about 10-40 wt.% Ti and/or Mn oxide, (d) about 1-5 wt.% of a Group IA metal oxide selected from the group consisting of K, Rb and Cs, and mixtures thereof, (e) about 1-10 wt.% Ce oxide such that said sintered combination comprises a series of spinels of Fe, Zn and/or Ti and/or Mn and said Group IA metal oxide in a cerium oxide matrix.
104. Fiato, R. A.; Slurried CO hydrogenation catalysts; U.S. 4,752,600, June 21, 1988. **Claim 1:** A slurry catalyst composition consisting essentially of: (a) TiO_2 , (b) the decomposition product of a ruthenium carbonyl complex which is $\text{Ru}_3(\text{CO})_{12}$, said decomposition product being formed by the decomposition of said $\text{Ru}_3(\text{CO})_{12}$ in the presence of a gas mixture of $\text{CO}:\text{H}_2\text{N}_2$ at a temperature of about 230°C to about 270°C and a pressure of about 230 to about 270°C and a pressure of about 4 to about 20 atm. for a sufficient period of time to form said decomposition product, said decomposition product being supported on said TiO_2 , and (c) an inert alkane hydrocarbon.
105. Iglesia, E., S. L. Soled and R. A. Fiato; Cobalt-ruthenium catalysts for Fischer-Tropsch synthesis; U.S. 4,822,824, April 18, 1989. **Claim 1:** A hydrocarbon synthesis process which comprises reacting hydrogen and carbon monoxide in

the presence of a catalyst comprised of cobalt and ruthenium on titania, at reaction conditions suitable for the formation of higher hydrocarbons, the catalyst being prepared by impregnating titania with solutions of cobalt and ruthenium salts, drying the impregnating support, reducing the cobalt and ruthenium, treating the reduced metals with an oxygen containing stream at conditions sufficient to form oxides of cobalt and oxides of ruthenium and reducing the cobalt and ruthenium oxides.

106. Wachs, I. E. and D. B. Yang; Catalysts comprising ruthenium on titania surface modified with Group VA oxide of vanadium, niobium or tantalum; U.S. 4,861,747, Aug. 29, 1989. **Claim 1:** A catalyst comprising ruthenium supported on a surface modified titania support wherein said support comprises an oxide of a metal selected from the group consisting of niobium, vanadium, tantalum or mixture thereof, in a non-crystalline form, supported on said titania.

107. Behrmann, W. C., C. H. Mauldin and K. B. Arcuri; Cobalt-titania catalysts. Process utilizing these catalysts for the preparation of hydrocarbons from synthesis gas, and process for the preparation of said catalysts; U.S. Patent 4,962,078, Oct. 9, 1990. **Claim 1:** A catalyst composition useful for the conversion of synthesis gas to liquid hydrocarbons which comprises cobalt dispersed and impregnated as a catalytically active layer upon the surface of a support, the support being at least about 80% by weight titania, the layer ranging in average thickness from about 0.2 mm to about 0.20 mm with the cobalt loading being about 0.04 g/cc to about 0.15 g/cc, calculated as metallic cobalt per packed bulk volume of catalysts, and having a productivity and methane selectivity at 200°C of at least 150 hr⁻¹ and no more than 10 mole %, respectively.

108. Mauldin, C. H. and K. L. Riley; Titania-supported catalysts and their preparations for use in Fischer-Tropsch synthesis; U.S. Patent 4,992,406, Feb. 12, 1991. **Claim 1:** A support composition for forming a catalyst useful for the conversion of synthesis gas to hydrocarbons which comprises titania in which there is incorporated from 0.1 to about 20 wt.% of an inorganic oxide binder selected from the group consisting of alumina and zirconia based on the weight of the titania-binder support, to provide a titania-binder support having a pore volume ranging from about 0.2 cc/g to about 0.5 cc/g, and surface area ranging from about 8 m²/g to about 70 m²/g.

109. Hildinger, H. W. and E. D. Carlson; Process for recycling and purifying condensate from a hydrocarbon or alcohol synthesis process; U. S. Patent 5,004,862, April 2, 1991. **Claim 1:** A process for purifying a condensate stream from a hydrocarbon synthesis or alcohol synthesis process which comprises: (a) contacting the condensate with a hot gaseous mixture comprising methane and steam to strip contaminants comprising lower molecular weight hydrocarbons and oxygenates; (b) recovering a gaseous stream comprising the contaminants and the gaseous mixture; and (c) separately recovering purified water.

110. Hildinger, H. W. and E. D. Carlson; Process for recycling and purifying condensate from a hydrocarbon or alcohol synthesis process; U.S. Patent 5,053,581, Oct. 1, 1991. **Claim 1:** A process for producing heavy hydrocarbons which comprises: (a) reacting CO and H₂ over a catalyst at reactive conditions in a hydrocarbon synthesis to form heavy hydrocarbons and a product condensate; (b) separately recovering the heavy hydrocarbons from the product condensate; (c) contacting the product condensate with a hot gaseous mixture comprising CH₄ and steam to strip the product condensate of contaminants, said contaminants comprising lower molecular-weight hydrocarbons and oxygenates; (d) recovering a gaseous stream comprising the contaminants and the gaseous mixture; and (e) converting the gaseous stream recovered in step (d) to CO and H₂ and utilizing at least a portion of said CO and H₂ in step (a).
111. Fiato, R. A.; Two stage process for hydrocarbon synthesis; U.S. Patent 5,028,634, July 2, 1991. **Claim 1:** A two stage hydrocarbon synthesis process comprising:
- (a) reacting in a first stage, hydrogen and carbon monoxide in the presence of a supported cobalt or ruthenium catalyst and obtaining a CO conversion to C₂+ hydrocarbons of at least 50% at reaction conditions including a pressure of at least 10 atmospheres;
  - (b) recovering a reaction product comprising hydrogen and carbon monoxide and separating liquid therefrom;
  - (c) reacting in a second stage, at a pressure below 10-12 atmospheres and no greater than the outlet pressure of the first stage, the remaining reaction products in the presence of a catalyst comprising catalytically effective amounts of cobalt supported on alumina at reaction conditions and
  - (d) wherein the second stage catalyst is at least as active for CO conversion to C₂+ hydrocarbons as the first stage catalyst at second stage reaction pressure.
112. Iglesia, E., H. Vroman, S. Soled, J. Baumgartner and R. A. Fiato; Selective catalysts and their preparation for catalytic hydrocarbon synthesis; U.S. Patent 5,036,032, July 30, 1991. **Claim 1:** A method for preparing a supported cobalt catalyst particle which comprises: (a) contacting a support particle with a molten cobalt salt, for a period sufficient to impregnate substantially all of the molten cobalt salt on the support to a depth of less than about 200 μ m; (b) drying the supported cobalt salt obtained in step (a); and (c) reducing the cobalt of the supported cobalt salt in step (b) to metallic cobalt by heating the salt in the presence of H₂, wherein the heating is conducted at a rate of less than about 1°C/min up to a maximum temperature ranging from about 200°C to about 500°C to produce a supported cobalt catalyst particle.
113. Hsu, E. C. and J. L. Robbins; Catalyst pretreatment method; U.S. Patent 5,070,064, Dec. 3, 1991. **Claim 1:** A liquid phase method for removing sub-1 micron particles adhering to catalyst particles the catalyst containing a Group VIII metal supported on an inorganic refractory oxide as a result of preparation of the

catalyst which comprises: (a) dispersing the catalyst particles to which the sub-1 micron particles adhere within a liquid comprising a FT; (b) agitating the dispersion and separating the sub-1 micron particles from the catalyst particles, and concentrating the sub-1 micron particles in the liquid phase; and (c) separating the sub-1 micron containing liquid phase from the particulate material.

114. Mauldin, C. H. and K. L. Riley; Titania catalysts,. their preparation, and use in Fischer-Tropsch synthesis; U.S. Patent 5,140,050, Aug. 18, 1992. **Claim 1:** A process for the conversion of synthesis gas to hydrocarbons at high activity which comprises contacting at reaction conditions a feed comprised of an admixture of carbon monoxide and hydrogen, in H₂:CO molar ratio equal to or greater than 0.5:1 at pressure greater than or equal to 80 psig, over a catalyst composition comprised of a catalytically effective amount of a Group VIII non-noble metal catalytically active for the conversion of synthesis gas to hydrocarbons dispersed upon a titania support in which there is incorporated from about 0.1% to about 10% of an inorganic oxide binder selected from the group consisting of alumina, and zirconia based on the weight of the titania-binder to support to provide a titania-binder support having a pore volume ranging from about 0.2 cc/g to about 0.55 cc/g and surface area ranging from about 8 m²/g to about 70 m²/g.
115. Soled, S. L., G. B. McVicker and W. E. Gates; Metal on rare earth modified silica alumina as hydrocarbon conversion catalyst; U.S. 5,248,409, Sept. 28, 1993. **Claim 1:** A catalytic hydroconversion process which includes hydroisomerization of at least a feedstream comprising: contacting and feedstream with a catalyst composition comprising an amorphous silica-alumina support having at least about 50 wt.-% silica, a rare earth oxide, and a metal selected from the group consisting of Group VIII noble metals, rhenium, and mixtures thereof.
116. Herbolzheimer, E. and E. Iglesia; Slurry bubble column; U.S. Patent 5,348,982, Sept. 20, 1994. **Claim 1:** A method for optimally operating a large diameter three phase (gas, liquid, solid) slurry bubble column having a diameter greater than 15 cm for FT synthesis over a supported cobalt catalyst in which solid particles are fluidized in the liquid phase by bubbles of the gas phase, comprising: (a) injecting the gas phase into said column at an average gas velocity along said column, U_g>2 cm/sec, such that the flow regime is in the substantial absence of slug flow; (b) fluidizing the solid supported cobalt catalyst particles of average diameter, d_p>5 :m, to the height, H>3m, of the expanded liquid in the column by operating with a catalyst settling velocity, U_s, and dispersion coefficient, D, such that

$$0.5 (U_s - U_L) \leq \frac{D}{H}, \text{ where } H > 3m$$

where

$$U_s = \frac{1}{18} d_p^2 \frac{\rho_s - \rho_l}{\mu} g f(C_p), \text{ where } d_p > 5 \mu m$$

and (c) maintaining plug flow in said column by operating with a gas phase velocity, U_g , expanded liquid height, H , and dispersion coefficient, D , such that $U_g \geq 0.2 D/H$, where $H > 3m$, $U_g > 2$ cm/sec, wherein D_s = effective density of the particles; D_l = density of the liquid; η = viscosity of the liquid; $f(C_p)$ = hindered settling function; ϕ = volume fraction of solids in the slurry (liquid plus solids); U_L = liquid velocity along the column; H = height of the expanded liquid in said reactor; g = gravitational constant; d_p = diameter of particles; m = meters.

117. Agestegua, C. R., S. L. Soled and S. Miseo; Catalysts for iso-alcohol synthesis from $CO + H_2$, U.S 5,387,570, Feb. 7, 1995. **Claim 1:** A catalyst composition consisting essentially of a solid solution or a coprecipitated mixture of a first oxide and a second oxide, wherein said first oxide is selected from the group consisting of yttria, rare earth oxides and mixtures thereof, and wherein said second oxide is a Group IIA oxide and a Group IB metal.
118. Clavenna, L. R., S. M. Davis, R. A. Fiato and G. R. Say; Structurally modified alumina supports, and heat transfer solids for high temperature fluidized bed reactions; U.S. 5,395,406, March 7, 1995. **Claim 1:** A composition of matter which comprises: a support components comprising particulate alpha alumina solids of fluidizable particle size of 30-150 microns modified by compositing a metal therewith to form particles represented by formulas (1) and (2), a composite particle being represented by formula (1), as follows;

with the core of the particle being represented by formula (2), as follows:

where in formulas (1) and (2), M is a Group IIA metal, x is a number ranging from about 0.01 to about 0.4 and is representative of the number of moles of the metal M per mole of Al_2O_3 , y is a number equal to or greater than zero, and x is greater than y .

119. Pruett, R. L. and J. S. Bradley; Transition metal bimetallic clusters of ruthenium with thallium, indium and gallium, U.S. 4,360,475, Nov. 23, 1982. **Claim 1:** A composition of matter comprising a bimetallic cluster compound of the formula $[M]_n[(Ru_6C-(CO)_{16})_2L]$ where M is alkali metal cation, alkaline earth metal cation, $N(RN)4+$, $P(RN)4+$ or $As(R^0)4+$ where RN is C_1 - C_{20} aliphatic, C_3 - C_8 cycloaliphatic, C_7 - C_{14} aralkyl or C_6 - C_{10} aryl, n is a number which satisfies valence requirements and L is Tl , In or Ga .
120. Iglesia, E., S. L. Soled and J. E. Baumgartner; Selective fixed-bed Fischer-Tropsch synthesis with high surface area Cu and K promoted, iron/manganese spinels; U.S. 5,118,715, June 2, 1992. **Claim 1:** A hydrocarbon synthesis process for preparing a product containing C_5+ hydrocarbons and less than about 30% CO_2 comprising contacting in a fixed-bed a pelletized catalyst composition

wherein the particle size is greater than about 200 microns average diameter, at a temperature of 200-240°C, the catalyst comprising at least one unsupported, single phase, iron-manganese spinel dual promoted with both copper and a Group IA or IIA metal, said spinel exhibiting a single phase being isostructural with Fe_3O_4 as determined by powder X-ray diffractometry, and possessing a BET surface area greater than 30 m^2/g and an Fe:Mn atomic ratio of at least 2/1, with a mixture of CO and hydrogen under conditions of pressure, space velocity, and elevated temperature for a time sufficient to produce said C_5+ hydrocarbons.

121. Behrmann, W. C., C. H. Mauldin and K. B. Arcuri; Cobalt-titania catalysts. Process utilizing these catalysts for the preparation of hydrocarbons from synthesis gas, and process for the preparation of said catalysts (C-2448); U.S. 5,128,377, July 7, 1992. **Claim 1:** A process useful for the conversion of synthesis gas to liquid hydrocarbons, which comprises contacting at reaction conditions a feed comprising carbon monoxide and hydrogen, in $\text{H}_2:\text{CO}$ molar ratio equal to or greater than about 0.5:1 at total pressure equal to or greater than about 80 psig, over a catalyst composition which comprises cobalt dispersed and impregnated as a catalytically active layer upon the surface of a support containing at least about 80 wt% titania ranging in average thickness from about 0.02 mm to about 0.20 mm, with a cobalt loading of about 0.04 g/cc to about 0.15 g/cc, calculated as metallic cobalt per packed bulk volume of catalyst and with a productivity and methane selectivity at 200°C of at least 150 hr^{-1} and no more than 10 mole%, respectively.

122. Say, G. R., J. H. Taylor, D. C. Long and R. A. Fiato; Synthesis gas generation of startup process (C-2556); U.S. 5,143,647, Sept. 1, 1992. **Claim 1:** A method for starting up a fluidized bed or spouted bed steam reforming partial oxidation process for converting a feed gas comprising methane to a product comprising hydrogen and carbon monoxide and unconnected methane which comprises the sequential steps of: (a) heating to reaction temperature the fluidized bed or spouted bed comprised of essentially inert particles, in the presence of oxygen, in an oxidizing atmosphere, and in the substantial absence of a reforming catalyst; (b) converting to a reducing atmosphere; and (c) introducing into the fluidized or spouted bed sufficient Group VIII metal containing catalyst and converting, in the presence of oxygen, the feed gas to the product.

123. Soled, S. L., E. Iglesia and R. A. Fiato; Copper promoted cobalt-manganese spinel catalyst and method for making the catalyst for Fischer-Tropsch synthesis; U.S. 5,162,284, Nov. 10, 1992. **Claim 1:** A composition of matter comprising a copper promoted cobalt-manganese spinel, the spinel having the formula: $\text{Co}_{3-x}\text{Mn}_x\text{O}_4$, where x is from about 0.5 to about 1.2.

124. Soled, S. L., S. Miseo, E. Iglesia and R. A. Fiato; Iron-zinc catalysts for the conversion of synthesis gas to alpha-olefins; U.S. 5,185,378, Feb. 9, 1993. **Claim 1:** A process for preparing a liquid product containing olefins and paraffins wherein the olefin/paraffin ratio is at least about 2.5/1, and the C_5+/C_4 -ratio is at least about 4.5/1 which comprises reacting in a slurry liquid, at suitable reaction

conditions, hydrogen and carbon monoxide in the presence of a catalyst comprising: iron, zinc, copper, an alkali metal selected from the group consisting of potassium, rubidium, cesium, and mixtures thereof, wherein the iron:zinc atomic ratio is at least a 5:1, and the alkali:copper atomic ratio is at least 2:1.

125. Soled, S. L., E. Iglesia and R. A. Fiato; Substituted cobalt catalysts for Fischer-Tropsch synthesis; U.S. 5,248,701, Sept. 28, 1993. **Claim 1:** A FT process for the conversion of synthesis gas to hydrocarbons which comprises activating a copper promoted, cobalt-manganese spinel catalyst having the formula $\text{Co}_3\text{Mn}_x\text{O}_4$, where x is from about 0.5 to about 1.2 by contacting the catalyst with a reducing atmosphere and contacting the activated catalyst in a reactor with hydrogen/carbon monoxide synthesis gas.

126. Chang, M. and C. A. Coulaloglou; Enhanced catalyst mixing in slurry bubble columns (OP-3723); U.S. 5,252,613, Oct. 12, 1993. **Claim 1:** A method for improving the axial distribution of catalyst in a hydrocarbon synthesis slurry bubble column which uses rising synthesis gas introduced by means of synthesis gas distribution means located at the bottom of said column to provide the majority of the energy used in distributing catalyst in said column, the improvement in axial distribution of catalyst being achieved by using a secondary fluid introduction means in said slurry bubble column at a location above the synthesis gas distribution means located at the bottom of said column to introduce a secondary fluid stream into said column.

127. Hsia, S. J.; External catalyst rejuvenation system for the hydrocarbon synthesis process; U.S. 5,260,239, Nov. 9, 1993. **Claim 1:** A process for practicing catalytic hydrocarbon synthesis and reactivation rejuvenation of deactivated hydrocarbon synthesis catalyst on a continuous basis, said process comprising combining catalyst and synthesis feed and hydrocarbon liquid in a hydrocarbon synthesis first vessel means to produce a reactor slurry comprising catalyst, synthesis feed and synthesis product, collecting deactivated catalyst from the top of the reactor slurry by means of a first downcomer-conduit means the top of which is fitted with gas disentrainment means and which is located just below the top surface of the reactor slurry, passing the deactivated catalyst down the first downcomer-conduit means from the top of the first vessel means to the bottom of a reactivation-rejuvenation second vessel means, said second vessel means having rejuvenating gas introduction means located at its bottom, forming a reactivating slurry of catalyst in reaction product and rejuvenating gas, wherein the deactivated catalyst is reactivated-rejuvenated in said second vessel means, collecting reactivated-rejuvenated catalyst from the top of the reactivating slurry by means of a second downcomer-conduit means the top of which is fitted with gas disentrainment means and which is located just below the top surface of the reactivation slurry and passing the reactivated-rejuvenated catalyst down the second downcomer-conduit means from the top of the second vessel means to the bottom of the first vessel means, all catalyst downward flows on both the first and second downcomer means occurring solely under the influence of gravity.

128. Pedrick, L. E., C. H. Mauldin and W. C. Behrmann; Draft tube for catalyst rejuvenation and distribution; U.S. 5,268,344, Dec. 7, 1993. **Claim 1:** A method for rejuvenating reversibly deactivated particulate hydrocarbon synthesis catalyst in a slurry phase reactor, said method comprising the use of substantially vertical draft tube means, open at both ends, fully immersed in the slurry containing the catalyst and injecting a hydrogen containing gas at or substantially near the bottom of said draft tube means thereby lifting catalyst in slurry from the bottom of the slurry phase reactor into and through the open bottom end of the draft tube means, rejuvenating catalyst in the presence of said hydrogen containing gas in the vertical draft tube means and ejecting the rejuvenated catalyst into the top of the slurry phase in the slurry phase reactor through the open top of the draft tube means.
129. Mitchell, W. N.; Rejuvenation of hydrocarbon synthesis catalyst; U.S. 5,283,216, Feb. 1, 1994. **Claim 1:** A method for rejuvenating a partially deactivated, Group VIII metal containing Fischer-Tropsch catalyst having an initial catalyst activity which comprises: suspending the catalyst in slurry liquid hydrocarbons and treating the suspended catalyst with hydrogen or a hydrogen containing gas at elevated temperatures and pressures and recovering a substantial portion of the metal catalyst activity.
130. Mitchell, W. N.; Activation of hydrocarbon synthesis catalyst; U.S. 5,292,705, March 8, 1994. **Claim 1:** A method for activating an essentially fresh, reduced cobalt containing Fischer-Tropsch catalyst which comprises treating the catalyst with hydrogen or a hydrogen containing gas in the presence of hydrocarbon liquids for a period sufficient to increase substantially the initial catalyst productivity.
131. Chang, M.; Enhanced gas separation for bubble column draft tubes; U.S. 5,332,552, July 26, 1994. **Claim 1:** A slurry bubble column reactor comprising a double walled vessel defined by an inner vessel wall having a peripheral circumferential top rim and a bottom edge, and an outer main containment vessel wall surrounding said inner vessel wall, said outer main containment vessel having a top and a bottom, and wherein the inner vessel wall and the outer vessel wall are substantially co-axial and have a space between them forming an annulus between said respective walls, the outer main containment vessel wall having a synthesis gas inlet means at the bottom, gas outlet means and product recovery means at the top, and a floor above the gas inlet means which floor is fitted with gas distribution means, the inner vessel wall serving as a main reactor zone, the peripheral circumferential top rim of the inner vessel wall having attached to it an inverted channel having an apex and two edges, the point of attachment of the inverted channel to the inner wall being along a first one of said two edges of said inverted channel, a second of said two edges of said inverted channel extending over the main reaction zone thereby creating a gas space within its inverted contour and which inverted channel has a gas vent extending out of, and upwardly from, said inverted channel, and having a liquid by-pass pipe extending from a point on one side of the inverted channel below the apex

of said inverted channel and between said apex and the edge of attachment to the inner vessel wall, to under said top rim of said inner vessel wall and which by-pass pipe empties into the annulus, and liquid exit means at the bottom of the annulus defined by openings in the bottom edge of the interior vessel wall and above the gas distributor means of the main containment vessel.

132. Clavenna, L. R., S. M. Davis, G. R. Say and R. A. Fiato; Synthesis gas from particulate catalysts, and admixtures of particulate catalysts and heat transfer solids; U.S. 5,348,717, Sept. 20, 1994. **Claim 1:** In a process for the production of hydrogen and carbon monoxide from a low molecular weight hydrocarbon by contact with a fluidized bed of catalyst at elevated temperature in the presence of oxygen, or both steam and oxygen, the improvement wherein the fluidizing bed is comprised of an admixture of a particulate consisting essentially of a non-leachable barium hexaaluminate solids of fluidizable particle diameter in concentration ranging from about 10 percent to about 99.9 percent, based on the weight of the admixture, and a catalyst comprised of a carrier component composited with a metal, or metals, component catalytic for the production of hydrogen and carbon monoxide from low molecular weight hydrocarbons when contacted with a fluidized bed of the catalyst, in concentration ranging from about 0.1 percent to about 90 percent, based on the weight of the admixture.
133. Clavenna, L. R., S. M. Davis and B. E. Beasley; Process for the reactivation of nickel-alumina catalysts; U.S. 5,356,845, Oct. 18, 1994. **Claim 1:** In a process for the production of hydrogen and carbon monoxide from a low molecular weight hydrocarbon by contact with a fluidized bed of nickel-on-alumina catalyst at elevated temperature in the presence of steam and oxygen, in a reaction zone operated in a net reducing atmosphere, the steps comprising: withdrawing a portion of said catalyst and contacting said catalyst with an oxygen-containing gas at a temperature elevated sufficiently to convert the nickel component of said catalyst to nickel aluminate, and disperse said nickel aluminate within the alumina support, without sintering and alumina support; and reducing said catalyst after contact with the oxygen-containing gas to the reaction zone to reduce the nickel aluminate component of the catalyst, and increase the activity of the catalyst vis-a-vis that of the catalyst initially withdrawn from the reaction zone.
134. Davis, S. M., L. R. Clavenna, G. R. Say and R. A. Fiato; High surface purity heat transfer solids for high temperature fluidized bed reactions; U.S. 5,360,778, Nov. 1, 1994. **Claim 1:** In a process for the preparation of a particulate heat transfer solid characterized as particulate refractory inorganic oxide solids containing silicon, or boron, or both silicon and boron impurities, the steps comprising: contracting, and treating, said particulate refractory inorganic oxide solids containing silicon in concentration no greater than about 0.5%, based on the total weight of the solids, and boron in concentration no greater than about 500 parts, per million parts by weight total solids, with an acid sufficient to reduce the concentration of silicon and boron in the outer peripheral surface layer of the

particles to no greater than about 5 atom percent silicon and boron, based on the total number of cations within said outer peripheral surface layer.

135. Behrmann, W. C., C. H. Mauldin and L. E. Pedrick; Hydrocarbon synthesis reaction employing vertical downcomer with gas disengaging means; U.S. 5,382,748, Jan. 17, 1995. **Claim 1:** A method for uniformly redistributing particulate catalyst in a slurry phase reactor, said method comprising using a substantially vertical conduit means open at both ends, fully submerged in the slurry of the slurry phase reactor, the bottom end of the substantially vertical conduit means is near the bottom of the slurry phase reactor and the top of the conduit means is topped by gas disengaging means which are below the top surface of the slurry in the slurry phase reactor and wherein the bottom of the substantially vertical conduit means is shielded by a baffle means which diverts gases rising from the bottom of the slurry phase reactor from entering into the bottom of the substantially vertical conduit whereby catalyst in slurry which passes down the substantially vertical conduit and is ejected from the bottom of said conduit near the bottom of the slurry phase reactor.
136. Koros, R. M., Bubble column, tube side slurry process and apparatus; U.S. 5,384,336, Jan 24, 1995. **Claim 1:** A hydrocarbon synthesis process comprising reacting a gaseous mixture of hydrogen and carbon monoxide at a pressure of 1 to 100 atmospheres and a temperature of about 175°C to about 400°C in the presence of a hydrocarbon synthesis catalyst dispersed in a liquid thereby forming a slurry liquid, wherein the catalyst dispersion is disposed in a plurality of vertically arranged elongated reaction tubes having an L/D (length/diameter) of at least about 10, each tube being surrounded by a common heat transfer medium disposed within the shell of a shell and tube reactor, the heat transfer medium not being in fluid communication with the slurry liquid.
137. Mitchell, W. N.; Activation of hydrocarbon synthesis catalyst; U.S. 5,389,690, Feb. 14, 1995. **Claim 1:** A FT process which comprises activating an essentially fresh, reduced cobalt containing FT catalyst with hydrogen or a hydrogen containing gas, the catalyst being dispersed in hydrocarbon liquids and subsequently using the catalyst in a FT process at FT reaction conditions.
138. Soled, S. L., E. Iglesia, R. A. Fiato and G. B. Ansell; Method for stabilizing titania supported cobalt catalyst; U.S. 5,397,806, March 14, 1995. **Claim 1:** In a FT process, under FT reaction conditions, including contacting with a feedstream comprising a CO and H₂ reaction mixture, a 400-750°C regeneration stable catalyst composition comprising cobalt on a substituted ternary metal oxide of titania having the general formula Co/Ti_{1-x}M_xO₂ wherein x is from 0.01 to 0.14 and M is selected from the group consisting of silicon, zirconium and tantalum, wherein the titania is an anatase polymorph.
139. Stark, T. M.; Pentane energy transfer medium in gas conversion; U.S. 5,409,960, April 25, 1995. **Claim 1:** A method for removing heat from a slurry FT hydrocarbon synthesis process reaction zone which comprises passing a cooling

medium comprising a C₄-C₁₀ normal, iso- or cyclic paraffin liquid in cooling tubes in indirect heat exchange through the slurry reaction zone, thereby vaporizing the cooling medium at its boiling point, the cooling medium being inert for FT processes, condensable, and vaporizing at a pressure greater than the pressure in the reaction zone, and recovering the vaporized cooling medium heat.

140. Wittenbrink, R. J., S. M. Davis and K. L. Riley; Supported Ni-Cu hydroconversion catalyst; Int. Pub. No. WO 97/03750, Feb. 6, 1997. **Claim 1:** A hydroconversion catalyst comprising nickel in an amount of less than about 15 wt.% catalyst and copper in a copper:nickel ratio of less than about 1:2 supported on an amorphous silica-alumina carrier having less than about 30 wt.% alumina, the carrier having a surface area of greater than about 200 m²/gm and a pore volume of less than about 1.0 mL/gm.

141. Davis, S. M. and D. F. Ryan; Distillate fuel production from Fischer-Tropsch wax; U.S. 5,378,348, Jan. 3, 1995. **Claim 1:** A process for producing middle distillate transportation fuel components from the waxy product of a hydrocarbon synthesis process which comprises: (a) separating the waxy product into a heavier fraction and at least one lighter fraction; (b) catalytically isomerizing the heavier fraction in the presence of hydrogen and recovering products with improved cold flow properties; (c) catalytically hydrotreating the lighter fraction and removing hetero atom compounds therefrom; (d) catalytically isomerizing the product of step (c) to produce jet fuel component having a freeze point of -30°F or lower.

144. Behrmann, W. C., K. B. Areuri and C. H. Mauldin; Surface supported cobalt catalysts, process utilizing these catalysts for the preparation of hydrocarbons from synthesis gas and process for the preparation of said catalysts; U.S. Patent 5,545,674, August 13, 1996. **Claim 1:** A process useful for the conversion of synthesis gas to liquid hydrocarbons less than about 10 mole% methane which comprises contacting at reaction conditions a feed comprised of carbon monoxide and hydrogen, in H₂:CO molar ratio equal to or greater than about 0.5:1 at total pressure equal to or greater than about 80 psig, over a catalyst composition having a productivity of at least 150 hr⁻¹ at 200°C and which comprises cobalt dispersed as a catalytically active layer upon the outer surface of an inorganic oxide support of a thickness of less than about 200 microns, with the loading of cobalt at least about 0.04 g/cc in said catalytically active layer, calculated as metallic cobalt per packed bulk volume of catalyst.

145. Davis, S. M., L. R. Clavenna, G. R. Say and R. A. Fiato; High surface purity heat transfer solids for high temperature fluidized bed reactions; U. S. Patent 5,496,531, March 5, 1996. **Claim 1:** In a process for the production of hydrogen and carbon monoxide from a low molecular weight hydrocarbon by contact with a fluidized bed constituted of a catalyst and particulate alpha alumina containing both silicon and boron impurities, at high temperature in the presence of steam, or oxygen, or both steam and oxygen, the improvement wherein the alpha alumina is comprised of particles of alpha alumina the outer peripheral surface

layer of which contains no greater than about 5 atom percent silicon and boron, based on the total number of cations within said outer peripheral surface layer, thereby improving resistance to sintering and agglomeration of the fluidized bed, said particles being produced by acid washing of the alpha alumina.

148. Beadle, S. W., W. H. Summerlin and E. T. A. Van Driessche; Airless cobalt demetalling in the cobalt flash combination catalyst cycle; U.S. Patent 5,410,090, April 25, 1995. **Claim 1:** A method for removing cobalt values from the crude product of a cobalt-catalyzed hydroformylation reaction formed from an olefinic feedstock, said crude product containing cobalt compounds in addition to an organic hydroformylation reaction product, which comprises: (a) contacting said crude product with an organic acid and water, in the absence of any oxygen-containing gases, thereby producing a substantially cobalt-free organic hydroformylation reaction product and a water soluble cobaltous salt aqueous product; (b) separating said substantially cobalt-free crude product from said water soluble cobaltous salt aqueous product; (c) diverting said substantially cobalt-free organic hydroformylation reaction product for further downstream treatment such as distillation or hydrogenation; (d) concentrating said water soluble cobaltous salt aqueous product thereby producing a concentrated aqueous solution of cobaltous salt and a substantially cobalt-free water containing said organic acid, whereby said concentrated aqueous solution of cobaltous salt is separated from said substantially cobalt-free water containing said organic acid; (e) recycling said substantially cobalt-free water containing said organic acid to step (a); (f) contacting said concentrated aqueous solution of cobaltous salt with an alcohol stream and synthesis gas, and passing this mixture to a preformer reactor where said concentrated aqueous solution of cobaltous salt is converted to a cobalt carbonyl; (g) contacting said cobalt carbonyl with a stream of stripping gas to entrain volatile cobalt compounds in said stripping gas and to generate as bottoms alcohol products and dissolved cobaltous salts, whereby said entrained volatile cobalt compounds are taken out overhead and the alcohol products and dissolved cobaltous salts are taken out as bottoms; (h) separating said alcohol products of step (g) from said dissolved cobaltous salts; (i) recycling said alcohol products from step (h) to step (f); (j) recycling said dissolved cobaltous salts from step (h) to step (a); and (k) contacting said volatile cobalt compounds from step (g) with said olefinic feedstock, whereby said volatile cobalt compounds are absorbed into said olefinic feedstock.
149. Beadle, S. W. and C. A. Poulin; Use of stripper reactor reflux as an initiator for preforming reaction of cobaltous salts to cobalt carbonyls, U.S. Patent 5,457,240, October 10, 1995. **Claim 1:** A method for producing higher aldehydes and higher alcohols which comprises: (a) hydroformylating an olefinic feedstock with synthesis gas in the presence of a cobalt-containing catalyst to form a crude product containing higher aldehyde, higher alcohol, secondary products and dissolved cobalt catalysts; (b) contacting said crude product with an oxygen-containing gas, an organic acid and water, thereby producing a substantially cobalt-free organic hydroformylation reaction product and a water soluble cobaltous salt aqueous product; (c) separating said substantially cobalt-free

crude product from said water soluble cobaltous salt aqueous product; (d) concentrating said water soluble cobaltous salt aqueous product, thereby producing a concentrated aqueous solution of cobaltous salt and a substantially cobalt-free aqueous solution; (e) separating said concentrated aqueous solution of cobaltous salt from said substantially cobalt-free aqueous solution; (f) contacting said concentrated aqueous solution of cobaltous salt with an alcohol and synthesis gas, and passing this mixture to a preformer reactor where said concentrated solution of cobaltous salt is converted to a cobalt carbonyl; (g) passing said cobalt carbonyl to a stripping reactor wherein said cobalt carbonyl is contacted with a stream of stripping gas to entrain volatile cobalt compounds in said stripping gas; whereby said entrained volatile cobalt compounds are taken overhead; and (h) recycling at least a portion of said entrained volatile cobalt compounds taken overhead in step (g) to said preformer reactor.

150. Vanderspurt, T. H. and J.-L. Kao; Noble metal large pore zeolite catalyst for methanol-ethanol coupling; U.S. Patent 5,493,064, February 20, 1996. **Claim 1:** An alcohol coupling process, comprising: contacting a vaporized mixture of starting alcohols of methanol in combination with a second alcohol selected from the group consisting of ethanol, n-propanol, and mixtures thereof with a carrier gas containing CO and H₂ in the presence of an alumina-bound highly dispersed metallic Pd-loaded, alkali metal cation exchanged L zeolite wherein the zeolite and alumina have an essential absence of strongly acidic catalytic sites and wherein said contacting is carried out at a temperature and partial pressure of CO and H of from about 300 to 400°C and from 3000 kPa to about 15,000 kPa at a sufficient pressure to minimize the decomposition of methanol to CO and H₂ and at a space velocity of from about 4000 hr⁻¹ to about 10,000 hr⁻¹ to produce isobutanol and n-propanol in the substantial absence of light gaseous alkanes and C₆₊ oxygenates.
151. Clavenna, L. R., S. M. Davis, R. A. Fiato and G. R. Say; Particulate solids for catalyst supports and heat transfer materials; U. S. Patent 5,395,813, March 7, 1995. **Claim 1:** As a composition, a fluidizable contact mass for the production of hydrogen and carbon monoxide from a low molecular weight hydrocarbon contacted with a fluidized bed of said contact mass at elevated temperature in the presence of steam, or oxygen, or both steam and oxygen, which comprises: an admixture of, a particulate, fluidizable precalcined zirconia heat transfer solid which contains from 0% to about 1% silica, based on the weight of the zirconia, in concentration ranging from about 10% to about 99.9%, based on the total weight of the admixture, wherein the zirconia component of the admixture has a Davison Index measurement of not greater than about 15, and a catalyst constituted of a refractory inorganic oxide support composited with a metal, or metals, component catalytic for the production of hydrogen and carbon monoxide from low molecular weight hydrocarbons, of fluidizable particle size in concentration ranging from about 0.1% to about 90%, based on the total weight of the admixture.

160. Davis, S. M., L. R. Clavenna, R. A. Fiato and G. R. Say; High performance alumina heat transfer solids for high temperature fluidized bed synthesis gas reactions; U.S. 5,360,777, Nov. 1, 1994. **Claim 1:** As a composition of matter, a heat transfer solid resistant to sintering and agglomeration for admixture with a catalyst to form a fluidized bed useful in the conversion of a low molecular weight hydrocarbon to hydrogen and carbon monoxide on contact therewith at high temperature in the presence of steam, or oxygen, or both steam and oxygen which comprises: alumina solids particles: (i) the outer peripheral surface layer of which contains no greater than about 5 atom percent silicon and boron, based on the total number of aluminum cations within said outer peripheral surface layer, while the bulk concentration of silicon in the particles does not exceed about 0.5%, based on the weight of the alumina solids, and the bulk concentration of boron in the particles does not exceed about 500 ppm, based on the weight of the alumina solids; (ii) the outer peripheral surface layer of which contains no more than 20 atom percent impurities based on the sum-total concentration of sodium, iron, calcium, and titanium as impurities; (iii) the tapped bulk density of the particles ranges from about 1.2 g/cc to about 2.5 g/cc; (iv) the Davison Attrition Index of the solids particles is no greater than about 12; and the sum total effect of these relationships between surface purity particle density, and attrition resistance is such as to provide a performance index categorized by the formula:

$$\text{Performance Index} = \frac{1}{(i)x(ii)x(iii)x(iv)} > 20.$$

161. Vanderspurt, T H. and R. J. Koveal; Isoalcohol synthesis; U.S. Patent 5,703,133, Dec. 30, 1997. **Claim 1:** A method for producing isobutanol and methyl butanols from syngas, comprising: (a) contacting a reactant stream containing syngas with a first stage catalyst having alkali promoted La-stabilized, highly dispersed microcrystalline Cu₂O having a particle size of ≤ 6 nm interspersed with metallic copper crystallites having a particle size of ≤ 25 nm, and zinc oxide crystallites having a particle size of ≤ 6 nm in the presence of an alumina structural promoter, wherein on a mol % alkali free metals only basis, Cu is present in from about 45% to about 55%, Zn from about 10% to about 20%, Al from about 10% to about 25%, La from about 5% to about 15% and wherein the alkali is between about 0% to about 1% K and from about 3% to about 6.5% Cs, wherein the first stage catalyst is produced by the process of: coprecipitating at a constant pH of from 0.7 to 11.0 at a temperature of from about 30°C to about 100°C in the essential absence of CO₂ from a solution of soluble metal salts of copper, zinc, lanthanum and aluminum with alkali hydroxide solution selected from the group consisting of LiOH, NaOH, KOH, CsOH and RbOH and mixtures thereof; aging the washed precipitate for from about 1 to 24 hrs at from to 50 to 90°C in the essential absence of CO₂; washing the precipitate in the essential absence of CO₂; drying the washed coprecipitate in air at up to about 120°C; calcining the dried coprecipitate in air for greater than 3 hrs at a temperature of from about 300 to 700°C; contacting the calcined coprecipitate with from 0.01% to 0.91% K and 3% to 6.5% Cs to form a promoted catalyst; drying the promoted catalyst at up to

120°C; recalcining the promoted catalyst at from about 300 to 700°C to produce a catalyst precursor containing highly dispersed CuO crystallites of up to about 10 nm; activating the promoted catalyst in flowing hydrogen for at least 1 hr at 175 to 185°C then for at least 1 hr at 250 to 270°C; wherein said contacting of reactant stream and first stage catalyst is carried out at a pressure of from about 850 psi (5,840 kPa) to about 1500 psi (10,310 kPa) a temperature of from about 240°C to about 340°C for a time sufficient to produce a product stream containing methanol, ethanol, propanol, and methyl butanols; (b) contacting methanol, ethanol and propanol from step (a) with a second stage catalyst having at least a first phase of mixed oxide crystallite containing from about 60 to 74 atomic % zirconium, from about 21 to 31 atomic % manganese and from about 5 to 9 atomic % zinc, and less than about 1 atomic % alkali, a second phase of zirconium doped hetaerolite containing from about 65 to 69 atomic % manganese, about 31 to 35 atomic % zinc, 0.5 to 5 atomic % zirconium, and optionally a trace atomic % alkali, and a third phase containing from about 20 to 55 atomic % manganese, from about 13 to 55% atomic zinc and 13 to 35 atomic % zirconium wherein the first phase mixed oxide crystallites have a zirconium oxide like structure have a particle size of at least about 40 D to about 100 D, the second phase of at least about 200 D to greater than about 2000 D and the third phase of at least about 1000 D to greater than 400 D at a pressure of from about 850 psi to about 1500 psi (10,300 kPa) a temperature of from about 340 to about 380°C to produce additional isobutanol and methyl butanols from the methanol, ethanol and propanol and trace ethylene and propylene.

162. Koveal, R. J and T. H. Vanderspurt; Isoalcohol synthesis catalyst; US Patent 5,691,268, Nov. 25, 1997. **Claim 1:** A syngas-to-alcohol catalyst, comprising: highly dispersed, alkali promoted, La stabilized, microcrystalline Cu₂O having a particle size of ≤ 6 nm in the presence of an alumina structural promoter, wherein on a mole % alkali free metals-only basis Cu is present in from 45% to 55%, Zn from 10% to 20%, Al from 10% to 25%, La from 5% to 15%, and wherein the alkali is from 0.01% to 0.91% K and from 3% to 6.5% Cs.
163. Apesteguia, C. R., S L Soled and S. Miseo; Catalysts for iso-alcohol synthesis from CO+H₂; US patent 5,508,246, Apr. 16, 1996. **Claim 1:** A syngas conversion process, having increased selectivity to methanol and isobutanol and conducted under syngas conversion conditions at pressures of about 20 to about 250 atmospheres, comprising contacting a carbon monoxide and hydrogen feedstream with a catalyst composition consisting essentially of a solid solution or a coprecipitated mixture of a first oxide and a second oxide, wherein said first oxide is selected from the group consisting of yttria, rare earth oxides and mixtures thereof and wherein said second oxide is a Group IIA oxide, and a Group IB metal.
164. Vanderspurt, T H., M A Greaney, D PI Leta, R J Koveal, M M Disko, A V Klaus, S K Behal and R. B. Harris; Isobutanol synthesis catalyst; US patent 5,707,920, Jan 13, 1998. **Claim 1:** A catalyst composition, comprising: a noble metal supported on at least a first phase having a poorly crystalline manganese and

zinc coped zirconium oxide phase containing about 71 to about 91 atomic % zirconium, about 10 to about 16 atomic % manganese and about 4 to about 8 atomic % zinc and a second phase of irregularly shaped hetaerolite crystals containing about 65 to about 69 atomic % manganese, about 31 to about 35 atomic % zinc and 0 to about 5 atomic % zirconium embedded in the first phase.

165. Herskowitz, M., Method for hydrocarbon synthesis reactions; US patent 5,652,193, July 29, 1997. **Claim 1:** A method for making a CO hydrogenation catalyst wherein said catalyst includes a metal selected from the group consisting of cobalt and ruthenium deposited in a porous, inorganic, refractory oxide support, said catalyst having said metal located in a rim on the outer surface of said support, said method comprising: (a) determining the rim thickness by: (i) determining intrinsic kinetic rate data including the intrinsic rate of reaction of carbon monoxide hydrogenation and the rate of CO conversion to methane for said catalyst; (ii) determining the thickness of said rim by relating the rates of diffusion of said carbon monoxide and said hydrogen to the intrinsic rate of reaction in said rim for a support geometry selected from the group consisting of a sphere, a ring, a cylinder, and a semi-circle and combinations thereof, such that said rim thickness optimizes both the rate of carbon monoxide hydrogenation and the reduction in methane selectivity; and (b) making a catalyst having a rim thickness determined in step (a).
166. Davis, S. M. and J. W. Johnson; Process for hydroisomerization of waxy hydrocarbon feeds over a slurried catalyst; EP 0 753 563 A1; 04/07/96. **Claim 1:** A hydroisomerization process for the conversion of a C₅₊ paraffinic feedstock to middle distillates which comprises contacting and reacting at hydroisomerization reaction conditions said C₅₊ paraffinic feedstock, and hydrogen, with a catalyst comprising a Group IB metal component, or a Group VIB metal component, or a Group VII metal component or a mixture of two or more of said metal components, supported on an acidic particulate solid, of average particle diameter in a range of from about 30 microns (30 :m) to about 150 microns (150 :m), dispersed in a paraffinic liquid hydrocarbon.
167. Wittenbrink, R. J., R. F. Bauman, P. J. Berlowitz, and B. R. Cook; Synthetic diesel fuel and process for its production; WO 97/14769, 24 April 1997. **Claim 1:** A material useful as a fuel heavier than gasoline or as a blending component for a distillate fuel comprising: 1 250-700°F fraction derived from a non-shifting FT catalyst process and containing at least 95 wt.% paraffins with an iso to normal ratio of about 0.3 to 3.0, ≤ 50 ppm (wt.) of sulfur and nitrogen less than about 2 wt.% unsaturates, and about 0.001 to less than 0.3 wt.% oxygen.
168. Wittenbrink, R. J., S. E. Silverberg and D F Ryan; High purity paraffinic solvent compositions, and process for their manufacture; WO 97/21787, 19 June 1997. **Claim 1:** A high purity solvent composition which comprises a mixture of paraffins of carbon number ranging from about C₈ to about C₂₀, has a molar ratio of isoparaffins:n-paraffins ranging from about 0.5:1 to about 9:1 and the

isoparaffins of the mixture contain greater than 50% of the mono-methyl species, based on the total weight of the isoparaffins of the mixture.

169. Stark, T M; Heat removal in gas conversion process, EP appl. 0 614 864 A1, 03/03/94. **Claim 1:** A method for removing heat from a hydrocarbon synthesis process reaction zone, which comprises passing a cooling medium through the reaction zone, in indirect heat exchange therewith, thereby vaporizing the cooling medium; the cooling medium being inert, condensible, and vaporizing at a pressure which is at least as great as the pressure in the reaction zone.
171. Hershkowitz, F. and G. Kiss; Unsaturates recovery and recycle process; U.S. patent 5,516,965, May 14, 1996. **Claim 1:** A process for recovering unreacted acetylene from an effluent stream of a process for synthesizing oxygenated hydrocarbons from unsaturated hydrocarbons, said stream containing unreacted unsaturated hydrocarbons, oxygenated reaction products, and low-boiling gaseous components selected from the group including CO, H₂, CO₂, H₂O, C₁-C₅ alkanes, nitrogen, helium, and argon, comprising: (a) absorbing the unreacted acetylene and the oxygenated hydrocarbons of the synthesis process effluent stream in a solvent wherein said solvent is an acetylene-depleted stream of the oxygenated product of said synthesis process; and (b) stripping the acetylene from the solvent to produce a first stream concentrated in acetylene and a second stream of oxygenated product depleted in acetylene, wherein said acetylene-depleted stream is the absorption solvent and the synthesis process product.
172. Clavenns, L. R., R A Fiato and G. R. Say; Particulate solids for catalyst supports and heat transfer materials, U.S. patent 5,476,877, Dec. 19, 1995. **Claim 1:** In a process for the production of hydrogen and carbon monoxide from a low molecular weight hydrocarbon by contact with a fluidized bed of catalyst at elevated temperature in the presence of steam, or oxygen, or both steam and oxygen, the improvement wherein the fluidized bed is comprised of an admixture of a particulate, fluidizable precalcined zirconia heat transfer solid which contains from about 0% to about 1% silica, based on the weight of the zirconia, in concentration ranging from about 10% to about 99.9%, based on the total weight of the admixture, wherein the zirconia component of the admixture has a Davison Index measurement of not greater than about 15 and a catalyst constituted of a refractory inorganic oxide support composited with a metal, or metals, component catalytic for the production of hydrogen and carbon monoxide from low molecular weight hydrocarbons, of fluidizable particle size in concentration ranging from about 0.1% to about 90%, based on the total weight of the admixture.
173. Herfbolzheimer, E., F J Kaiser, Jr and E. Iglesia; Catalyst fluidization improvements; U.S. patent 5,157,054, Oct. 20, 1992. **Claim 1:** A slurry phase hydrocarbon synthesis process for the conversion of hydrogen and carbon monoxide at reaction conditions to products which comprises: injecting a gas comprising hydrogen and carbon monoxide at or near the bottom of a bubble

column containing a slurry liquid, a catalytically active first solid and at least a second solid, dispersing the solids in the slurry liquid, all of the energy thereof being supplied by the gas, in the absence of liquid product recycle, the amount of the second solid being sufficient to increase the bed height of the first catalytic solid by at least 10%, and recovering liquid product.

174. Long, D. C.; Staged hydrocarbon synthesis process; U.S. patent 5,498,638, March 12, 1996. **Claim 1:** A once through hydrocarbon synthesis process which comprises reacting in a first stage or stages, a feed comprising hydrogen and carbon monoxide, and optionally CO₂, in the presence of a non-shifting hydrocarbon synthesis catalyst containing cobalt or ruthenium, recovering the product therefrom, condensing liquids from the product and reacting the remaining gases in a subsequent stage or stages in the presence of a hydrocarbon synthesis catalyst having shifting activity, and recovering the products therefrom.
175. Long, D. C.; Staged hydrocarbon synthesis process; EP appl. 0 679 620 A2, 26/04/95. **Claim 1:** A substantially once-through hydrocarbon synthesis process which comprises reacting in a first stage or stages, a feed comprising hydrogen and carbon monoxide, and optionally CO₂, in the presence of a non-shifting hydrocarbon synthesis catalyst, recovering the product therefrom, condensing liquids from the product and reacting the remaining gases in a subsequent stage or stages in the presence of a hydrocarbon synthesis catalyst having shifting activity, and recovering the products therefrom.
176. Taylor, J. H., and G. R. Say; Production of synthesis gas via fluidized bed/fixed bed process combination; U.S. patent 5,421,840, June 6, 1995. **Claim 1:** In a process for the production of hydrogen and carbon monoxide, the steps comprising: contacting, in a first reaction zone, low molecular weight hydrocarbons comprising methane, oxygen, and steam, at high temperature in a net reducing atmosphere, with a fluidized bed of catalyst, or catalyst and a solids diluent, to convert from about 85% to about 92% of the hydrocarbons to hydrogen and carbon monoxide and form a reaction mixture of hydrogen, carbon monoxide and unreacted hydrocarbons, oxygen and steam, withdrawing said reaction mixture as an effluent from said first reaction zone, and contacting said effluent, in a second reaction zone, with a fixed bed of catalytic metal solids with a void fraction of at least about 0.9 to convert, sufficient of the unreacted hydrocarbons, oxygen, and steam and increase the hydrocarbon conversion to a level ranging from about 0.5% to about 5% above that obtained in said first reaction zone.

ADDENDUM - EXXON FISCHER-TROPSCH WORK

Fischer Synthesis Process

A patent (A.1), a continuation of four prior applications with the first dated October 3, 1989, claimed a method for hydrocarbon synthesis reactions. This patent relates to the use of a catalyst of the "rim" type, as the terminology is used by Exxon. These are catalysts where the active metal(s) are deposited in the outermost layer of the support particle, and in a manner that the interior of the support particle is essentially devoid of the metal(s). This approach is widely used in the manufacture of auto exhaust catalysts that are shaped into spheres, cylinders, etc. The specific experiments were conducted with a 6 wt.% cobalt and 0.5 wt.% ruthenium on silica or titania support; since the surface area of the catalyst used in the example was reported to be about 20 m²/g it is assumed that the support was titania. The description of the preferred embodiment includes a derivation of the theoretical aspects of the determination of the rim loaded thickness needed to optimize CO conversion and/or minimize methane production. This theory has been included in several of the reviews of Fischer-Tropsch synthesis that have recently been published by Exxon workers. It is surprising that the authors of these reviews are not inventors of this method for hydrocarbon synthesis reactions and that the inventor (M. Herskowitz) is not an author of the review articles.

The outer layer containing the catalytic metal has a thickness determined so as to optimize CO conversion to heavy hydrocarbons so that conversion to methane is maintained at a predetermined level. The inventor maintains that it is not possible to simultaneously maximize CO conversion and minimize methane conversion. However it is possible to define a rim thickness so as to optimize one of these products. The

thickness of the rim-loaded catalyst is determined by relating the rate of diffusion of CO and H₂ to a rate of reaction in the porous inorganic oxide for a predetermined support geometry, partial pressures and temperatures.

The fluxes of the two reactants at steady state must be equal since there is no accumulation; thus,

$$\beta D_{e,CO} [dC_{CO}/d\chi] = D_{e,H} [dC_H/d\chi] \quad [A.1]$$

where the flux is expressed as a product of the effective diffusivity, D_e , and the concentration gradient. β is the stoichiometric coefficient and is equal to 2.07 in the reported work. Since hydrogen diffuses more rapidly than CO, the relative concentration of hydrogen should increase from the surface to the center of the catalyst pellet.

The differential mass balance inside the pores of the catalyst pellet of carbon monoxide, the limiting reactant, is

$$[D_{e,CO} (1/\chi^s)] d/d\chi[\chi^s (dC_{CO}/d\chi)] = \rho_p r_{CO} \quad [A.2]$$

where χ is the radial position measured from the external surface toward the center, ρ_p is the pellet density, C_{CO} is the CO concentration in the liquid-filled pores and r_{CO} is the intrinsic rate of reaction on the active sites. The shape factor, s , is equal to two for a sphere and to unity for a cylinder; the treatment can be extended to other pellet shapes.

The boundary condition on the external surface is:

$$C_{CO} = P_{CO,b}/H_{CO} \quad [A.3]$$

where $P_{CO,b}$ is the CO partial pressure in the bulk gas phase and H_{CO} is the Henry's Law constant. The other boundary condition can be defined for two cases as:

$$\text{inert core} \quad dC_{CO}/d\chi = 0 \quad \chi = \chi_i \quad [A.4]$$

$$\text{hollow core} \quad C_{CO} = P_{CO,b}/H_{CO} \quad \chi = \chi_i \quad [A.5]$$

This derivation assumes that external mass transfer resistance is negligible and that the pellet is isothermal. Experimental data verified that these are valid assumptions.

The intrinsic rate expression (small particle, diffusion free case) for cobalt or ruthenium on titania or silica support is

$$r_{CO} = k_1 \exp(-E_1/RT) [P_{CO}^a P_H^b / (1 + k_2 P_{CO} + k_3 P_H)^c] \quad [A.6]$$

where k_1 , k_2 , k_3 , E_1 , a , b , and c are calculated from experimental rate data. [In this and other Exxon patents there are many typos that are usually obvious but sometimes cause concern. Thus, in the above equation we have modified the equation given in the patent by replacing 1 in the original with a and 2 with c to produce equation [A.6].] The inventor indicates that the kinetic parameter, k_1 , usually depends only on the metal concentration on the support; presumably the dispersion must also be included. The inventor indicates that in certain cases such as cobalt on titania, it is also a function of water partial pressure:

$$k_1 = A[(1 + k_4 P_{H_2O}) / (1 + (k_5 P_{H_2O})^2)] \quad [A.7]$$

where A is the activity of the catalyst.

Henry's Law can be used to express equation [A6] in concentrations of CO and H_2 :

$$C_{CO} = P_{CO}/H_{CO} ; C_H = P_H/H_H \quad [A.8]$$

Integrating equation [A1] allows the expression of the hydrogen concentration in terms of the carbon monoxide concentration:

$$C_H = [P_{H,b}/H_H] - [\beta D_{e,CO}/D_{e,H}][(P_{CO,b}/H_{CO}) - C_{CO}] \quad [A.9]$$

or

$$H_H C_H / P_{H,b} = 1 - \gamma [1 - (H_{CO} C_{CO} / P_{CO,b})] \quad [A.10]$$

where

$$\gamma = (\beta D_{e,CO}/D_{e,H})(H_H/H_{CO})(P_{CO,b}/P_{H,b}) \quad [A.11]$$

Substituting equations [A6] and [A7] into equation [A8] and expressing in dimensional-less form yields

$$\phi = (\chi_s - \chi_c)[\rho k_1 \exp(-E_1/RT) [P_{CO}^a P_H^b / D_{e,CO} (k_2 P_{CO,b})^c]^{1.2} \quad [A.12]$$

The Thiele modulus, ϕ , is the ratio between the maximum rate of reaction and the maximum rate of diffusion. Likewise, γ expresses the ratio between the maximum rate of diffusion of the two reactants; when $\gamma = 1$ the ratio C_{CO}/C_H remains constant and when it is less than one the ratio decreases.

Equation [A.2] is solved to yield the concentration profiles in the pores of the catalyst pellet. This concentration profile is then integrated over the volume of the pellet and this is used to calculate the effectiveness factor which is the ratio of the actual reaction rate (global rate) averaged over the pellet and the maximum reaction rate calculated for the surface conditions:

$$\eta_{CO} = [1/V \int_{VP} r_{CO} dV] / [R_{CO}(P_{HP_{CO}} P_{H_2O})] \quad [A.13]$$

The effectiveness factor for methane can also be obtained in a similar manner using the rate of methane production, r_{CH_4} :

$$\eta_{CH_4} = [1/V \int_{VP} r_{CH_4} dV] / [R_{CH_4}(P_{HP_{CO}} P_{H_2O})] \quad [A.14]$$

and r_{CH_4} is obtained from kinetic measurements:

$$r_{CH_4} = k_4 \exp(-(E_2 - E_1)/RT) [P_H / (1 + k_2 P_{CO} + k_3 P_H)] r_{CO} \quad [A.15]$$

Assuming an isothermal reactor for simplicity, η_{CO} and η_{CH_4} are used in a reactor mass balance to calculate the carbon monoxide conversion and methane selectivity:

$$y_{\text{CO},i}(G_f/M_i)(dX_{\text{CO}}/dZ) = \eta_{\text{CO}} \rho_B r_{\text{CO}} \quad [\text{A.16}]$$

$$y_{\text{CO},i}(G_f/M_i)(dX_{\text{CH}_4}/dZ) = \eta_{\text{CH}_4} \rho_B r_{\text{CH}_4} \quad [\text{A.17}]$$

where $Y_{\text{CO},i}$ is the carbon monoxide mole fraction in the feed, G_f is the mass velocity, M_i is the molecular weight of the feed, ρ_B is the bed density and X_{CO} and X_{CH_4} are the carbon monoxide and methane conversion, respectively.

Using a 6% Co/0.5% Re catalyst of different pellet sizes and a feed with $\text{H}_2/\text{CO} = 2$, the CO conversion and CH_4 selectivity were measured. These conversion data were used to estimate the CO and H_2 diffusivities using the following procedure:

- a. values of $D_{e,\text{CO}}$ and $D_{e,\text{H}}$ were assumed;
- b. effectiveness factors η_{CO} and η_{CH_4} were calculated from equations [A.9] and [A.10] and the solution of equation [A.2] given the inlet conditions of the reactor;
- c. the CO conversion and conversion to methane were calculated by integrating equations [A.16] and [A.17]; since the effectiveness factors are functions of the partial pressures of CO, CH_4 and H_2O they must be recalculated along the length of the reactor taking into account of the changes in the partial pressures;
- d. methane selectivity was calculated from the ratio of conversion to methane, X_{CH_4} and carbon monoxide conversion, X_{CO} ;
- e. the calculated carbon monoxide conversion and the methane selectivity were compared with the experimental values for the various pellet sizes; and
- f. the effective diffusivities are adjusted to give the best fit of the experimental data.

An example of the agreement between the calculated and the experimental data for catalysts with a range of diameters is shown in figure A.1.

In one example the experiments were performed in a 3'x0.5" reactor that was packed with 1 mm diameter spherical particles uniformly loaded with 6%Co-0.5%Re. Data were obtained as the reaction temperature and the H₂/CO ratio were varied and the CO conversion and CH₄ selectivity obtained as described above. When the initial H₂/CO ratio is less than 2, the ratio will decrease along the catalyst bed and, since methane selectivity depends upon this ratio, it will decrease down the bed.

Simulations of carbon monoxide conversion and methane selectivity were made for various thickness of the rim loaded metals. As shown in figure A.2, both conversion and methane selectivity increase with increasing rim thickness. However, the important point is that these two factors increase rapidly from a low to high value and that the rim thickness where this increase occurs is different for the two factors.

In another simulation, the carbon monoxide conversion and methane selectivity were determined for two pellet shapes: ring and cylinder. As shown in figure A.3, the rim thickness needed to obtain the maximum CO conversion and a low methane selectivity depends upon the pellet shape. Thus, the cylindrical shape provides a much greater difference between the rapid increase in the two factors than the ring shape does.

The inventor claims a method for making a catalyst by determining the rim thickness which optimizes both the rate of carbon monoxide hydrogenation and the reduction of methane selectivity.

Long (A.2,A.3) claims a substantially once-through hydrocarbon synthesis process which comprises reacting in a first reactor or stages, a feed comprising

hydrogen and carbon monoxide, and optionally CO_2 , in the presence of a non-shifting hydrocarbon synthesis catalyst. The effluent is treated to recover the product from the first reactor by condensing the liquids and then reacting the remaining gases in a subsequent stage or stages in the presence of a hydrocarbon synthesis catalyst having shift activity, producing and recovering additional products.

A basis for this invention is that "The shift reaction can, however, be suppressed if the feed contains higher amounts of CO_2 relative to CO, and CO_2 is known to be added to $\text{H}_2 + \text{CO}$ synthesis gas feeds for hydrocarbon synthesis. Synthesis gas feeds can contain up to 10% CO_2 , that is, about 0.1-10% CO_2 ." The feed to the first stage(s) has H_2/CO in a 1.5:1 to 1.5:1 mole ratio, preferably 1.9: to 2.3:1, and CO_2 in the range 1.0-10 mole%, preferably 5-10 mole%. This mixture is subjected to synthesis with a non-shifting catalyst, preferably cobalt on alumina, silica or titania (preferred), and preferably promoted by metals as Ru, Rh, Ce or Hf, most particularly Rh (A.4). Conversion of CO in the first stage(s) are preferably at least 90%. Following conversion by the non-shifting catalyst, the liquid products, containing C_5+ hydrocarbons, water, oxygenated compounds and small amounts of dissolved gases.

The feed for the stage 2 reactor(s) with shift catalyst is illustrated in Table A.1. Based on our calculations, the mole fraction of water in the feed is 0.0024 (1.83 mm if operating at 20 atm). For a water-vapor saturated stream, we estimate the temperature of the separation to be -10 to -15°C, a surprisingly low temperature. The gas shown in Table A.1 is fed to a stage 2 reactor(s) where subsequent hydrocarbon synthesis produces a product with an olefin:paraffin ratio of 1.5:1 to 4:1, the lower ratios being favored for higher hydrocarbons and the higher ratios favored for the lower carbon number hydrocarbons. The H_2/CO ratio entering the stage 2 reactor(s) will be

essentially the same as the stage 1 reactor(s) because of the non-shifting character in the stage 1 operations. However, because of the conversion in stage 1 reactor(s), less gas will enter stage 2 reactor(s) with the result that the relative concentration of CO₂ will be higher in stage 2 than in stage 1 reactors. Sufficient hydrogen must be present in the feed to stage 2 reactor(s) to react with both CO and CO₂. Reaction conditions in stage 2 reactor(s) will be similar to those in stage 1 reactor(s); e.g., 10-35 bar, 220-340°, SHSV 200-2000 dry feed (water less than 5 vol% of feed).

Slurry Reactor

Herbolzheimer et al. (A.5) claim the use of a second solid in a slurry phase hydrocarbon synthesis process. A gas is injected at or near the bottom of the bubble column containing a slurry liquid, a catalytically active first solid and at least a second solid. The energy to maintain the dispersion of the solids is supplied by the gas in the absence of liquid recycle. The second solid is added in sufficient quantity to increase the bed height by at least 10%.

The authors state that slurry phase reaction, particularly those occurring in bubble columns, are well-known and do not need to be discussed. In column 6, line 23, the authors state that, "Slurry reactors are well known..." This is surprising since it would appear to imply that at the time of filing this patent [February 25, 1991] the use of slurry reactions are well known and, since bubble column reactors are also well known, only specific improvements to the operation of slurry bubble column reactors should be patentable inventions. Catalyst settling is a problem that can be encountered in bubble column reactors. Particles tend to settle to the bottom because of the influence of gravity. Opposing the settling tendency is the dispersion forces created by the rising

bubbles of gas injected at or near the bottom of the reactor. The balancing effect of these two forces results in an exponential distribution of catalyst solids concentration.

The authors utilize the data employing a dispersion coefficient and the settling velocity. D , the dispersion coefficient, depends on the superficial gas velocity through the system and on the effective diameter of the reactor column. The authors do not define this term in more detail, and presumably are considering the dispersion coefficient for the solids. The settling velocity of the catalyst particles, U_s , is given as

$$U_s = U_o(1 - c)^n \quad [A.18]$$

where

$$U_o = d_p^2(\rho_s - \rho)g/18\mu \quad [\rho_s \text{ is given as } \rho_s \text{ in the patent}] \quad [A.19]$$

where c is the volume fraction of solids in the slurry, d_p is the particle diameter, ρ_s is the density of the solids, g is the gravitational constant, μ is the viscosity of the suspending liquid, and n is a constant ranging from 4 to 8.

In the description, they indicate that most reactors operate in a regime somewhere between plug-flow and fully-backmixed (or CSTR) conditions. A plug-flow condition can be attained by using fixed-bed catalyst or a very large L/d (where L and d are the length and effective diameter of the reactor, respectively). In the plug-flow reactor the concentration (or partial pressure) of hydrogen and carbon monoxide, the reactants for Fischer-Tropsch Synthesis, decrease along the path of reactor flow due to reaction, and this decreases the driving force of the reaction. On the contrary, complete backmixing results in the same concentration of reactants along the entire length of the reactor resulting in a constant driving force and reflects the relatively low driving force at exit conditions.

Productivity is generally favored in plug-flow systems and selectivity is favored in backmixed systems. Later Exxon patents pertain to the operating conditions for plug-flow bubble column slurry reactors .

In the preferred mode for this patent, there is an absence of liquid throughput; thus, in the preferred mode, all of the energy from maintaining solids as a dispersion in the liquid is provided by the injection of gas at or near the bottom of the slurry reactor.

The catalysts utilized in the examples are typical of those described in many Exxon, and other, patents. The preferred catalyst is cobalt supported on titania and promoted with rhenium. The preferred catalyst particle size is in the range of 20 to 100 microns.

The data described in the examples were obtained in a 5 meter tall, non-reactive bubble column with 15 cm internal diameter (i.e., the L/d ratio was greater than 20, corresponding to nearly plug-flow conditions). Nitrogen gas was injected vertically into the column through a half inch hole at the bottom of a conical insert. This cone was used to insure fluidization of all the particles charged to the system. Pressure and temperature were monitored at 1 meter intervals along the column length, and slurry samples were withdrawn at these locations. The slurry liquid was C₂₀-C₄₀ paraffinic wax produced by Fischer-Tropsch synthesis using a cobalt catalyst. The solid was either TiO₂ or glass beads. No liquid was added during the measurements.

The solids distribution of 80 micron glass beads in FT product was determined at a temperature of 400°F (204°C) and 280 psig (for gas velocities below 8 cm/sec) or 150 psig (for gas velocities above 8 cm/sec). The decay length of the particle concentration profile was obtained by taking the slope of a line segment joining the data points when plotted as the logarithm of the solids concentration versus height. In figure A.4, the

decay length in each zone is plotted versus the average concentration in the zone for superficial gas velocities of 2-16 cm/sec.

They correlated the data by

$$D/U_s(\text{feet}) = 0.2(1 + 20c^2 + 3000c^4)/U_o(\text{cm/sec}) \quad [\text{A.20}]$$

for $U_g < 4$ cm/sec and

$$D/U_s(\text{feet}) = 1.2(1 + 3c^2 + 500c^4)/U_o(\text{cm/sec}) \quad [\text{A.21}]$$

for $U_g < 4$ cm/sec.

U_o is Stokes settling velocity and c is the volume fraction of solids in the slurry.

The results of the above experiment with glass beads was then used in models to predict solids distribution for several examples of various solids combinations. For catalyst and inert solids of the same density (2.7 g/cm^3) and diameter (50 microns) that are (1) dispersed in a solvent with a liquid viscosity of 0.9 cp and density of 0.7 g/cm_3 , (2) with an average catalyst loading of 0.05 by volume (gas-free basis), (3) an expand bed height of 30 feet, (4) a gas inlet velocity of 8 cm/sec, and (5) an overall conversion of 0.8, they obtained catalyst distributions with 0, 0.05, 0.1, 0.2 and 0.3 volume fraction of inert solids added.

The data in figure 5.A show that with only catalyst the effective bed height is about 13 feet, and with the catalyst more heavily concentrated at the bottom of the reactor. The addition of even a small amount of inerts increase the bed height. As the inert solids content is increased the bed expands further in height and the catalyst concentration profile becomes flatter.

In another example, they use the same catalyst and inert solid except the inerts are 1 micron in size. This example would be approximated by the use of 80 micron iron catalyst spheres made up of 1 micron particles that, because of attrition, produce

individual 1 micron fines. Effects similar to those of equal sized particles are obtained. A similar calculation was made using an active catalyst of density 2.7 g/cm^3 and lower activity catalyst with a density of 1.0 g/cm^3 . They also made calculations for the case when the original activity is decreased by factors of 2, 4, and 6. The use of the less active component also causes the bed to expand.

In the examples provided, the authors do not provide an identification of the meaning of the curves for volume fraction of catalyst vs. height in figures A.2-A.5 of the patent or in the figure legend. Thus, the reader must assume the identity of the curves.

It appears that this patent is the basis for the several patents that pertain to inert solids. For example, a structurally modified alumina prepared by incorporating a Group IIA metal or metals, particularly Mg or Ba, is claimed to have increased resistance to sintering and agglomeration (A.6). These materials are considered as aiding catalyst fluidization, as a catalyst support, and as heat transfer agents in syngas production or utilization in the slurry phase (A.7-A.12).

Stark (A.13,A.14) was issued a patent to cover the use of pentane (or similar light hydrocarbon) to remove the exothermic heat of reaction of the Fischer-Tropsch process and to expand the pentane to recover the energy to drive air plant compressors. Steam/water is the usual material for heat removal, and is utilized in the commercial reactors at Sasol. However, Stark indicates that it is desirable to have a coolant that has a boiling point and vaporizes at a pressure higher than the reaction pressure; this will ensure that no problem will arise if a leak allows coolant to enter the reaction zone. In order for vaporization to occur with pentane, it is necessary that the coolant side be below the critical conditions (197°C ; 44.1 atm. (679 psi)).

Stark (A.13,A.14) claims a method for removing heat from a hydrocarbon synthesis process reaction zone. A cooling medium is passed through the reactor zone in an indirect heat exchange, thereby vaporizing the cooling medium. The cooling medium is chosen so that it possesses the properties of inertness, condensable and vaporizes at a pressure which is at least as great as the pressure in the reaction zone.

Water/steam is frequently employed as the heat transfer medium. However, the authors claim that there is a reasonable expectation of leaks in a F.T. reactor because of the presence of numerous tubes and welds. In the case of water/steam, the reactor pressure is higher than the water/steam side so that F.T. products will leak into the cooling section whenever a leak occurs. The accumulation of products in the cooling side will eventually require the unit to be shut down for cleaning and/or repairs. In this instance, the cooling medium is chosen to have a higher vapor pressure than inside the reactor so that any leakage will be from cooling side to reactor. An appropriate cooling medium is n-pentane, a product of the F.T. synthesis.

The high pressure energy is recovered from the cooling medium through an expander. Preferably a substantial portion of the energy recovered from the expander is used to drive compressors for an air plant which separates oxygen from nitrogen.

The U.S. patent, but not the European patent application, indicates that the F.T. synthesis is carried out in a slurry phase system.

Hydrocracking and Hydroisomerization

Davis et al. (A.15) claim a hydroisomerization process for the conversion of a C₅₊ paraffinic feedstock to middle distillates. This involves contacting and reacting the feedstock and hydrogen at hydroisomerization reaction conditions with a catalyst comprising a Group IB, VIB or Group VIII metal component, or two or more metals,

supported on an acidic particulate solid with an average particle diameter of the size range 30 to 150 μm which is dispersed in a paraffinic liquid hydrocarbon.

Davis et al. (A.15) report that in normal hydrocracking with large catalyst particles, secondary reactions, arising from diffusional limitations, produce large amounts of gas and naphtha, and decrease the yield of the desirable middle distillate fractions. To overcome this limitation, staged fixed-bed reactors are operated at relatively low space velocities. They cite an earlier process [U.S. Patent 5,378,348] utilizing a separation into two boiling range fractions (500°F^- and 500°F^+) and separately hydroisomerizing to make middle distillates.

The hydroisomerization of the present invention is conducted in a slurry phase, preferably with greater than 25% catalyst slurry of particles in the micron size range (preferably 40-60 micron). The catalyst is bifunctional, possessing metallic hydrogenation and acidic functions. The metal oxide support, preferably a silica-alumina material, is prepared as described in reference -[U.S. Patent 3,843,509].

It is reported that one slurry reactor can be used to obtain approximately as much conversion as in three packed bed reactors in series under similar reaction conditions. An additional advantage of the slurry reactor is that a water-steam cooling coil can be used to remove the exothermic heat of reaction and to control the temperature. Using a packed fixed-bed reactor, a complex system of traps and quenching techniques are required to control the heat that is released during the reaction.

Data for the conversion of n-hexane show that the conversion decreases with increasing hydrogen pressure. At a given temperature, the fraction of single methyl branches decreases with increasing feedstock conversion; significant amounts of multi-methyl branched compounds appear at higher feedstock conversion. In contrast, in a

fixed bed reactor undesirable cracked products result at higher conversion levels. Even with the slurry technology, the fraction of cracking increases with feedstock conversion at levels above about 80%.

The kinetics of the Fischer-Tropsch wax cracking with a Pd/silica-alumina catalyst was obtained to design a reactor for a commercial scale process. They report that conversion followed zero order kinetics with an apparent activation energy of 30-35 kcal/mole for the conversion range of 30-70%.

Davis and Ryan (A.16) claim a process for producing middle distillate transportation fuels from a waxy product of a hydrocarbon synthesis process. The process consists of:

1. separating the product into a heavier (500°F^{+}) and at least one lower (500°F^{-}),
2. catalytically isomerize the heavier products in the presence of hydrogen,
3. catalytic hydrotreat the lighter fraction to remove heteroatoms (primarily O), and,
4. catalytically isomerize the product from step (3) to a product with a freeze point of -30°F or lower.

The authors indicate that a cobalt catalyst tends to produce heavier products, e.g., containing C_{20+} , whereas ruthenium tends to produce more distillate type products, e.g., $\text{C}_5\text{-C}_{20}$. A typical product slate for a cobalt catalyst is given as (the values may vary by $\pm 10\%$ for each fraction) is given in Table A.2.

Surprisingly, they found that hydrotreatment of the heavier fraction (containing about 0.45 wt% oxygen) prevents the production of a product with the excellent cold flow properties that was formed by hydroisomerization of the untreated material. They indicate the need to limit the conversion for the 700°F^{+} to the 700°F^{-} products to the 35-

80% range as a measure to limit cracking to produce gases and thereby a lower yield of distillates.

The lighter fraction can be the 320-500°F or, preferably, the entire liquid fraction boiling below 500°F. Following a conventional hydrotreatment, the naphtha is flashed off and the remaining material is hydroisomerized using a catalyst appropriate for light fractions, such as the ones described in reference A.17.

The most active catalysts were those materials containing a surface silica additive. However, it is stated that selectivity is more important than activity. Activity was improved when a 4% surface $\text{SiO}_2/\text{CoNiMo}/10\%\text{SiO}_2\text{-Al}_2\text{O}_3$ catalyst was used at 700 psig rather than 1,000 psig. Increasing the LHSV to 3.0 and increasing the temperature to provide activity similar to that of LHSV = 0.5 to 1.0 dramatically effected the products; the yield of jet fuel was decreased in favor of gas and naphtha production and the jet fuel had an increased freeze point. The cause for this was not understood but it was speculated that diffusional problems were the major factor.

An international patent application (A.18) claims the production of a high purity solvent composition which comprises a mixture of paraffins of carbon number ranging from about C_8 to C_{20} . The solvent has a molar ratio of iso-/n-paraffins ranging from about 0.5:1 to 9:1 and the isoparaffins of the mixture contain greater than 50% of the mono-methyl species. This patent application employees catalysts and processing schemes that are included in reference (A.19).

The Fischer-Tropsch product was obtained from the conversion of a synthesis gas ($\text{H}_2:\text{CO} = 2.11\text{-}2.16$) with a titania supported cobalt-rhenium catalyst. The reaction conditions were in the range of 422-428°F, 287-289 psig and feed linear velocity of 12 to 17.5. The alpha of the Fischer-Tropsch synthesis was 0.92.

The 700°F+ boiling fraction was hydroconverted over a Pd-silica-alumina catalyst (0.5 wt.% Pd, 38 wt.% Al₂O₃) to produce 39.4 wt.% conversion of the 700°F+ to 700°F- materials (Table A.3).

Wittenbrink et al. (A.20) describe a processing scheme whereby some oxygenates (primary alcohols) remain in the finished fuel. These oxygenates function to improve the lubricity of the diesel fuel.

The process scheme illustrated in their figure A.6 leads to some confusion. Shown leaving the Fischer-Tropsch reactor (vessel 2) are two streams: 3 (700°F+; 370°C) and 4 (700°F-). It is reported that the reactor is operated in the range 422-428°F (217-220°C) and 287-289 psig using a titania supported cobalt/rhenium catalyst (A22). The syngas had a composition of H₂/CO = 2.11-2.16. The alpha for FTS was 0.92. The FTS products were separated into three fractions having approximate boiling ranges: (1) C₅-500°F (designated F-T cold separator liquids); (2) 500-700°F (F.T. hot separator liquids) and 700°F+ (F.T. reactor wax). It appears that streams 3 and 4 in figure A.6 must be sent to a fractionator (not shown in the figure) to generate three streams.

The hydroisomerization and recombining of fractions are the same, or essentially the same, as described by Davis et al. (A.15) above.

References

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- A.3. D. C. Long, European Patent Office Publication No. 0 679 620 A2, April 26, 1995.
- A.4. See, for example, U.S. 4,637,993; U.S. 4,717,702; U.S. 4,477,595; U.S. 4,663,305; U.S. 4,822,824; U.S. 5,036,032; U.S. 5,140,050; U.S. 5,292,705.
- A.5. E. Herbolzheimer, F. J. Kaiser, Jr., and E. Iglesia; U. S. Patent 5,157,054, October 20, 1992.
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- A.13. T. M. Stark, U.S. Patent 5,409,960, April 25, 1995.
- A.14. T. M. Stark, European patent application Number 94301541.2.
- A.15. S. M. Davis, J. W. Johnson, C J. Mart, D. F. Ryan and R. J. Wittenbrink; European Patent Application EP 0 753 563 A1, filed April 7, 1996.
- A.16. S. M. Davis and D. F. Ryan, U.S. Patent 5,378,348, January 3, 1995.
- A.17. U.S. Patent 5,187,138]
- A.18. WO 97/21787
- A.19. U.S. Patent 5,378,348
- A.20. R. J. Wittenbrink, R. F. Bauman, P. J. Berlowitz and B. R. Cook, International Publication No. WO 97/14769, April 24, 1997.
- A.21. U.S. Patent 4,568,663.

Table A.1			
Reactor Simulation Results			
		Stage 2 Product	
	Stage 2 Feed	Shifting Catalyst	Non-shifting
Component Rates, Moles/Hr			
H ₂	11584	3021	6781
CO	2823	564	524
CO ₂	16324	15065	16326
H ₂ O	113	4887	2400
Hydrocarbon + Alcohol	13701	14045	13924
Inert	2434	2434	2434
Moles Converted			
CO		2259	2299
CO ₂		1259	-2
Total		3518	2297
% (CO+CO ₂) Converted		18.4	12.0
Hydrocarbon + alcohol		344	223
Yield, Moles/Hr			

Table A.2

Typical Product Slate from FT Process Liquids Produced with a Cobalt Catalyst (from
ref. A.17)

Fraction	Wt.%
IBP-320°F	13
320-500°F	23
500-700°F	19
700-1050°F	34
1050°F+	11
TOTAL	100

Table A.3	
Fischer-Tropsch Synthesis conditions	
Operating Conditions	
Temperature, °F	638
LHSV, v/v/h	1.2
Psig	711
H ₂ treat rate, SCF/B	2,100
Yields, Wt.%	
C ₁ -C ₄	0.97
C ₅ -320°F	10.27
320-500°F	14.91
500-700°F	29.99
700°F+	43.86
TOTAL	100
700°F Conversion, Wt.%	39.4
15/5 Distillation Yields, Wt.%	
IBP-650°F	50.76
650°F+	49.24

Figure A.1. Model predictions for methane selectivity as a function of pellet radius compared to experimental data (6% CO-0.5% Re catalyst; $T = 200^{\circ}\text{C}$; $(P_{H_2}/P_{CO})_{\text{feed}} = 2.0$; $P_t = 19 \text{ atm}$) (from ref. A.????).

Figure A.2. CO conversion and methane selectivity as a function of rim thickness for spherical particles ($d_p = 1.0 \text{ mm}$; $T = 200^{\circ}\text{C}$; GHSV = 770 v/v/hr; --- $A = .6 \times 10^{-5} \text{ mole/s/s}\cdot\text{g}\cdot\text{atm}^2$;)) $A = 1.2 \times 10^{-5} \text{ mole/mole/s/s}\cdot\text{g}\cdot\text{atm}^2$) (from ref. A.1).

Figure A.3. CO conversion and methane selectivity as a function of rim thickness for ring (---) and cylinder (—) pellets ($d_p = 1.0$ mm; $T = 200^\circ\text{C}$; GHSV = 770; $A = 1.2 \times 10^5$ mole/s $\cdot$ g $\cdot$ atm² (from ref. A.1).

Figure A.4. Plot of decay length versus volume fraction solids concentration (#, 2 cm/sec; G, 8 cm/sec; +, 4 cm/sec; X, 12 cm/sec; *, 6 cm/sec; $\diamond$, 16-18 cm/sec).

Figure A.5. A plot of volume fraction versus bed height when a second inert solid to a first catalytically active solid in a bubble column, the inerts being of the same density and diameter as the catalytic solid.

Figure A.6. Schematic of the process (from ref. A.21).

ATTACHMENT XI

Listing of Open Literature Description of Exxon FT Work

A listing of papers by Exxon personnel, and including two by E. Iglesia identified by * that were published after he left Exxon but covering work that was conducted at Exxon. The synopsis will be brief since the results and conclusions in these papers are reviewed in papers XI.1, XI.12, XI.15 and XI.26.

The polymerization of the C_1 monomer produces a distribution described by the Anderson-Schulz-Flory (ASF) distribution. Thus, each carbon number surface species has a probability of continuing the chain growth or terminating the polymerization to produce a product. The ASF mechanism assumes that the ratio of chain propagation r_p , and termination, r_t , are independent of the hydrocarbon chain length. The resulting hydrocarbon selectivity predicted is described as:

$$m_i = \alpha m_{i-1} = (1 - \alpha) \alpha^{i-1} \quad [1]$$

where m_i is the mole fraction of hydrocarbon containing i carbon atoms and α is the probability for chain growth and is related to the probability for chain growth and termination as

$$\alpha = r_p / (r_p + r_t). \quad [2]$$

According to the ASF mechanism, a plot of the logarithm of the mole fractions of the hydrocarbons produced versus the number of carbon atoms in the hydrocarbon should result in a straight line with a single slope given by the chain growth probability, α . Much of the data generated, both in small and large reactor systems, exhibit two values of α . Recently an explanation has been given for this deviation of the hydrocarbon selectivity from that predicted by the ASF reaction mechanism has been

offered by workers at Exxon (XI.1,XI.15,XI.18,XI.26). The explanation termed as the Transport-Enhanced Olefin Re-adsorption (TEOR) model is briefly outlined below.

The normal ASF chain growth scheme is outlined in Figure 1. This mechanism for hydrocarbon production has been modified by the Exxon workers first as shown in figure 2 and later as shown in figure 3. The modified mechanism is claimed to be applicable for iron, cobalt and ruthenium catalysts, although data for iron has not been included.

This mechanism distinguishes between paraffins and olefins formed by termination of the hydrocarbon chain on the catalyst surface. Further, the olefins formed can re-adsorb back onto the catalyst surface and re-enter the chain growth process. This process of re-adsorption is quantified by a re-adsorption rate (r_R). Finally, the olefins formed can be hydrogenated, at least partially on other catalytic sites (rate given by r_S) to paraffins. The effective rate of chain termination is then

$$r_t = r_o + r_H - r_R \quad [3]$$

where r_o is the rate of termination to olefins and r_H is the rate of termination to paraffins. Thus olefin re-adsorption serves to decrease the effective rate of termination.

The rates of chain growth, olefin termination, paraffin termination, hydrogenation and olefin re-adsorption are assumed to be independent of chain length, i.e., the number of carbon atoms in the hydrocarbon. The value of the chain growth parameter, α , is then

$$\alpha = r_p / (r_p + r_o + r_H - r_R) \quad [4]$$

Note that due to the independence of the rates with chain length, this modified mechanism by itself cannot predict two or more values of the chain growth probability with increasing number of carbon atoms in the hydrocarbon.

The pores inside a catalyst particle are filled with the heavier hydrocarbon products (presumably liquid under reaction conditions) from the FTS. In the TEOR model it is assumed that this limits or exerts a strong influence on the diffusion of the FTS hydrocarbon products (both olefins and paraffins) out of the pores. The effect of diffusion resistance is to increase the time spent in a catalyst pore by the FTS hydrocarbon products. The diffusivity of individual hydrocarbons is dependent on their molecular weight or chain length or the number of carbon atoms. In the TEOR model, the dependence of diffusivity is assumed to be an exponential function of the number of carbon atoms:

$$D = D_0 e^{-0.3i} \quad [5]$$

where D_0 is a constant.

As the diffusivity increases with chain length, the time spent inside a catalyst pore is longer for a hydrocarbon containing, for instance, 20 carbon atoms than for a hydrocarbon containing 10 carbon atoms. Thus the olefins containing 20 carbon atoms have a greater chance to re-adsorb on to the catalyst surface and re-enter the chain growth process than olefins containing 10 carbon atoms. Hence, the rate of re-adsorption for a C_{20} olefin is greater than the rate of re-adsorption of a C_{10} olefin, i.e., the re-adsorption rate for heavier olefins is enhanced by transport limitations. Then, according to equation [4], the probability for chain growth, α , should increase with the number of carbon atoms in the hydrocarbon.

The diffusivity of light olefins (C_2 - C_{10}) in the liquid-filled catalyst pores is fairly high so that the re-adsorption rate of these olefins is relatively unaffected. Thus, a single value of the chain growth probability, α , is obtained for these hydrocarbons. For hydrocarbons containing higher than 10 carbon atoms, the rate of diffusion becomes

increasingly significant. Hence, the rate of re-adsorption, and thus the chain growth probability (α), increases with the hydrocarbon chain length. The increasing rate of olefin re-adsorption with hydrocarbon chain length finally reaches the rate of olefin termination, i.e.,

$$r_R = r_o \quad [6]$$

at a sufficiently high value of the number of carbon atoms (C_{25} or greater) in the olefin. At this point no more olefins are desorbed from the catalyst surface and the resulting probability for chain growth becomes

$$\alpha = r_p/r_p + r_H \text{ for } C_{25}+ \text{ olefins} \quad [7]$$

Thus, for $C_{25}+$ hydrocarbons, the chain growth probability does not depend on the hydrocarbon length and once again approaches a constant value.

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ATTACHMENT XII

Review of Fischer-Tropsch Work by Gulf Oil

The Gulf-Badger process leads from the catalysis research work on Fischer-Tropsch synthesis work and the reaction engineering analysis conducted by Gulf Oil, and later the process and engineering design provided by Badger (XII.1). A simplified process scheme is shown in Figure XII.1 (XII.2). The process was first discovered from exploratory work conducted by Gulf in the early 1970s. As Gulf continued to discover large reserves of natural gas, the need to convert remote natural gas to transportation fuels became important (XII.1). Since the exploratory research was successful, fundamental engineering and development work were undertaken, in the early 1980s. Because of its experience with others in the Fischer-Tropsch Synthesis, the Badger Company was invited to participate in some of the experimental work on reactor development and later provided the process engineering as well as the basis for the process economics (XII.2).

The initial involvement by Badger was because they had experience with fluid bed reactors and already had two of them set up in their lab. Gulf management wanted rapid development and did not want to delay to build their own reactors. Gulf researchers apparently advised against using the cobalt catalyst in a fluidized bed reactor but the work progressed to the point where 100 g batches of catalysts were prepared. The catalyst proved to be so active they had to strip insulation off the reactors when the reaction started to go out of control.

More money was spent on the fluid bed work in six months than Gulf had spent in the previous six years. With the result, of course, that the catalyst behaved just as Gulf researchers had predicted. The unit ran fine for half a day or so but then it began

to be difficult to keep the catalyst suspended. The catalyst had to be hydrogen-stripped once or twice a day, and the methane make was so high during those stripping periods that the overall selectivity to liquids was rather poor.

At the same time, the go-ahead for fixed bed development was given, and Gulf continued with Badger because they were already familiar with the catalyst and process. The scale-up of the fixed bed process of the catalyst manufacture by Davison were successfully accomplished.

Two types of reactors - two fluid-phase fixed bed and fluidized bed - were seriously considered. Because of the high molecular weight products that are produced by Gulf's most promising catalysts and thermal instability of the reactor, the fluidized bed reactor design concept presented real problems. Therefore, the Gulf Oil reaction engineering staff selected a fixed bed reactor. Its design and operation were critical, but success was quickly achieved.

The proprietary catalyst (in 1983) was inherently stable when combined with the proper reactor design and operation. Catalyst activity decay was avoided when stable, parametrically insensitive conditions and operation were achieved. The catalyst could be regenerated to the original activity by controlled oxidation and reduction.

The catalyst activity is an important property. It has a direct impact on the reactor design and operation as well as on capital and operating costs. The catalysts activity and selectivity in the developed reactor determine the reactor size that is required to produce a given quantity of desirable product, and to convert a given volume of synthesis gas, per day.

Operating conditions also influence the catalytic conversion and selectivity, and thereby the product distribution. An increase in temperature increases the reaction rate

whereas decreasing the H_2/CO ratio at constant temperature and pressure decreases the rate with the Gulf catalyst (XII.2). It was found that a $10^\circ C$ increase in temperature would just about compensate the rate loss for a decrease in H_2/CO ratio from 2 to 1.5. A substantial increase in reaction rate results from increasing the total pressure. The results for increasing pressure and temperature are illustrated in Figures XII.2 and XII.3 (XII.2). Representative data are summarized in Table XII.1 (XII.2). The Gulf-Badger reactor design has a constrained range of performance and acceptable operation.

Production of C_5+ products depends upon both the activity and selectivity of the catalyst, and is a product of these two factors. Thus, some of the effects that increase activity may decrease productivity.

Pilot plant data for a reactor, consisting of a single, commercial-size reactor (1" x 40') tube show that reasonable temperature control can be achieved. Conditions that are representative of those used at Gulf are (XII.2):

Temperature	200-225°C
Pressure	250 psig
H_2/CO feed ratio	1.5-2
Feed space velocity	500-1,000/hr.
CO conversion	40-60% per pass
Selectivity to C_5+	<u>ca.</u> 70-75% of carbon converted

A typical product make from a reactor operating under such conditions are illustrated in Table XII.2.

Two reactor concepts were tested during the pilot plant work - a tubular fixed bed and a fluidized bed at Badger. The latter was not satisfactory. Details on only the fixed bed reactor were given in reference XII.2. Gulf's pilot plant consisted of two reactor

sections in series (Figure XII.4, ref. XII.2). After initial operation, temperature of the hot spot in the Gulf Oil reactor did not exceed that of the average temperature by more than 5°C. The illustrated CO conversions depended linearly upon temperature, as did the relative rate (Figures XII.5 and XII.6; ref. XII.2). The productivity of C₅+ hydrocarbons did not increase linearly with temperature due to the relative increased production of light (C₁ - C₄) gaseous products (Figure XII.7; ref. XII.2).

A demonstration unit was designed (in 1983) that would produce approximately 15 b/d of naphtha, 15 b/d of diesel fuel and 7 b/d of wax from 350,000 scf of natural gas (Figure XII.7; ref. XII.2). Natural gas was compressed to the reformer pressure and mixed with recycle CO₂, heated and passed through a zinc oxide bed to remove sulfur compounds. The natural gas was obtained by drilling a well at the laboratory site. It then entered a steam-methane reformer and was converted to synthesis gas. Carbon dioxide was removed in an amine scrubber after the gas was cooled and compressed. The gas then passed through a membrane separation system to adjust the H₂/CO ratio. Hydrogen would be used as fuel in the demo plant but could be utilized for upgrading in a commercial operation.

Gulf-Badger Process - Patent Literature

A series of catalysts was prepared that demonstrated a beneficial effect of a minor amount of ruthenium on a catalyst containing a major amount of cobalt for the low pressure synthesis of higher hydrocarbons from synthesis gas (XII.3).

A standard reference cobalt catalyst was prepared according to a published procedure (XII.4) whereby solution I (49.4 g. Co(NO₃)₂•6H₂O; 11.0 g. Mg(NO₃)₂•6H₂O and 1.5 g. Th(NO₃)₄•4H₂O dissolved in 250 ml water) and solution II (35 g. K₂CO₃ in 250 ml water) were heated to boiling. Solution I was added rapidly with vigorous stirring to

solution II, and immediately thereafter, 20 grams of dry powdered kieselguhr was admixed with stirring which continued for 10 minutes. The mixture was filtered and washed with distilled water until no evidence for nitrate ion was observed in the wash water. The solid was dried at 120°C for 16 hours, calcined in air at 350°C for 16 hours, then reduced in flowing hydrogen at 350°C for 3 hours. A second catalyst was prepared following the same procedure except that 0.35 g. of RuCl_3 was added to solution; this catalyst had the following composition: Co (31.6 wt.%); Mg (3.25 wt.%); ThO_2 (1.98 wt.%); Ru (0.53 wt.%); and kieselguhr (62.64 wt.%).

These two catalysts were subjected to synthesis runs using the same experimental conditions ($\text{H}_2/\text{CO} = 2$; upflow reactor with preheater for feed gas; atmospheric pressure; gas hourly space velocity based on the total amount of charge gas was 250; g.c. analysis). A series of experiments were conducted at various reaction temperatures with the CO conversion levels shown in Figure XII.9. It is seen that a measurable conversion is obtained only at a temperature of about 125°C or higher. On the other hand, the same catalyst except that it contains Ru, exhibits appreciable conversion at 50°C and maintains this superiority with increasing reaction temperature. The products from the runs at 220°C with the standard Co catalyst and the Ru containing catalyst were analyzed. The products from the standard catalyst exhibited an ASF distribution, with an alpha value of 0.85 (Figure XII.10). The products from the Ru containing catalyst exhibited a product distribution that contained significantly heavier hydrocarbons; the alpha value, based on the curve in Figure XII.10, was 0.98. Thus, the addition of Ru to the standard catalyst resulted in a significant increase in the catalytic activity as well as producing a significantly heavier products. The data indicated that the presence of Ru essentially eliminated the production of

methane and ethane (however, this conclusion is on a relative basis). In addition, the C_{9+} product from the standard catalyst contained 29% of olefinic product compared to 4% with the Ru containing catalyst. The gaseous products were found to contain about 15 volume percent CO_2 for the standard cobalt catalyst but only traces of this gas were obtained with the Ru containing catalyst. While it is not stated how the samples were collected, the low value for the C_{9-11} product fraction, relative to lower and higher carbon number products (Figure XII.10), suggests that the products consisted of gaseous and liquid fractions that were subsequently analyzed separately, resulting in loss of some C_{9-11} hydrocarbons.

Similar catalysts were prepared. For catalyst 3, about equal amounts of alumina and magnesia were added to replace kieselguhr in the above Ru containing catalyst (31.6 wt.% Co, 2.0 wt.% thoria, 0.5 wt.% Ru, 32.9 wt.% alumina and 32.9 wt.% magnesia). The other catalyst (4) contained a lower amount of Co and no thoria; at the same time alumina was substituted for the kieselguhr and the amount of magnesium oxide was increased. This catalyst (XII.4) contained 17.77 wt.% Co; 0.70 wt.% Ru, 40.77 wt. % alumina and 40.77 wt.% MgO .

The three catalysts were compared for methane production at various reaction temperatures; these results are compiled in Table XII.3. Referring to Table XII.3, it is apparent that the presence of Ru significantly decreased the amount of methane produced at all reaction temperatures. All Ru containing catalysts produced only traces of CO_2 . Substituting gamma-alumina for kieselguhr had little, if any, effect on methane production; likewise, the removal of thoria and an increase in magnesia had little effect on methane production.

As shown in Table XII.4, it is noted that the "% selectivity for C₉₊ fraction" increased, and the % olefin in the fraction decreased, when Ru was present in the catalyst.

It appears that another Gulf worker later repeated Kobylinski's work with precipitated Co and CoRu catalysts, as well as one with the 20Co-0.5Ru-1La₂O₃ composition. Ru was found to confer better dispersion and activity, just as it did for the impregnated catalysts, but that there was no appreciable change in product distribution in standard week-long tests. Apparently a problem with the GC analysis, such as getting drops of liquid product in with the vapor phase products impacted the reported data. The precipitated catalysts were found to have activities per unit weight of metal that were intermediate between those of catalysts made by aqueous impregnation and those made by nonaqueous impregnation.

High octane gasoline and diesel fuel are produced from synthesis in a two stage process (XII.5). In the first stage, synthesis gas is converted to straight chain paraffins that have a boiling range that falls mainly in the diesel fuel range. A cobalt catalyst, preferably containing a Group IIIB or IVB metal oxide, is supported on gamma- or eta-alumina, or a mixture of these two aluminas. The C₅-C₉ straight chain portion of the product from the first stage is converted in the second stage to highly aromatic plus branched chain paraffinic gasoline using a platinum group metal catalyst. The most preferred metal oxide for use in the catalyst for the first stage is thoria. The support should have low acidity, meaning a Brønsted acidity with H₀ ≤ 1.5, which is less than 5 micromole per gram (about 10¹⁶ acid sites per m² of surface area). The deleterious effect of acidity is the isomerization and cracking of intermediate alkenes, removing them from chain growth and producing a low molecular weight product. **This latter**

statement implies that higher molecular weight alkenes readsorb on the catalyst to react with synthesis gas (or other alkenes) to produce higher alkenes. In addition, the production of low molecular weight products requires either that low molecular weight alkenes do not readsorb to undergo subsequent chain growth or that the low molecular weight products produced by cracking are alkanes, and not alkenes.

The catalyst for the first stage was defined by hydrogen chemisorption and should adsorb at 25°C from 125 to 300 micromole per gram of total catalyst. The chemisorption of hydrogen is illustrated in Figure XII.11 and shows a maximum for a catalyst that is receded in flowing hydrogen at 350°C. The maximum hydrogen adsorption corresponds to a dispersion, d , of cobalt of 0.066; that is, 6.6% of the Co atoms are located on the surface of cobalt metal crystallites.

The support must be of high purity and have a surface area in excess of 50 m²/g, and preferably in the range of 150 to 225 m²/g. High purity means that the support will contain negligible amounts of sodium, sulphate, silicon, phosphates or other material having a deleterious effect on the metal dispersion or the production of high molecular weight hydrocarbons.

The preparation of the catalyst was accomplished using a nonaqueous, organic impregnation solution containing the soluble cobalt and Group IIIB or IVB salts in order to achieve the necessary metal loading and distribution. The alumina was calcined in air prior to impregnation, preferably in 5h 400 to 600°C range. Suitable solvents include ketones, such as acetone or methyl ethyl ketone; the lower alcohols; amides, amines, ethers, hydrocarbons or mixtures thereof. A mixture of ethanol and acetone (4 parts

acetone; 1 part ethanol) is preferred and is used in an amount that will fill the pore volume; a maximum amount would be equivalent to five times the total pore volume.

The impregnated material is dried (25 to 45°C) to remove solvent to "dryness" and the material is then calcined in air, preferably 225 to 275°C. The impregnation, drying and calcination steps are repeated until the desired metal loading is obtained. The catalyst is slowly reduced in hydrogen. In the first reduction step, the catalyst is heated slowly (0.5 to 5°C/min) to a maximum temperature of 180 to 220°C and held at this temperature for about 24 hours. The second reduction step is accomplished by heating at a rate of 5 to 20°C per minute to the optimum temperature. Initially the reduction step is accomplished in a diluted hydrogen stream (e.g., 5% hydrogen in nitrogen); gradually the hydrogen concentration is increased to provide pure hydrogen.

While it is stated that the reactor type utilized is not critical, a fixed bed, with gas downflow, was preferred.

The catalyst for the second stage could be a typical naphtha reforming catalyst; that is, a platinum group metal supported on alumina using halogen to impart acidity.

The catalyst which gave the hydrogen adsorption data that is shown in Figure XII.11 contained the following composition by weight: 100Co/18ThO₂/200Al₂O₃. This catalyst was evaluated for activity using a flow of 240 cm²/g/hr of CO and the same flow of H₂. Data were obtained for the above catalyst and are summarized in Tables XII.5 and XII.6.

The conversion depends upon temperature as is shown in Figure XII.12 (the numbers in parentheses are the total gas flow rate (cm²/g/hr)). Thus, at a flow rate of 1:1 synthesis gas of 1.22 NL/g/hr; the conversion of CO was 6.5%. The activation energy was calculated using the data in Figure XII.12 to be 15 kcal/mole. The product

distribution changed slightly to favor lower weight products as the temperature increased (Figure XII.13). The product distribution did not adhere to the ASF plot except perhaps for the lowest temperature run; in all instances the C_2 - C_4 products were much too low to approach fitting an ASF plot. It was not possible to fit the data in Table XII.2 with an ASF distribution.

This patent covers the activation of a promoted or unpromoted supported cobalt catalyst (XII.6). The catalyst is prepared using cobalt carbonyl and the support is either silica or alumina. The activation procedure comprises three steps: (1) reduction in hydrogen, (2) oxidation in an oxygen-containing gas, and (3) reduction in hydrogen, all three steps conducted at temperatures less than 500°C. This activation comprising reduction, oxidation and reduction has been called "ROR". It has been found that the addition of promoter, such as lanthanum or manganese (and oxides of the lanthanides and actinides), reduces the activity of the unpromoted catalyst. However, if in addition to the above promoters, ruthenium is also incorporated the ROR activation results in an increase in activity above that of the unpromoted cobalt catalyst.

The cobalt carbonyl is added by an impregnation technique using a non-aqueous solvent. If desired, the addition of promoter can be accomplished by co-impregnation along with cobalt. In the preferred procedure, the promoters (metal oxide and/or ruthenium) are added prior to the cobalt carbonyl.

Thus, the promoter is added to the calcined support as described in ref. XII.5. The impregnated catalyst, preferably using the incipient wetness technique, is dried slowly in air. The slow drying procedure is used so as to spread the metals over the entire support. After drying in air, the catalyst is calcined by heating slowly in flowing air to, preferably, 250 to 300°C. The drying and first calcination can be accomplished

separately, or done in a combined step. The calcination step is accomplished at a slow heating rate, preferably 0.5 to 1.0°C/min., and held at the final temperature for up to 20 hours (2 h. is preferred). If necessary, the impregnation, drying and calcination steps are repeated to provide the optimum metals loading.

Following the calcination, the catalyst is impregnated with an organic solution containing cobalt carbonyl. Prior to impregnation, the catalyst is not exposed to the atmosphere sufficiently for the support to be rehydrated. If more than one impregnation is required, the catalyst must be subjected to a reduction-reoxidation treatment, the first two steps of the ROR procedure.

The preferred procedure for the ROR process is:

- (1) Slowly heat to about 200°C and hold at this temperature for about 20 hours (starting with about 5% H₂ in nitrogen and increase gradually to pure H₂), then heat to the optimum reduction temperature (about 350°C) and hold for about 24 h. Reduction should be slow enough to prevent the volatilization of cobalt carbonyl and to prevent the water vapor from exceeding 1% in the exit gas.

Passivation is effected at room temperature using diluted air.

- (2) The oxidation step is conducted as described in ref. XII.5.
- (3) The oxidized catalyst is reduced as described in step (1) above.

The advantage of the ROR technique was illustrated by the preparation of three catalysts: (A) cobalt carbonyl was impregnated onto Ketjen gamma-alumina; (B) impregnating gamma alumina with cobalt and ruthenium nitrates (20 wt.% Co and 0.5 wt.% Ru); and (C) impregnating gamma-alumina with nitrate salts to give a material containing 25 wt.% Co, 0.5 wt.% Ru and 1.0 wt.% lanthanum oxide. The three catalysts

were tested at 185°C; $H_2/CO = 1.85$ (atmospheric pressure), producing the results shown in Table XII.7.

The ROR treatment of the cobalt carbonyl catalyst provided a more active catalyst than the other two preparations and the selectivity of the cobalt carbonyl catalyst for C_5+ hydrocarbon is comparable to the ruthenium-promoted cobalt catalyst.

Hydrogen adsorption studies showed that the ROR treatment produced lower dispersions of Co than just hydrogen reduction. Thus, catalyst A had a metal dispersion of 0.29 following a reduction in hydrogen, but only 0.13 following the ROR treatment. Thus, the activity per metal site increased rather than the number of sites.

The activity of a silica-supported catalyst prepared using cobalt carbonyl is higher than that of an alumina-supported catalyst; however, the selectivity for C_5+ hydrocarbons is lower. The ROR treatment of the silica-supported material improves the C_5+ hydrocarbon selectivity.

This patent provides additional data to support the view that the reduction-oxidation-reduction, "ROR", technique provides superior activity over the same catalyst when it is just treated with hydrogen (XII.7). Data is also presented to show the improvement in activity when ruthenium is incorporated into the cobalt catalyst. The data shown in Table XII.8 was obtained at 1 atm pressure with [the patent gives the gas composition as weight percent but it surely is molar percent] a 35% CO and 65% H_2 synthesis gas mixture.

As shown in Table XII.8, the use of ruthenium significantly improved the catalyst activity as compared to the test of a catalyst that did not contain ruthenium. Even when the Co/Ru molar ratio exceeded 200/1, the catalyst activity increased in excess of 100

percent over that in which ruthenium was absent. Likewise, the ROR activation led to a catalyst that exceeded the activity of a hydrogen treated material by 24-34 percent.

Data were also presented to show the benefit of Ru for a catalyst prepared by precipitation of cobalt, ruthenium and lanthanum oxide onto an alumina support by the addition of potassium carbonate. In this case the use of the ROR treatment improved the catalyst activity. However, when the amount of ruthenium exceeded 0.5 wt.%, the activity showed a decline of 4%.

A method of catalyst preparation is given which consists of an aqueous impregnation using a solution of a cobalt salt, drying the impregnated material and then employing a nonaqueous, organic impregnation solution of salts of ruthenium and a Group IIIB or IVB metal (XII.8).

A supported catalyst was prepared using a microspheroidal gamma-alumina commercially available from Harshaw; this alumina had an average particle diameter of about 60 microns. After calcination at 600°C, the alumina was impregnated with a cobalt nitrate solution. The material was dried at 120°C and then impregnated with thorium nitrate and ruthenium acetylacetonate dissolved in an acetone-ethanol (=2:1 ratio) solution. Excess solvent was removed at reduced pressure at room temperature in a rotary evaporator. The catalyst was then dried by heating to 90°C with the nitrate salt melting with evolution of water in the temperature range of 50-60°C. Prereduction and passivation was conducted using a hydrogen flow of 720 ml/g/hr. The catalyst was heated to 100°C at 1°C/min and maintained at this temperature for 1 hr and then heated at the same rate to 200°C. After holding at the latter temperature for 2 hr., the catalyst was heated at 10°C/min to 360°C and held at this temperature 16 hrs. After cooling below 200°C, the catalyst was flushed with nitrogen and the temperature lowered to

room temperature. Air was then bled into the nitrogen (1:50 air:nitrogen with flow of 50 mL per minute per 5 g catalyst for 16 hr). The final reduced catalyst contained 21.9 wt.% Co, 0.5 wt.% Ru, 2.2 wt.% ThO_2 and 75.4 wt.% alumina.

The activity of the catalyst was obtained using a 1/2" fluid bed reactor where 50 grams of catalyst was heated to a temperature of 350°C in a flow of hydrogen (N L/g/hr) and held at this temperature overnight. The hydrogen flow was reduced to 0.3-0.4 L/g/hr and an equal flow of CO was introduced (if $\text{H}_2/\text{CO} = 2$, the hydrogen flow was doubled). The results of runs are summarized in Table XII.9.

The results show that, for similar conditions, an increase in the H_2/CO ratio from 1 to 2 caused a decrease in the C_5+ hydrocarbon yield and an increase in the amount of methane. An increase in pressure from 15 to 30 psia caused an even greater decrease in the C_5+ hydrocarbons and increase in methane; an increase in temperature had a similar effect.

A recent paper by Haddad and Goodwin (XII.16) on the CoRu catalyst claimed to obtain no change in activity from a ROR treatment. Looking at their catalyst preparation, they claimed to add 20% Co as the nitrate apparently in one step. This would appear to require the use of a supersaturated cobalt solution. In most catalysts, the alumina does not have enough pore volume to accommodate that much cobalt nitrate. The fact that they saw no ROR effect could be taken to mean that they had not produced an alloy catalyst whereas measurements of Curie point changes showed that the Gulf workers had done so. Goodwin reports TGA studies after a wide range of precalcination and reduction temperature, but none for an RO-treated catalyst. Gulf workers usually found a 100°C lowering in the reduction temperature for an RO-treated catalyst, compared to a fresh one - more evidence of a drastic change in properties.

The best proof of the advantage of ROR was obtained on a large scale - after one year of operation and several hydrogen strippings, the catalyst in the demo plant was regenerated (mainly for experience with recalcination). It was then 50% more active than it had been after initial startup and this made operation with the regenerated catalyst even more difficult. After the plant was shut down Gulf workers tested catalysts from about 20% of the reactor tubes and the catalysts, except for one tube, had the expected catalytic properties.

This patent relates to the use of a mixture of a catalyst active for the Fischer-Tropsch synthesis and one that effects alkene isomerization and/or cracking to produce gasoline from synthesis gas (XII.9). The Fischer-Tropsch synthesis catalyst is any one of the many examples that are comprised of cobalt alone or promoted by ruthenium and/or Group IIIB or IVB metal oxides. The acid cracking/isomerization catalyst is a silicalite-1 type (see XII.10 - XII.12).

An example utilized a catalyst containing 50 wt.% silicalite and 50 wt.% of a catalyst with the composition $100\text{Co}/18\text{ThO}_2/200\text{Al}_2\text{O}_3$ (example of conversion data given above). The particles were separately ground to give a particle size 100 mesh, mixed and then wetted, and then comminuting and sieving the resultant mixture to provide uniform 30-40 mesh particle size. Tests were conducted using 0.5 g samples of the prereduced catalyst by reducing in hydrogen at 360°C in hydrogen 2.4 L/g/hr at one atmosphere. The hydrogen flow was then reduced to 0.48 L/g/hr and an equal flow of CO ($\text{H}_2/\text{CO} = 1:1$). The tests were effected at 185°C and one atmosphere pressure to provide the data in Table XII.10.

The impact of the addition of silicalite to the Fischer-Tropsch catalyst is apparent (Figure XII.14). The ASF plot shows that $\alpha = \sim 1$ for the C_3+ hydrocarbons; however

the amount of methane is much above and the C_2 products much below the values expected for conformity to the ASF plot. When silicalite is added to the Fischer-Tropsch catalyst, the data do not fit the ASF distribution. Methane and the C_2 -products are slightly higher than was obtained with the Fischer-Tropsch catalyst alone. More importantly, the C_3 - C_{10} hydrocarbon products significantly deviate from the ASF distribution. Thus, it is apparent that the acid catalyst has effected a significant amount of isomerization and cracking of heavier hydrocarbons to lighter, gasoline range hydrocarbons.

The fraction of n-alkane in each carbon number hydrocarbon fraction provides a surprising distribution (Figure XII.15). When the catalyst contains only the Fischer-Tropsch component, the amount of n-alkane drops from about 75% for C_2 to about 20% for C_3 and then slowly increases with increasing carbon number to approach 60% for the C_{10} carbon number fraction. In this respect, the cobalt catalyst, when operated at 1 atmosphere, exhibits a distribution that is very similar to the one obtained for an iron catalyst at 1 atmosphere or at intermediate pressure levels (XII.13). However, when the silicalite catalyst is present, the alkane fraction deviates from the one obtained for Fischer-Tropsch synthesis. Up to carbon number 6, a similar trend is obtained for both catalysts; however, above carbon number 6 there is significantly less n-alkane when the silicalite is present. The apparent explanation for this is that the products have increasing fractions of isoalkanes, isoolefins and internal olefins as the carbon number increases above C_4 , thus lower fractions of n-alkanes and 1-olefins. Isomerization to iso or internal olefins is not possible with C_2 and C_3 . The degree of olefin reincorporation may be strongly influenced by the degree of substitution at the double bond. Ethylene readsorbs the most readily because it has two free CH_2 groups. Among the 1-olefins,

readsorption and chain initiation declines slowly with carbon number. Internal olefins readsorb poorly because they have no free CH₂ group, but they can isomerize back to 1-olefins and that gives them a small path towards readsorption. Isoolefins are also relatively unreactive. Although some have a free CH₂, if they have two substituents on the adjacent carbon that appears to be enough to make readsorption difficult.

All that is needed then to lower the effective chain growth probability among C₄+ chains is for the 1-olefins, produced as primary products, to be isomerized to internal olefins or isoolefins. That removes them from the F-T reaction. With a catalyst that does this (almost any acidic catalyst), one can observe a large drop in chain growth probability between C₃ and C₄.

The isomerization to isoolefins requires a strong acid site and it was found that this reaction declined fairly quickly with time over silicalite or ZSM-5. However, the isomerization to internal olefins, which requires only moderate acidity, persisted for as long as any of the composites were run, and it was sufficient to alter the ASF distribution.

A layered aluminosilicate (montmorillonite-type structure) containing cobalt substituted into the crystal lattice was activated for the Fischer-Tropsch reaction using a sequential reduction-oxidation-reduction (ROR) technique (XII.14). A Group VIII noble metal, such as ruthenium, is also added by impregnation prior to the final reduction step.

The hydrothermally produced cobalt aluminosilicate has the following general formula prior to its activation:

[it is 3x+y in the patent]

where n is between 0.02 and 4 (prefer 2 to 3); x is up to about 1 (prefer 0.1 to 0.1); $n+x$ between 0.02 and 4 (prefer 2 to 3); y is between 0.05 and 2 (prefer 0.5 to 2); and z is up to about 10. In the above the predominant amount of Al, Co, OH, and F are in the octahedral layers, and the Si and minor amounts of Al are in the tetrahedral layers. Ammonia and water are located between the layers. Water and ammonia are lost in the pre-activation calcination. The reduction is carried out in hydrogen (or other reducing gas) and the oxidation process is preferable accomplished in air or diluted air. The activation is accomplished in three steps - the ROR process described earlier.

A catalyst is prepared using a saturated aqueous solution of 161 g of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ in two liters of water that is slurried with 1.84 g of a silicic acid solution providing a $\text{Si/Al}=4.7$ ratio. The silica-alumina gel was precipitated by adding the slurry to 1 L of ammonium hydroxide with a pH of 8. The gel was washed with distilled water to remove chloride. A 50 g sample of the washed gel was slurried with 225 ml of water containing 60 g of cobalt acetate, 0.78 g of ammonium fluoride, and 0.42 g of HF while stirring and maintaining the pH at 8.0 by adding ammonium hydroxide as needed. The mixture was heated at 300°C in an autoclave (1,240 psig) for four hours. After drying at 120°C, the gel was calcined at 500°C for 4 hrs and produced a hard, wine-red solid with $\text{SiO}_2/\text{Al}_2\text{O}_3 = 0.30$. The catalyst was reduced at 400°C for 2 hr in hydrogen and then reoxidized at 500°C. A hydrogen reduction at 600°C (16 hr.; 8.5% wt. loss) then reoxidized in air at 500°C (8.1% wt. gain). A final reduction was effected at 400°C for 16 hours.

This catalyst was utilized at 1 atm. in a 0.5 g. catalyst bed using a hydrogen:carbon monoxide = 1:1 with a feed of 0.48 l/g/hr. Three temperatures were utilized following activity stabilization to produce the results shown in Table XII.11.

The major products in the C₅+ hydrocarbons were found to be isoalkanes and isoalkenes. The alkenes contained a high fraction of internal alkenes.

The catalyst is a rare earth promoted layered complex metal silicate composition characterized as having repeating units with a structural formula

where x is a number from 0 to 1 (fraction of Ru in Ru+Ni); a is the valence of nickel, b is the valence of ruthenium; n is a number defined by

$$6/[a(1-x) + bx]$$

and w is a number ranging from 0 to 4 (XII.15). The preferred catalyst is a rare earth promoted nickel chrysotile.

These catalysts produce much methane in addition to higher carbon number hydrocarbons. Typical examples, using H₂/CO = 2.5; 350 GHSV; 210°C; and atmospheric pressure, are shown in Table XII.12.

Low concentrations of thoria are needed but higher (30% or more) are not beneficial, and may have a slight detrimental effect. The inclusion of low concentrations of thoria greatly increase the amount of C₂+

Typical examples, using H₂/CO = 2.3; 400 GHSV; 204°C; and atmospheric pressure, to define the differences in rare earth promoters, if any, are shown in Table XII.13.

The results show that there is a synergistic benefit in conversion when a mixture of two rare earth promoters are used. Thus, thoria incorporation provides a CO conversion of 31.5% and lanthana 25%; rather than the expected intermediate value for CO conversion when a mixture of thoria and lanthana are incorporated, the CO conversion is 71.5%. A similar result is obtained when thoria and praseodymium is utilized.

Slurry Phase Synthesis

A patent (XII.17) claimed a process for the conversion of synthesis gas using a finely divided catalyst (ca. 10-110 microns) dispersed in a fluid medium. The catalyst consisted essentially of cobalt and ruthenium on a support. In subsequent claims the support was identified as alumina or silica. Another subclaim indicated that the fluid is a liquid medium which could be a synthetic hydrocarbon liquid or a hydrocarbon conversion product. The activation known as ROR (reduction in hydrogen, oxidation, reduction in hydrogen) was claimed. A promoter could be selected from the group consisting of Rh, Pt, Pd, Ir, Os, Ag and Au. The use of these catalysts produced a product with less than 16 wt.% methane. The catalyst cobalt concentration covered was from about 5 to about 25 wt.% and the promoter in an amount from about 0.01 to 0.5 wt.% based upon the total catalyst weight.

The patent contains examples of conversions in fixed-bed reactors with a catalyst prepared to have various particle sizes. A catalyst was prepared that had a particle size that one normally encounters in fixed-bed operations (1/16th inch (0.16 cm) extrudate) and then this catalyst was ground to produce average particle sizes of 0.28 and 0.54 mm. The found that both catalyst activity and product selectivity changed with particle size. In particular, the fraction of methane decreased and the amount of C₅+ increased with decreasing particle size of the catalyst (Figures XII.16 and XII.17); over the particle sizes tested it appears that both selectivities change linearly with particle size. It appears that the methane production of the three catalyst sizes extrapolates to a common value of about 4 wt% at very small particle size (Figure XII.16). Likewise, the C₅+ selectivity appears to approach about 87 wt.% at very small particle size. This means that the C₂-C₄ yield is about 9 wt.% for the very small particle size catalyst. As

expected, the rate of reaction increased as the particle size was decreased (Figure XII.18). For the smallest particle size (0.24 mm) the reaction rate increased by a factor of 1.94 for an increase in temperature of 10.5°C, a factor close to the rule of thumb of a doubling in reaction rate for every 10°C increase in temperature. At 195°C, the rate decreased by 27% when the H₂/CO ratio was decreased from 2.0 to 1.5.

The authors indicate that the catalyst prepared using an organic solvent has higher activity than one prepared in the same manner but using an aqueous solution. The authors indicate that the catalyst may contain Group IIIB or IVB metal oxide as a promoter, with oxides of the actinide and lanthanide series being preferred. Especially preferred metal oxides are La₂O₃, CeO₂, ZrO₂, TiO₂, HfO₂, or ThO₂. MnO₂ and MgO are also listed as preferred promoters. The amounts of these promoters can be from about 0.05 to 100 parts by weight to 100 parts by weight of cobalt. It appears that the patent covers only catalysts using these oxides as promoters, and not as the support material.

The support should have low acidity. Its surface area should be at least about 40 to 50 m²/g but not so high that "permit reactant materials to enter the interstices of the catalyst." A preferred surface area is in the range of 150 to 225 m²/g. The support should be high purity, meaning having low concentrations of components having deleterious effects on the cobalt catalyst.

The process is outlined in figure XII.19 and does not differ significantly from one used by Kölbel and coworkers (XII.18). In the reactor, the catalyst particles are suspended in a liquid medium having sufficient viscosity to ensure that the particles remain in suspension and having a volatility that is low enough to avoid loss due to vaporization within the reactor. The catalyst is present from about 2 to 40 wt.%. The catalyst density can be in the range of 0.25 to 0.90. The gas flow enters at a rate

sufficient to suspend all of the catalyst particles in the system without settling. The gas flow rate will be selected depending upon the slurry concentration, catalyst density, suspending medium density and viscosity, and particular particle size utilized. Suitable gas flow rates include, for example, from about 2 to 40, preferably from about 6 to 10 cm/sec. The pressure range covered is from about 1 to 70 atm. Light hydrocarbon products, such as C_{20} and below, are withdrawn overhead through a line designated 32 in Figure XII.19. A portion of the heavier products and catalyst slurry is withdrawn through line 38 and is passed to a separation zone. A concentrated catalyst/slurry fraction is returned to the reactor while a portion of the catalyst/slurry may be passed through a regeneration zone (54) before being returned to the reactor. Heavy products with low catalyst concentration are revolved through line 44. Separation by filtration can be utilized for separating catalyst from the suspending liquid (vessel 40).

The data obtained in the slurry reactor were compared to a run in the fixed bed reactor with the same catalyst formulation. The catalyst for the fixed bed reactor was supported on 1/16 inch extrudate alumina which contained about 20 wt.% Co, 0.5 wt.% Ru and 1.0 wt.% of a rare earth oxide composite containing 66 wt.% La_2O_3 , 24 wt.% Nd_2O_3 , 0.7 wt.% CeO_2 , 8.2 wt.% PrO_2 and 1.1 wt.% other rare earth oxides. The synthesis gas ($H_2/CO = 2.03:1$ with methane diluent of 19.1 mole %) passed through the 1" i.d. reactor at a maximum stable temperature of 215°C with a pressure of 275 psi (18.7 atm., 1895 kPa). For the slurry reactor, alumina which contained about 12 wt.% Co, 0.3 wt.% Ru and 0.6 wt.% of a rare earth oxide composite containing 66 wt.% La_2O_3 , 24 wt.% Nd_2O_3 , 0.7 wt.% CeO_2 , 8.2 wt.% PrO_2 and 1.1 wt.% other rare earth oxides was in the form of 20-105 microns (less than 140 mesh; average particle size 52 microns). A liquid with a viscosity of 8 centistokes ($8 \times 10^{-6} \text{ m}^2/\text{s}$) was composed mainly

of C₄₀-C₅₀ isoparaffins. Gas entered at the bottom through a stainless steel screen in the form of small bubbles. Hydrocarbon was removed from the top through a heated line. The pressure was 160 psig (10.7 atm) and the gas flow with H₂/CO = 1.95 was 1826 cm/s. Initially the temperature was 225°C but was increased and held at several higher temperatures to obtain additional conversion data.

The increase in conversion with increasing temperature gives an activation energy of 20.5 kcal/mol (85.7 kJ/mol) (Figure XII.20). This value of the activation energy is surprisingly close to that reported for a fused iron catalyst (20.0 kcal/mol; 83.6 kJ/mol) and a precipitated iron catalyst (20.9 kcal/mol; 87.4 kJ/mol) (XII.19). At 225°C, methane is 8.4 wt.% of the product and increases to 15.6 wt.% at 240°C. As the temperature increases, the C₅+ fraction gradually decreases (Figure XII.21) and the C₅-C₂₀ fraction increases, indicating that the alpha value decreases with increasing temperature; however, there is not sufficient data to obtain reliable values of alpha (Table XII.14).

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Table XII.1						
Evaluation of G-B Catalyst in Pilot Fluid Bed Reactor Data Taken at 25 Hours on Stream (from XII.2)						
Run	Temp., °C	Pressure, (psig)	H ₂ /CO	Syngas Space Velocity, cm ³ /g/h	Per Pass CO Conversion, %	Selectivity to C ₅ + ^a
First	195	15	2.0	600	25	74
Second	195	30	2.0	1200	22	82
Third	195	30	2.0	1200	16	74
	215	30	2.0	1200	44	71
Fourth	215	60	2.0	1950	41	72
Fifth	205	30	1.5	1200	17	72
Sixth	215	30	3.0	1200	76	55
Seventh	205	30	2.0	1200	23	67
Eighth	205	30	2.0	1800	25	73
Ninth	215	40	1.5	1600	25	72
a. C ₅ + expressed as percent of carbon selectivity basis. b. At some point, every run had one or more reactor "run aways." They all failed.						

Table XII.2	
Typical Data from Fixed Bed Pilot Plant (XII.2)	
Temperature, °C	210
Yields, Wt.% of Hydrocarbon Product	
CH ₄	13.7
C ₂ H ₄ to C ₄ H ₁₀	11.6
C ₅ -C ₈ (naphtha)	25.4
C ₉ -C ₂₀ (distillate)	33.4
C ₂₁ + (wax)	14.2
Oxygenates	1.7

Table XII.3					
Influence of Ru on Catalyst Performance (from ref. XII.3)					
Experimental Conditions:			H ₂ :CO = 2:1, GHSV = 380		
		% Selectivity to CH ₄ Catalyst from Example			
Ex. No.	Temp., °C	1 (Co)	2 (Co + Ru)	3 (Co + Ru)	4 (Co + Ru)
18	200	9.8	0 ^a	0	0
19	300	27.5	0	0	0
20	400	48.0	0	1.2	0.5
21	450	87.0	10.1	21.0	25.0
a. The low selectivities (zero) are most likely not real.					

Table XII.4									
Influence of Ru on the Production of C ₉ ⁺ (from ref. XII.3)									
		% Selectivity to C ₉ + Fraction Catalyst from Example Number in Table XII.3				% Olefins in C ₉ + Fraction Catalyst from Example Number in Table XII.3			
No.	Temp., °C	1	2	3	4	1	2	3	4
22	200	41	88	87	--	29	4	5	3
23	300	30	75	71	73	32	10	9	7
24	400	18	41	38	34	48	30	26	21

Table XII.5					
Products Using a Prerduced Co-Th-Alumina Catalyst (from ref. XII.5)					
Example No.	2	3	4	5 ²	6 ³
Temp., °C	175	185	195	205	194
H ₂ /CO	1:1	1:1	1:1	1:1	2:1
CO Flowrate (cm ³ /gram/hour)	155	155	270	610	270
CO Conversion Rate (cm ³ /gram/hour)					
To CO ₂	0.2	1.1	1.6	2.9	(1.3)
To Hydrocarbons	19	41	61	79	(120)
CO Conversion (Percent)	13	27	23	13	44
Product Distribution (Carbon Atom %)					
CH ₄	4	5	6	8	9
C ₂ -C ₄	6	7	8	10	9
C ₅ -C ₈	23	25	29	34	24
C ₉ -C ₂₀	62	59	50	44	49
C ₂₁ +	5	4	7	4	9
2. Separate run. 3. Not aged at 205°C.					

Table XII.6	
Alpha Values for Runs Shown in Table XII.5 (From ref. XII.5)	
Run Number	Alpha, Based on C ₅ -C ₈ /C ₉ -C ₂₀
2	0.89
3	0.82
4	0.83
5	0.79
6	0.74

Table XII.7				
Impact of ROR (reduction-oxidation-rereduction) of a Co Catalyst (from ref. XII.6)				
	CO Conversion Rate (cc/gram Co/hour)		C ₅ + Liquid (Wt.%)	
Catalyst	R350	ROR	R350	ROR
A	1230	1485	73	81
B	790	1190	80	79
C	690	960	81	--

Table XII.8					
Influence of Ru on Activity of a Co Catalyst (from ref. XII.7)					
		Co/Ru Ratio		195°C CO Conversion Rate (cc/gram metal/hour)	
Test No.	Ru (Wt.%)	(Wt.)	(Molar)	R350 (F)	ROR (G)
1	0.0	---	---	382	476
2	0.05	400	693	780	968
3	0.10	200	346	879	1093
4	0.50	40	69	1034	1415
5	1.00	20	35	930	1286

Table XII.9 Influence of Temperature on a Co-Th-Alumina Catalyst (from ref. XII.8)					
Example No.	2	3	4	5	6
Temp., °C	195	195	195	205	215
Pressure, psia	15	15	30	30	30
H ₂ /CO	1:1	2:1	2:1	2:1	2:1
CO Flowrate (cm ³ /gram/hour)	310	310	735	735	735
CO Specific Rate (cm ³ /gram/hour)	70	95	102	200	257
C ₅ + Synthesis Rate (mg/gram/hour)	38	48	47	83	97
Product Distribution Carbon (Atom %)					
CH ₄	6	10	15	19	22
C ₅ +	88	79	73	64	58
C ₉ -C ₂₀	57	45	41	32	25
C ₂₁ +	9	5	6	4	1
CO ₂	2	2	1	2	2

Table XII.10 Influence of Silicalite on the Product Distribution (from ref. XII.9)				
	Co/ThO ₂ /Al ₂ O ₃		Co/ThO ₂ /Al ₂ O ₃ + Silicalite	
Carbon No.	Carbon Atom %	Wt.% n-Paraffin in Fraction	Carbon Atom %	Wt.% n-Paraffin in Fraction
1	4.7	(100)	11.3	(100)
2	0.7	50	1.8	75
3	2.5	15	8.4	24
4	3.5	20	23.2	25
5	5.0	25	23.1	35
6	6.1	33	14.9	45
7	6.8	46	9.0	38
8	7.5	56	4.8	22
9	8.5	58	2.3	13
10	9.4	62	0.9	5
11+	45		1	

Table XII.11			
Products from the Conversion of Syngas with a Co-Silica-Alumina Catalyst (from ref. XII.14)			
	Temperature, °C		
	175	185	195
Yield, Wt. %			
C ₁ -C ₄	22	25	34
C ₅ -C ₁₁	54	60	57
C ₁₂ +	24	15	9
Relative Rate, mg/g/hr ^a			
C ₁ -C ₄	0.3	0.5	1.1
C ₅ -C ₁₁	0.7	1.2	1.8
C ₁₂ +	0.3	0.3	0.3
a. The units or the numerical values are probably in error. They may be specific rates (mg/g cat/hr) but if this is the case, the magnitude of the values are questionable. In any event, it appears that the rates are only about one-tenth that of a good Co-Al₂O₃ catalyst. The low activity may be due to the difficulty of reducing Co in the above catalysts.			

Table XII.12				
Effect of Thoria Concentration on Product Composition (from ref. XII.15)				
			Mol % Selectivity to	
Example No.	Wt. % ThO ₂	% CO Conversion	CH ₄	C ₂₊
30	0.5	31.1	92.0	8.0
31	1.5	29.0	55.0	45.0
32	2.0	30.5	57.0	43.0
33	3.0	33.2	57.5	42.5
34	5.0	31.0	54.3	45.7
35	10.0	28.6	55.5	44.5
36	20.0	21.4	58.2	41.8
37	30.0	11.2	50.3	49.7

Table XII.13				
Relation of Catalyst Composition to Conversion and Product Selectivity (from ref. XII.15)				
Exempl e No.	Catalyst	Wt.% Rare Earth	% CO Conversion	% Selectivity to C ₂₊
11	Ni-Chrysotile	0	17.0	0
38	Th-Ni Chrysotile	2	31.5	43.0
39	La-Ni Chrysotile	2	25.0	39.0
40	Ce-Ni Chrysotile	2.5	32.5	32.1
41	Pr-Ni Chrysotile	2	35.3	35.0
42	Th + La-Ni Chrysotile	2 + 2	71.5	49.0
43	Th + Pr-Ni Chrysotile	2 + 2	69.1	48.0

Table XII.14					
Conversion Data for Syngas Conversion Using Fixed-Bed and Slurry Reactors (from ref. XII.17)					
Test Number	1	2	3	4	5
Reactor Type	fixed-bed	slurry	slurry	slurry	slurry
Temperature, °C	215	225	230	235	240
CO Conversion rate (ccCO/g/h)	215	649	808	992	1210
CO Conversion, %	45.3	8.4	10.4	12.8	15.6
Product Yields, Methane, wt. %	26.6	10.5	11.5	12.5	14.0
C ₅ -C ₂₀ (mg/g/h)	67	325	400	478	560
C ₅ +, wt. %	60.0	79.0	78.0	76.0	73.0

Figure XII.1. G.B. process, remote natural-gas conversion (from ref. XII.2).

Figure XII.2. Effect of pressure on catalyst activity (relative rate based on data as given in Table XII.1) (from ref. XII.2).

Figure XII.3. Effect of temperature on catalyst activity (relative rate) (from ref. XII.2).

Figure XII.4. Schematic diagram of the pilot plant remote-gas-to-diesel fixed-bed process (from ref. XII.2).

Figure XII.5. Effect of temperature and H_2/CO on carbon monoxide conversion (from ref. XII.2).

Figure XII.6. Catalyst activity (from ref. XII.2).

Figure XII.7. Catalyst productivity (specific rate) (from ref. XII.2).

Figure XII.8. G.B. demonstration plant, block-flow diagram (from ref. XII.2).

Figure XII.9. The impact of Ru (# data points) on a Co (MgThO_x) catalytic conversion as a function of temperature (data from XII.3).

Figure XII.10. Anderson-Schulz-Flory plot of the products from the synthesis using a Co catalyst and one also containing Ru, Mg and Th) (data from XII.3).

Figure XII.11. Co dispersion measurements as a function of temperature (data from XII.5).

Figure XII.12. Dependence of CO conversion on the temperature (numbers in figure are the GHSV) (data from ref. XII.5).

Figure XII.13. Hydrocarbon product distribution for a cobalt catalyst as a function of temperature (data from XII.5).

Figure XII.14. Anderson-Schulz-Flory plot of the products from the Fischer-Tropsch synthesis with a cobalt (Th, Al₂O₃) catalyst alone (F) and physically admixed with a silicate zeolite catalyst (G) (data from XII.9).

Figure XII.15. Wt% N-alkane in the carbon fractions of the products from Fischer-Tropsch synthesis with cobalt (Th, Al_2O_3) catalyst (F) and physically admixed with silicate zeolite (G) (data from XII.9).

Figure XII.16. Methane production for synthesis in fixed-bed reactor with different particle size catalysts (from XII.17).

Figure XII.17. C₅+ product selectivity for three particle size catalysts in fixed-bed reactor (●, 185°C, H₂/CO = 2; ▲, 195°C, H₂/CO = 2; □, 195°C, H₂/CO = 1.5) (from XII.17).

Figure XII.18. Reaction rate for CO conversion in fixed-bed reactor for three particle size catalysts (●, 185°C, H₂/CO = 2; ▲, 195°C, H₂/CO = 2; □, 195°C, H₂/CO = 1.5) (from XII.17).

Figure XII.19. Process schematic for slurry reactor system using cobalt catalyst (from XII.17).

Figure XII.20. Arrhenius plot for CO conversion in slurry reactor with Co catalyst (data from XII.17).

Figure XII.21. CO conversion and C₅+ product selectivity for FTS using slurry reactor and cobalt catalyst (data from XII.17).

ATTACHMENT XIII

Review of Fischer-Tropsch Work by Statoil

Three patents on Fischer-Tropsch synthesis catalysts assigned Den Norske Stats Olijeselskap A.S., Norway by Norwegian and U.S. investigators are summarized below (XIII.1-XIII.3). These individuals summarize the background for their invention. Anderson's book (XIII.4) is taken as the main background for the inventions and consider this book to indicate that the common Fischer-Tropsch (FT) catalysts are nickel, cobalt and iron. Nickel is considered to be active but it produces mainly methane. Among the Group VIII metals (old U.S. Periodic Table nomenclature), ruthenium is a very active catalyst and produces mainly hydrocarbons. Ruthenium is considered to have higher activity than Fe, Co or Ni at low temperatures. Other metals which possess high activity are considered to produce oxygenates and the patentees cite rhodium as an example (XIII.5). Osmium is considered to have moderate activity and Pt, Pd and Ir to have low activity (XIII.4,XIII.6,XIII.7).

These investigators recognize that others have used various combinations of metals for Fischer-Tropsch Synthesis (FTS). For example, nickel-doped cobalt has a higher productivity of methane than cobalt alone (XIII.8). On the other hand, Kobylinski taught that the addition of small amounts of ruthenium to a cobalt catalyst provided a material with a higher activity and with lower methane production than a similar catalyst comprised of cobalt without the ruthenium (XIII.9). Other work has documented that the activity is higher when ruthenium is added to the catalyst but the lower methane make is not as well documented.

These investigators indicate that, "In general, the catalysts [of combinations of metals] of these [prior] teachings have activities and selectivities which are within the

ranges of the individual components." They also note that the combination of a metal with certain oxide supports may lead to higher productivity of products, presumably due to the increase in surface area of the active metal component. The authors cite the case of using titania to support cobalt or cobalt-thoria (XIII.10) with a resulting increase in activity for the production of hydrocarbons and, by implication, attribute this beneficial effect to strong-metal-support-interactions (SMSI) (XIII.11).

Statoil investigators also indicate that a patent (XIII.12) teaches that combinations of cobalt, rhenium and thoria or cobalt and rhenium supported on titania are useful for hydrocarbon production. The patent indicates that similar improvements in activity can be obtained when using other inorganic oxide supports; however, the inventors indicate that titania is the only support specifically discussed in reference 12. These workers indicate that, "The typical improvement [reported in reference 12] in activity gained by promotion of cobalt metal supported on titania with rhenium is less than a factor of 2."

The major teaching of the Statoil patent is that the choice of support for Co is critical, "and the addition of a small amount of rhenium to an alumina—supported cobalt catalyst gives a much greater improvement in activity than the addition of rhenium to cobalt supported on any other inorganic oxide. To be effective as a support for cobalt, the alumina should possess low acidity, high surface area and high porosity. The method of adding the active metals to the alumina support is, according to the inventors, not critical.

Included in inventions by the Statoil investigators is the finding that it is beneficial to include a small amount (0.1 - 5%, preferably 0.1 to 2 wt.%) of a metal oxide promoter

in addition to cobalt and rhenium. The inventors conclude that the most preferable metal oxide is La_2O_3 or a mixture of lanthanides rich in La.

After preparation, the catalyst is calcined in a specified manner ultimately to attain a preferred temperature between 250 and 350°C for 2-5 hours. To activate the catalyst, it is reduced in hydrogen, again using a specified heating ramp to attain a preferred temperature of 300-400°C and holding at this temperature for 6-24 hours. Catalyst passivation and rereduction cycles may be carried out.

Catalyst testing was accomplished with a $\text{H}_2/\text{CO} = 2$ synthesis gas. A fixed-bed reactor (0.5 g catalyst) was utilized at atmospheric pressure and temperatures of 185, 195 and 205°C [a standard testing procedure involved 9.82 hr at 195°C, 4.3 hr at 205°C, 4.5 hr at 185°C and 9.5 hr at 195°C]. The flow rate of synthesis gas was 1.68 L/g catalyst/hr. Catalysts were compared using results obtained during the period of 10 and 30 hours-on-stream.

A series of identical catalysts (12 wt.% Co, 1 wt.% rare earth oxide), except for the content of rhenium, were prepared. For the alumina supported catalyst, there was a greater than 3-fold increase in CO conversion as Re content increases to about 1 wt.% and then a gradual decline in CO conversion was noted for further increases in Re content Figure XIII.1). The incorporation of these amounts of Re did not substantially increase the production of either methane (10-14%) or CO_2 (0.6-1.3%).

Two series of catalysts were prepared in which the Co loading was increased, one series with and one without rhenium. Re was added so as to keep the wt.% Co/wt.% Re constant at 12 for 3, 6 and 9 wt.% Co; for the 20 and 40 wt.% Co formulations, the ratios were 0, 4, 20 and 0, 8, 20 and 40, respectively. The impact of Re is evident in Figure XIII.2 (apparently the data for the 20 and 40% Co are for Co/Re

ratio of 20 samples in Table V of reference XIII.1). This patent indicates that the improvement in activity due to the addition of rhenium increases as the cobalt content increases.

The Statoil investigators report that,

"The catalysts in Table VII (Table XIII.1 of this report) were prepared to test the teaching that various inorganic supports are acceptable for preparing cobalt plus rhenium F-T catalysts. An examination of the data in Table VIII (Table XIII.2 of this report) leads to the surprising conclusion that the type of support is extremely important and that vast differences in activity exist between catalysts prepared on one support and catalysts of the same catalytic metals content on another support. More surprisingly, only cobalt plus rhenium on alumina showed a commercially attractive activity level and selectivity."

Some may question the conclusion that a selectivity that includes 13-18 wt.% methane is a commercially attractive catalyst.

The MgO and Cr₂O₃ supports provide catalysts with very low activity. The zirconia and silica-alumina supported catalysts showed improved but low activity and poor selectivity for C₂⁺. For silica and titania supports, the cobalt only catalysts exhibited activities similar to an alumina supported cobalt catalyst. However, for the addition of rhenium to the alumina, titania and silica cobalt catalysts, a significant improvement was observed only for the material employing alumina as a support. The authors report that, "This [latter] result is surprising and would not have been predicted based on teachings in the prior art." [This does not appear to be in complete agreement with some Exxon patents.]

The "Weisz Window" provides a rule-of-thumb estimation of the productivity needed for commercial operation as $10^{-5} - 10^{-6}$ mole sec^{-1} (cm^3 reactor) $^{-1}$ (XIII.13). In the following we assume: (1) a fixed-bed reactor, (2) the density of the alumina supported catalyst as 2 g/cm^3 , (3) the flow of syngas as 1.88 NL/hr/g and (4) $\text{H}_2/\text{CO} = 2$. From Table XIII.2 for the Re containing catalyst (example 8), the CO conversion is 33%. Thus we calculate that the conversion of CO is 0.209 NL/hr/cm^3 . Using this value, we calculate that the conversion of CO is 0.52×10^{-5} mole/ cm^3/sec ; this is close to the value of the Weisz Window. If the rate increases directly with pressure, then the conversion is in the Weisz Window at 10 atm.

The incorporation of alkali in the cobalt catalyst impacts both the activity and hydrocarbon product distribution. For a catalyst containing Co, Re and rare earth oxide, the incorporation of alkali caused (1) a decrease in CO conversion and (2) an increase in the alpha value of the products (Tables XIII.3 and XIII.4; Figures XIII.3 and XIII.4). However, the conclusion that the alpha value depends upon the K/Co ratio depends entirely upon the two data points obtained for the lowest to K/Co ratios. If these two points are not reliable (or are not considered), the K/Co ratio has no impact upon the value of alpha. The question of promotion changing activity and selectivity is complicated for a cobalt catalyst. Anderson pointed out that selectivity changes can be effected by changing reactor pressure (XIII.14).

van Berge and Everson (XIII.15) point out that the data in reference 1 were obtained at different conversion levels, and thus different reactor partial pressures, and that the chain of chemical promotion by K, Na, Cs and Rb could not be regarded as conclusive. Studies performed at Sastech (XIII.16) are reported to confirm the ineffectiveness of chemical promotion of cobalt Fischer-Tropsch catalysts.

The loss of activity with increasing alkali content allows one to calculate, assuming one K eliminates 1 site, that only 4.5 atomic % of the Co is catalytically active. At first glance, it appears that the data are consistent with each potassium eliminating one catalytic site, or some constant fraction of a site (Figure XIII.4). However, it must be realized that the addition of alkali causes an increase in $\ln \alpha$, and a corresponding increase in the average molecular weight of the products. The average number of growing chains, and the average number of catalytic sites, is directly proportional to the average molecular weight of the growing chains (e.g., the average molecular weight of the products). Hence,

$$\overline{\text{No. of Sites}} \propto \overline{M.W.} = 1/(1 - \alpha).$$

When this is taken into account, the catalytic sites decrease more rapidly than the increase in K, or at least those catalytic sites that initiate chain growth must do so (Figure XIII.5).

During the past few years, Statoil has obtained patents related to a catalytic multi-phase reactor, and specifically to catalyst wax separation (XIII.17-XIII.21). An example of such a reactor is illustrated in Figure XIII.6 (XIII.17). "This is a solid/liquid slurry reaction apparatus which comprises: a reaction vessel **(11)**, a filter member **(13)** in contact with the slurry **(16)** defining a filtrate zone which is separated from the slurry and having an outlet **(23)** for filtrate product **(32)**; means for establishing a mean pressure differential across the filter member; means for causing fluctuations or oscillations about the mean pressure differential; and means for introducing gaseous reactants or other components in the form of gas bubbles into the slurry (XIII.17)."

One of the claims is for a filter element **(22)** which comprises a fine meshed screen, helically wound threads, fine vertical threads or sintered metal particles (XIII.17). The hydrostatic pressure preferably results from the filter member being submerged in the slurry.

The pulsating pressure can be applied directly to the filtrate or to the gas space above the filtrate, preferably by the action of a reciprocating piston in a cylinder. The pressure fluctuation may be of the order of 10 to 200% differential (preferably 2 to 5 mbar).

The filter element material and catalyst are preferably selected so that the maximum hole or pore size of the filter element is of the same order of the catalyst particle size. It might be expected that catalyst would plug the filter but this is found not to be the case. Of course, the particle size of the catalyst may be much larger than the maximum hole or pore size of the filter.

In operation, products pass through the filter element **(12)** to form a product filtrate **(32)** which is free of catalyst. Any gaseous products and unconverted reactants that pass through the filter element can be vented through outlet **(31)** and subsequently through **(17)**. The product filtrate **(32)** leaves through level device **(23)** and outlet **(24)** to collect in **(25)** for regulated continuous or periodic removal.

In an example, a reactor of 4.8 cm x 2 m dimensions was filled with approximately 10 wt.% of a Co on alumina catalyst (30 to 150 μm). The gas (H_2 , CO and N_2) was fed at a superficial gas velocity of 4 cm/s. The temperature was 230°C and pressure was 30 bar.

The filter unit was located in the upper part of the reactor and comprised of Sika stainless steel sintered metal cylinder Type R20 produced by Pressmetall Krebsöge

Gmbh. The filter had an outer diameter of 2.5 cm, a height of 25 cm and an average pore diameter of 20 μm .

The slurry was effected using a poly- α -olefin liquid. Fischer-Tropsch product **and a poly- α -olefin that was fed to the reactor** were both withdrawn through the filter unit (ratio of Fischer-Tropsch and poly- α -olefin not specified). Liquid withdrawal rate varied from 2.5 to 320 g/hr, depending on Fischer-Tropsch synthesis rate and feed rate of poly- α -olefin. The experiment lasted for about 400 hrs and approximately 30 liters was withdrawn through the filter unit. Most would therefore conclude that the test was of a short duration compared to the length of time that a commercial unit must operate. Furthermore, the product was diluted with start-up solvent that was added during the run. Thus, it appears that this example is applicable to a limited process scheme, and not for all process schemes.

A solid/liquid slurry reaction apparatus with a filtration section has been submitted for patent coverage (XIII.22) and is illustrated in figure XIII.7. The teachings of this patent application is based upon a recent report identified only as "a report issued by the United States Department of Energy." The DOE report addressed the question of catalyst/wax separation in Fischer-Tropsch slurry reactor systems and concludes:

"Internal filters immersed in the reactor slurry, as used in some bench-scale or pilot-scale units, do not work successfully due to operational difficulties. A reactor with a section of its wall as a filter may be operable for a pilot plant but is not practicable for commercial reactors. Internal filters are subject to plugging risks, which may cause premature

termination of the run, and commercial plants are not allowed to take chances."

The patent applicants have discovered that, contrary to the teachings of the DOE report, "...it is possible to provide a continuous reaction system for a Fischer-Tropsch synthesis in which it is not necessary to perform the solid/liquid separation in an external filter unit. Furthermore, a sufficiently high flow rate of filtrate for commercial operation can be achieved."

The description in the patent application indicates that the filter screen and the catalyst are similar, or identical, to those described in the previous patent application (XIII.17). In this instance, however, the filter screen has been made a part of the slurry reactor wall or, as shown in figures XIII.8 and XIII.9, it may be incorporated in multiple locations of the slurry reactor wall. In the example shown in figure XIII.7, a conical section **(15)** is included as an expansion chamber to prevent the slurry from foaming over and to define a gas space **(16)** above the reaction zone. The cone-shaped portion **(15)** may contain additional means (that are not shown nor specified) for breaking up or reducing foam formation.

The invention was described and was then further illustrated with the following example. Experiments in a laboratory using an apparatus similar to that shown in figure XIII.7 were carried out. The length and diameter of the unit were 1250 mm and 55 mm, respectively. The filter member had a mean pore size of 30 μm and a length of 200 mm. A heat transfer oil (diethyl benzene (95%) and minor amounts of other alkyl benzenes) and 20 wt.% alumina were used as the slurry phase. The alumina particles initially had a cut-off at 53 μm . The experimental conditions in the example were: 1 bar pressure, 20-25°C and 6 cm/s superficial gas velocity. After an initial start-up period,

the separation capacity became approximately constant at a level of 750-800 kg/m²h. The calculated pressure differential was approximately 5 mbar. After 40 days of operation, there was only a slight decrease in separation capacity.

The section of the DOE report that was quoted above was concerned with an operating slurry bubble column reactor for Fischer-Tropsch synthesis at a commercial scale operation. The example provided by the patent applicants was for a cold model with only an alumina solid and without Fischer-Tropsch synthesis. It would appear that the patent applicants have not shown by their example anything that would be contrary to the teachings of the DOE report since the patent applicants did not operate at any of the conditions necessary for a commercial Fischer-Tropsch plant that is currently being operated successfully.

Another patent application (XIII.19) relates to a vessel that contains a number of vertical reaction tubes, each suitable for multi-phase catalytic conversions (figure XIII.10). In this application, the above DOE report is quoted and the teaching that the applicants have provided a means of accomplishing this. Each reactor tube has essentially the features of the reactor described in the previous reference XIII.ref. 18). In operation, the gas is preferentially fed to each multi-phase catalytic reactor. These reactors are held in place by plates **(18)** and **(14)**; in effect these two plates and the vessel wall **(12)** provide the vessel to hold the heat transfer liquid/vapor.

The filter section of each reactor tube is located above the top plate **(14)**, which serves to hold a level of the wax following separation from the catalyst slurry. In another version, a sieve **(34)** surrounds each filter and is utilized to maintain a minimum wax level for each reactor tube so that the tube does not lose liquid level so that the

reactor tube is depleted of liquid. Thus, the sieve extends above the level of the wax filtrate that is maintained on plate **(14)**.

The heat exchange medium is preferably a liquid at its boiling point; water is the preferred medium since the heat of reaction can be recovered as steam to be used to generate electricity or provide heat for plant operations.

In the only example of the patent application, a slurry bubble column Fischer-Tropsch reactor **is simulated** using a two phase quasihomogeneous one dimensional model. They use typical catalyst performance data contained in US 4,801,573. The simulations are utilized to **calculate** optimum values for the reactor and its operation. **Experimental data of an operating Fischer-Tropsch reactor are not provided in the application.** Since the DOE report was for an operating reactor that actually effects a separation of wax and catalyst, it is difficult to understand how the applicants can show that they have provided a solution to the problems enumerated in the DOE report.

A patent application (XIII.20) describes a separation device that has as its main object the prevention of gas from being entrained in the liquid phase in cases where it is desirable to separate gas and liquid or immiscible liquids.

A recent patent application describes a method of regenerating a catalyst in a Fischer-Tropsch synthesis reaction (XIII.21). Examples of regeneration procedures are reviewed and the conclusion is that "These arrangements all suffer the drawback that a separate source of H₂ gas must be provided to achieve regeneration." The present invention (XIII.21) is to overcome this drawback. While the use of hydrogen could be a drawback, it would appear to be so only from an operational viewpoint. For example, Sasol produces a nearly pure hydrogen stream by a pressure swing adsorption process.

It would be a disadvantage to utilize a stream of pure CO since this stream is not available in a normally operating Fischer-Tropsch plant.

Schematic sections through a slurry reactor (figure XIII.12) and a slurry reactor with a separate regeneration vessel (figure XIII.13) are shown. Details of the slurry reactor (figures XIII.12 and XIII.13) are not provided in this patent. To effect regeneration, the feed parameters of the synthesis gas are adjusted to increase the conversion of CO in the synthesis gas until the H_2/CO ratio of the gas leaving the reaction zone exceeds 10:1 and then maintaining this conversion level during the regeneration mode for some period of time to effect regeneration to a desired level. Preferable, the CO conversion is between 95 and 100%, most preferable 100%. Thus, the preferred H_2/CO ratio is 20/1, and most preferably, greater than 30/1. To achieve this high hydrogen/CO ratio, the flow is decreased, preferably slowly, so that the conversion increases to attain the desired level. Alternatively, hydrogen could be increased in the synthesis gas by modification of the generation step of the synthesis gas.

At the high conversion level, the reaction changes from synthesis to a regeneration mode. The regeneration mode is characterized by: high H_2/CO ratio, low C_{5+} selectivity and high CO_2 selectivity. This is taken to indicate a high water gas shift rate due to the high hydrogen partial pressure. Experimentally, it has been found that a few hours of regeneration is normally sufficient; however, it may take longer for more severely deactivated catalysts.

When a separate regeneration vessel is used, "normal" conditions for synthesis are maintained on the synthesis side and the high hydrogen (100% CO conversion)

condition is maintained on the regeneration side. Preferably, there is a flow of deactivated and regenerated catalyst between the two sides.

Two examples are given for the regeneration. In the first example, a catalyst containing 12% Co and 0.5% Re on alumina are used at 220°C and 20 bar (2 MPa) total pressure in a continuous slurry stirred tank reactor (CSTR). The reactor volume is 2 L and is half-filled with slurry. The H₂/CO inlet synthesis gas ratio was 2; the exit gas was also close to this value. The initial stable hydrocarbon activity is set relative to 1; note that this is based on hydrocarbon production. The CO conversion was 63% at this hydrocarbon production level of 1.

After the catalyst had operated for a few days, the catalytic activity had declined so that the relative hydrocarbon productivity activity number had declined to 0.69. At the relative activity number of 0.69, the CO conversion was 68% at a flow rate of 2100 NL/kg cat./hr. It is not clear whether this flow rate is for synthesis gas or for CO only; in the following we shall **assume that the flow is for CO only**. The C₅₊ selectivity was 89.4%. At this stage of catalyst deactivation, a decrease of the flow rate to 1050 NL/kg cat/hr resulted in an increase in CO conversion to 88% with a C₅₊ selectivity of 89.9%.

To establish a regeneration mode at this point (0.69 relative activity), the flow rate was reduced to 750 NL/kg cat/hr and the CO conversion was 99%. The exit H₂/CO ratio was 14/1. This regeneration mode was maintained for 10 hours and was then brought back to the Fischer-Tropsch mode by increasing the flow rate to 2100 NL/kg cat/hr. The reaction continued to produce a C₅₊ selectivity of over 88%. The relative activity at these final Fischer-Tropsch conditions was 0.77. This value is above the value of 0.69 for the deactivated catalyst but still considerably below the value of 1.0 for the fresh catalyst.

Example 2 is for a catalyst that contains 20% Co and 1% Re on alumina; however, the data are less extensive than for example 1. They report that the 20 wt.% Co catalyst was brought back to the initial level following 24 hours of the regeneration mode whereas 10 hours for the 12 wt.% Co catalyst only restored the activity to 77% of the initial activity.

The hydrocarbon production of the deactivated catalyst (relative activity of 0.69) in Example 1 corresponds to 0.983 g hydrocarbon/g cat/hr. For the fresh catalyst (relative activity of 1.0) the hydrocarbon productivity is calculated by us to be 1.29 g hydrocarbon/g cat/hr. For the reactivated catalyst (relative activity 0.77) the productivity is 1.16 g hydrocarbon/g cat/hr.

If it is assumed that the catalyst productivity is linear in Co content, the productivity of the deactivated 20 wt% Co catalyst would be 1.49 g hydrocarbon/g cat/hr and that of the fresh and regenerated catalyst would be 2.15 g hydrocarbon/g cat/hr.

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Table XIII.1 (from ref. XIII.1)						
			Weight of Materials in Impregnating Solution, g		Composition of Finished Catalyst, Wt.%	
Example No.	Support	Weight of Support, g	Co(NO ₃) ₂	HReO ₄ *	Co	Re
28	Silica	20	13.47	---	12	---
29	Silica	20	13.62	0.38	12	1.0
30	Titania**	25	16.84	---	12	---
31	Titania**	24.64	16.78	0.46	12	1.0
32	Titania***	25	16.84	---	12	---
33	Titania***	24.64	16.78	0.46	12	1.0
34	Chromia	20	13.47	---	12	---
35	Chromia	21.3	14.51	0.40	12	1.0
36	Magnesia	21.59	14.54	---	12	---
37	Magnesia	14.54	10.67	0.29	12	1.0
38	Silica- alumina	20	13.47	---	12	---
39	Silica- alumina	20	13.62	0.38	12	1.0
40	Zirconia	20	13.47	---	12	---
41	Zirconia	20	13.62	0.38	12	1.0
* Weight of 82.5% perrhenic acid solution. ** Calcined at 500°C. *** Calcined at 600°C.						

Table XIII.2 (from ref. XIII.1)

Example No.	Co %	Re %	Support	CO Conversion %	C ₂ ⁺ Selectivity %	CH ₄ Selectivity %	CO ₂ Selectivity %
1	12	---	Al ₂ O ₃	12	90.0	8.9	1.1
8	12	1	Al ₂ O ₃	33	87.7	11.4	0.9
28	12	---	SiO ₂	11	90.1	8.7	1.2
29	12	1	SiO ₂	12	88.1	10.7	1.2
30	12	---	TiO ₂ [*]	11	87.6	11.8	0.6
31	12	1	TiO ₂ [*]	17	86.5	12.8	0.7
32	12	---	TiO ₂ ^{**}	11	87.6	11.7	0.7
33	12	1	TiO ₂ ^{**}	17	85.8	13.5	0.7
34	12	---	Cr ₂ O ₃	1	83.5	15.5	1.0
35	12	1	Cr ₂ O ₃	2	80.8	12.3	6.9
36	12	---	MgO	0.3	20.0	30.0	50.0
37	12	1	MgO	0.3	19.1	30.9	50.0
38	12	---	SiO ₂ /Al ₂ O ₃	5	76.3	22.2	1.5
39	12	1	SiO ₂ /Al ₂ O ₃	6	78.6	19.8	1.6
40	12	---	ZrO ₂	4	80.9	16.3	2.8
41	12	1	ZrO ₂	7	78.8	18.7	2.5

* Support calcined at 500°C.

** Support calcined at 600°C.

Table XIII.3 (from ref. XIII.1)										
Example No.	Wt. of Al_2O_3 , g	Type of Alkali	Weight of Material in Impregnation Solution, g				Composition of Finished Catalyst, Wt. %			
			(a)	(b)	(c)	(d)	Co	Re	RE	Alkali
42	300.0	---	1039.65	17.21	13.99	---	40	2.0	1.0	0.0
43	75.0	K	260.46	4.31	3.50	0.34	40	2.0	1.0	0.1
44	75.0	K	256.36	4.25	---	0.67	40	2.0	---	0.2
45	175.0	K	609.03	10.08	8.20	1.59	40	2.0	1.0	0.2
46	100.0	K	349.50	5.79	4.70	1.83	40	2.0	1.0	0.4
47	100.0	K	354.03	5.86	4.76	4.64	40	2.0	1.0	1.0
48	60.0	Na	205.49	3.40	---	0.93	40	2.0	---	0.24
49	60.0	Cs	209.55	3.47	---	2.12	40	2.0	---	1.36
50	65.0	Rb	225.38	4.23	---	1.71	40	2.0	---	0.87
51	20.0	---	13.78	0.38	0.62	---	12	1.0	1.0	---
52	20.0	K	13.80	0.38	0.62	0.06	12	1.0	1.0	0.1
53	20.0	Li	13.64	0.38	---	0.11	12	1.0	---	0.05
54	20.0	Li	13.80	0.38	0.62	0.12	12	1.0	1.0	0.05
55	20.0	Cs	13.67	0.38	---	0.10	12	1.0	---	0.3
56	20.0	Cs	13.83	0.38	0.62	0.10	12	1.0	1.0	0.3
(a) $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (b) 82.5% HReO_4 solution, except for example 50 which was 72.9% HReO_4 (c) Rare earth nitrates (RE) (see example 1) (d) LiNO_3 , NaNO_3 , KNO_3 , RbNO_3 or CsNO_3										

Table XIII.4 (from ref. XIII.1)					
	Alkali				
Example No.	Type	Content Wt. %	CO Conversion %	CH ₄ Selectivity %	Product Alpha*
42	---	---	52.5**	14.2**	0.75**
43	K	0.1	52 50	8.6 11.1	0.86 0.79
44	K	0.2	43	9.3	0.83
45	K	0.2	51 44 41	9.5 11.6 9.4	0.84 0.84 0.81
46	K	0.4	30 35	7.3 7.8	0.87 0.85
47	K	1.0	12 9 6	7.0 7.9 6.2	0.88 0.85 0.87
48	Na	0.24	21	8.3	0.82
49	Cs	1.36	14	8.5	0.86
50	Rb	0.87	11	7.3	0.86
51	---	---	31.7***	10.9***	0.77***
52	K	0.1	19 22	7.6 9.8	0.78 0.84
53	Li	0.05	31	11.7	0.78
54	Li	0.05	27	12.0	0.78
55	Cs	0.3	21	11.1	0.83
56	Cs	0.3	21	10.3	0.84
* Calculated by plotting $\ln(W_n/n)$ vs. n, where n is carbon number and W_n is the weight fraction of the product having a carbon number n, and determining the slope of the line. ** Average of 21 tests. *** Average of 6 tests.					

Figure XIII.1. Effect of rhenium on CO conversion catalysts containing 12% cobalt (from ref. XIII.1).

Figure XIII.2. Effect on conversion of adding rhenium to cobalt on alumina catalyst (from ref. XIII.1).

Figure XIII.3. Alpha versus K/Co (from ref. XIII.1).

Figure XIII.4. Percent CO conversion versus K/Co (from ref. XIII.1).

Figure XIII.5. Percent CO conversion versus K/Co (from ref. XIII.1) and our decrease calculated assuming α is related directly to the site density.

Figure XIII.6. Slurry reactor with internal filter for wax/solids separation from ref. XIII.17).

Figure XIII.7. Slurry reactor incorporating a filtration system into the reactor wall (from ref. XIII.22).

Figure XIII.8. Slurry reactor incorporating multiple filtration systems into the reactor wall (from ref. XIII.22).

Figure XIII.9. Slurry reactor incorporating multiple filtration systems into the reactor wall (from ref. XIII.22).

Figure XIII.10. A multi-phase catalytic reactor with multiple tubes for slurry phase reactor systems (from ref. XIII.19).

Figure XIII.11. Schematic of sleeve on reactor tube in Figure 10 to maintain slurry level in each reactor tube (from ref. XIII.19).

Figure XIII.12. Schematic of slurry phase reactor with internal wax/catalyst separation unit that can be used for regeneration of a Fischer-Tropsch catalyst (from ref. XIII.21).

Figure XIII.13. Schematic of slurry phase reactor with external wax/catalyst separation unit that can be used for regeneration of a Fischer-Tropsch catalyst (from ref. XIII.21).

ATTACHMENT XIV

Review of Fischer-Tropsch Work by Rentech

Rentech has obtained eight patents to date [October 10, 1996] [XIV.1-XIV.8].

The drawings, background of the invention and objectives of the invention are identical [except for combining some paragraphs and minor changes in a few paragraphs such as "A further object ..." rather than "It is yet another objective..."]

The background provides a brief description of earlier work [XIV.9-XIV.14]. They indicate that today there are two primary methods for producing syngas from methane: steam reforming and partial oxidation. The primary advantage of partial oxidation over steam reforming is indicated to be that the reaction is self-sustaining and the only heat that must be added is the initial preheating of the reactants. Another advantage is that a lower ratio of H_2/CO is produced, and that it more nearly matches that needed for the FTS. In addition, the CO_2 and/or hydrogen need not be removed from the syngas prior to the synthesis.

The authors indicate that "...the Fischer-Tropsch reactor must typically be able to convert at least 90% of the incoming carbon monoxide."

They discuss the advantages of the two materials they consider to be attracting the most attention: cobalt and iron based catalysts. They indicate that, theoretically, a cobalt catalyst can produce higher conversion yields than an iron based-catalyst since the cobalt catalyst can approach 100% carbon conversion efficiency but that an iron catalyst tends toward 50% carbon conversion to hydrocarbons due to the extent of the water-gas-shift (WGS) reaction. They indicate that cobalt is much higher in cost, and this is likely to increase even further if the demand for cobalt increases to meet widespread development of Fischer-Tropsch synthesis (FTS).

It is indicated that recycle of the tail-gas is usually utilized to achieve 90% conversion of CO. Too much water is considered to be an inhibitor for FTS and the maximum attainable in single-pass operation is 70% CO conversion. On the other hand, the WGS activity of the iron catalyst permits operation at 90% conversion per pass without difficulty. It has been reported, contrary to this view, that even with an iron catalyst, the rate of CO conversion may decline rapidly at CO conversions above about 60% [XIV.15].

The present inventions are claimed to "...include a solution to the problems of reducing the formation of excess hydrogen from the reformer or partial oxidation unit and increasing the conversion efficiency for the entire carbon input to the system when using specifically prepared promoted iron catalysts." The patents demonstrate the use of recycle of the carbon dioxide produced during the FTS to the reformer in order to control the excess hydrogen and to improve the carbon conversion efficiency problems.

It is stated that olefins, alcohols and aldehydes are readsorbed on the catalyst and thereby participate in further chain growth. Naphtha and light diesel fractions are considered to be rich in olefins and to contain relatively large amounts of alcohols. Thus, the authors indicate that it is possible to force the reaction toward higher molecular weight by recycle of olefins, alcohols and aldehydes.

It is also proposed to convert the excess hydrogen as well as the carbon dioxide that is produced through the WGS reaction in a second FTS reactor.

A schematic of one of the process schemes is provided in figure 1. Indicated in this process is the recycle of carbon dioxide and/or recovered gas (streams 9 and 19).

The preferred catalyst is a precipitated iron catalyst that is promoted with a predetermined amount of potassium and copper. The amount of promoters depends upon the desired extent of chain growth and the product molecular weight distribution.

The preferred catalyst is unsupported. To accomplish catalyst preparation, iron and copper metal is dissolved in nitric acid. However, to minimize the emission of oxides of nitrogen, oxygen is bubbled through the solution while the metals are being dissolved.

The catalyst precursor was prepared by precipitation by the addition of ammonium hydroxide (ambient temperature) to the hot (up to 150°C copper/iron solution to produce a pH of 7.4. After cooling to 80°F, the pH is adjusted to 7.2. The slurry is pumped to a holding tank, the solid settles and the solution is removed; subsequent washings to remove ammonium nitrate are with "high quality water free of chloride". A drum filter, with water spray bars, is used to complete the washing and collection of the slurry. Aqueous potassium carbonate of the desired amount is added to the slurry and it is then thoroughly mixed. Drying, such as in a spray drier, is used to produce spherical catalyst in the size range of about 1 to 5 up to about 40 to 50 microns. The last step is heating to 600°F in a fluidized bed to remove residual moisture and to convert the hydrous iron oxide to hematite (Fe_2O_3).

The authors report that "Determining the "best" activating procedure for a catalyst is difficult at best..." In their study, high activity of the catalyst was correlated with the presence of iron carbides after the activation procedure. The most effective procedure used carbon monoxide at 325°C at 0.1 atm. pressure. The authors indicate that it may be preferable to activate in synthesis gas, and give a recipe for doing this in a controlled manner. They heat the catalyst precursor in an inert gas to 500°F and then to 540°F in

synthesis gas until the heat of reaction becomes sufficient to heat the catalyst bed at a faster rate than the applied external heat; at this point heating is terminated and cooling is effected to keep the temperature at 540°F until the CO conversion is 90%. At this point the temperature is lowered to the desired reaction temperature (450 to 525 °F) and the reactor pressure is raised from the activation pressure of 150 psig to below about 450 psig. The flow rate is adjusted to a space velocity in the range of 240 to 300 per hour.

It was reported that the activity and selectivity of the iron catalyst is improved by exposure to a hydrogen-rich synthesis gas at elevated temperature and pressure. The production of water is believed to prevent over-carburization of the catalyst, and thereby inducing the improved activity and selectivity [XIV.16].

The authors prefer a reactor design similar to that utilized by Bureau of Mines workers [XIV.17]. The gas distributor may consist of orifices or of porous metal spargers. Preferably a design using concentric rings of manifolds arranged to conform to the reactor; i.e., the largest diameter ring is at the highest and the smallest diameter at the bottom of the reactor. The reactor diameter should be selected to give a superficial velocity (actual volumetric flow rate of feed gases divided by empty reactor cross-sectional area) between about 0.02 to 0.2 meters per second. This flow should expand the bed by 30 to 45% over that of no flow conditions.

The authors prefer between 5 and 15 wt.% by weight of iron in the slurry, more preferably between 7.5 and 12.5, and most preferably 10 wt.% iron. This corresponds to 30 to 90 grams of iron per liter of expanded bed, and the most preferred is 60 g/L.

Heat removal utilizes heat exchanger tubes that commence about 1 meter above the gas distributor and extends to the top of the expanded slurry. Pressurized steam is the preferred heat transfer medium.

The preferred iron catalyst particle is between 10 and 40 microns, with 30 microns being most preferred. The preferred ratio of potassium (as carbonate) to iron is about 0.010 (0.005 and 0.015). The copper to iron ratio is preferably about 0.010.

The means of removing wax from the catalyst employed a cross flow filter. The advantage of this means is that the flow velocity of the slurry through the porous filter tubes is about 10 feet/sec and this slows down the rate of building a catalyst layer on the tube wall. When the flow has declined to a predetermined level, an inert gas is used to pressurize the shell side to remove the layer of catalyst into the slurry stream, which flows back to the reactor. They described rates for a cross-flow filter from Mott Metallurgical Corp., a filter and procedure which were found to be unsuitable for the operation at the LaPorte, Texas plant.

Catalyst can be removed from the reactor periodically by employing a slipstream.

The gaseous product stream (20, figure 1) can be used directly for process heat.

The quality of the diesel obtained from the Fischer-Tropsch synthesis are illustrated in Tables XIV.1 and XIV.2.

According to the data, the material contains 3.05 wt.% oxygen and the average carbon number is C_{14} . Assuming that the oxygen is distributed on the same basis as the hydrocarbons, then we calculate that the F/T diesel must contain about 38 wt.% alcohols in order to contain 3.05 wt.% oxygen. This value for the alcohol content appears consistent with the composition included at the bottom of Table V of U.S.

Patent 5,324,335. This would appear to be the highest content of alcohols that has been reported for Fischer-Tropsch products.

One of the catalysts utilized in the studies produces a chain-growth probability of 0.73 for carbon numbers from 1 to 9. Like Satterfield and coworkers, the patents reported that two different chain-growth probabilities were obtained.

In example 1, the authors indicate a means of calculating the carbon conversion efficiency for the overall process which is defined as the rate of production of carbon contained in the C_{5+} product in the FTS divided by the carbon atoms in the process feed. The authors state that, "Table VIII lists the product yields and carbon efficiency along with operating parameters for Example 1 and several examples discussed below." However, Table VIII does not contain a column giving efficiencies and the yield given in Table VIII is for C_{7+} rather than C_{5+} as given in the definition. It is not obvious how one can obtain the efficiencies, as defined, from the data in Table VIII. Efficiencies are given in some of the examples together with some indication of the mode of recycle; these are compiled in Table XIV.3 by the reviewer.

The carbon dioxide produced in the FTS can be recovered by absorption from the FTS tail gas and can then be recycled to the gasifier, vented to the atmosphere or stored for later sale or use.

When additional diesel fuel is desired, the wax can be heated to 410°C to effect thermal cracking. It was shown that the diesel from wax cracking contained only 0.16% oxygen whereas the diesel produced in the FTS contained 3.05% oxygen.

After removing the carbon dioxide, the tail gases from the FTS can be recycled to the FTS reactor to "...enable further chain growth of olefins and alcohols."

Examples 2 through 11 were ..."modeled using the conditions listed. The modeling is based on the experience with various conditions used in pilot plant studies and represents the expected results using the conditions employed."

In Example 2, the authors write that, "The large carbon dioxide content (approximately 18%) of the gases leaving the separation vessel is undesirable for the synthesis reactor feed. Therefore, the next step in synthesis gas preparation is reduction of the carbon dioxide content to less than about 5% by volume, and in the example to less than 2%."

Examples 3-10 involve various carbon dioxide and/or light gas recycle and some of these results are summarized in Table XIV.3.

In example 11 it is stated that, "...it was found that the tail gases from the Fischer-Tropsch reactor which consist chiefly of hydrogen and carbon dioxide can be converted to liquid hydrocarbons in a second Fischer-Tropsch reactor... A test was conducted in a small slurry reactor using the same iron-based catalyst that was used in the Fischer-Tropsch synthesis. The temperature, pressure and space velocity were also kept the same. The carbon dioxide conversion was 25% for a feed having hydrogen to carbon dioxide ratios of 2:1 and also 1.5:1. Conversion of the hydrogen was 42%, and 88% of the carbon monoxide produced in the water gas shift reaction was converted to hydrocarbons in the Fischer-Tropsch reaction. The chain growth (α) was the same as in the conventional Fischer-Tropsch synthesis."

Apart from the claims, references XIV.1, XIV.6 and XIV.7 are essentially identical. The patent of reference XIV.1 claims the production of an oxygen containing diesel fuel using FTS. The claims in references XIV.6 and XIV.7 cover a variety of

carbon dioxide and/or light gaseous product recycle schemes that include both stream(s) and the fraction of each stream to be recycled.

Another grouping of three patents are essentially identical except for the claims [XIV.2-XIV.4]. These three patents are to show, "Several Fischer-Tropsch reaction schemes using a promoted iron catalyst in a slurry reactor produce oxygenated naphtha and diesel fractions on distillation that reduce particulate emissions in diesel engines. High carbon conversion efficiencies and optimum chain growth are characteristics of the process."

These three patents are identical to the above three patents up to the Detailed Description of the Invention and, apart from the one difference described below, this section is the same in the two sets of three patents. In references XIV.2-XIV.4 the paragraph in references XIV.1, XIV.6 and XIV.7:

"The steam reforming reactor 5 can be of conventional design employing a commercial nickel catalyst such as obtained from Katalco and designated **23-1**. Preferably, the reactor should be operated at from about 1292°F (700°C) to about 1652°F (900°) at system pressure of about 12 psia (82.7 kPa) to about 500 pais (3447 kPa). The flow of input gases through the reactor catalyst bed should be approximately 300 lbs/hr/ft³ catalyst."

has been replaced by examples of approaches to reduce the amount of carbon monoxide in town gas to a specified level, for example 10% by volume.

It is shown that the water gas shift reaction could be used to reduce the level of CO in the output from the gasifier; however, this approach significantly reduces the heating value of the resulting town gas. It is shown that the removal of the CO₂

produced during the WGS will increase the heat content of the town gas but, in order to have 10% CO in the product, the extent of WGS must be even greater.

The objective of these patents [XIV.2-XIV.4] is to replace the shift reactor with a FTS reactor to remove the excess CO. Thus, a portion of the gas from the gasifier is fed to the FTS reactor while about 20% of the gas bypasses the FTS reactor (Case III in ref. XIV.2-XIV.4). The composition of the blending streams and the town gas are shown in Table XIV.4.

In addition to the town gas, the FTS produces 11.8 barrels of hydrocarbon liquids having five or greater carbon atoms (based on 1.0 MMSCF feed from the gasifier).

Removing the CO₂ will permit the heating value of the town gas of Case III to be increased but this will require a greater fraction of the effluent from the gasifier passing through the FTS reactor (Table XIV.5).

In this instance 12.6 barrels of C₅₊-hydrocarbons will be obtained.

In another scenario, a WGS reactor is included in the process that can be utilized when the FTS reactor is inoperable or, in another scenario, both the FTS and WGS reactors can be utilized in parallel.

The catalyst activation and the test results of this group of three patents [XIV.2-XIV.4] are identical to those in the first group of three patents [XIV.1,XIV.6,XIV.7]. The examples in references XIV.2-XIV.4 are essentially the same as those in references XIV.1, XIV.6 and XIV.7.

Reference XIV.2 claims a method of thermally cracking a wax produced by a FTS reaction using an iron-based catalyst in a slurry reaction at a temperature of 770°F (410°C) for a sufficient period of time to produce diesel and naphtha fractions.

Reference XIV.3 claims a method for preparing and activating with synthesis gas a material that is catalytically active for Fischer-Tropsch synthesis.

Reference XIV.4 claims a FTS method suitable for producing a diesel product that is cleaner than commercially available that is derived from crude oil and having a cetane number which is higher than 45 and aromatics less than 1% and the same product that contains more than 2 wt.% oxygen.

The final two patents [XIV.5,XIV.8] are essentially identical to each other and, except for a section describing the use in conjunction with power generation and the claims, are identical to references XIV.2-XIV.4. The Fischer-Tropsch processes are used in combination with electric power generation. The example considers a 300 MW off-peak power production rate (during 17 hours of the 24 hour day) in a plant with a thermal efficiency of 33%. The feed gas requirements for the peak and off-peak conditions are 14.87 and 11.15 million standard cubic feet per hour (MMSCFH), respectively. This requires a FTS reactor to handle 3.72 MMSCFH of coal gas during off-peak hours. To prevent slurry bed slumping, the FTS reactor would require an additional 0.45 MMSCFH during peak operation. During peak operation, the FTS conditions would be changed from 250 to 100 psi to maintain an adequate superficial velocity in the FTS reactor. The average production of liquid hydrocarbons would be about 2100 barrels per day.

Reference XIV.5 claims: (1) a FTS process for producing liquid hydrocarbons from a synthesis using an iron catalyst in a slurry reactor with recycle of CO₂ to the gasifier, (2) claim 1 using coal derived synthesis gas and (3) the method of claim 2 wherein the FTS is used in combination with an electric power generation system.

Reference XIV.8 has one claim for a diesel fuel additive for reducing particulate emissions by utilizing the oxygenates in the FTS product so that the diesel contains at least 2 wt.% oxygen.

The discussion in the sections of these patents provides an excellent overview of FTS using an iron catalyst and of process concepts to improve the efficiency of carbon utilization. At times it is difficult for the reader to easily discern whether the data is from modeling or produced by experiment. Rentech has operated a 6-inch 8-foot tall slurry reactor both with and without CO₂ removal in advance of the FTS reactor [XIV.8]. In 1992 it was reported that the longest run was for a two-week period but it is understood that subsequent runs have been made for periods of 60 days or more; however, data for these longer runs do not appear to be available in the public domain.

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- XIV.18. C. B. Benham, "A decade of research and development in Fischer-Tropsch applications, Pittsburgh Coal Conf, October 15, 1992.

Table XIV.1			
	No. 1 Diesel ASTM (1)	No. 2 Diesel ASTM (2)	F/T Diesel
Cetane Index ASTM 976-80	45 min.	40 min.	62
Sulfur Wt.% ASTM D129-80 90% Distillation	.50 max	.50 max	<0.0001*
Temperature °F ASTM D56 Viscosity @ 40°C	550°F-max.	540°F-min. 640°F0Max.	556°F
cSt.	1.4 min.	1.9 min.	1.8
ASTM D445-82	2.5 max.	4.1 max.	
Conradson Carbon on 10%; ASTM D189-81 Wt.%	.15 max.	.35 max.	.02
Flash Point °F, min. Corrected to 760 mm Hg ASTM D56-82	100°F	125°F	122°F
Aromatic Content, Vol. %; ASTM D1319	8% min.	33%	less than 1%
API Gravity ASTM D1298	38-41	34.7	48.7
BTU/lb ASTM D240	16,000-17,000	19,810	19,371
Oxygen Content, Wt.%	N/A	N/A	3.05%
* Analyses were below limits of detection. (1) ASTM D975-81, #1 Diesel (2) ASTM D975-81, #2 Diesel			

Table XIV.2			
Test	Method		Results
Flash Point, °F	ASTM D56		122
API Gravity @ 60°F	ASTM D1298		48.7
Sulfur Content, Wt.%	Horiba Analyzer		<0.0001
Kinematic Viscosity @ 40°C, cSt.	ASTM D445-82		1.80
Distillation Range	ASTM D86	IBP 90% FBP	314 566 627
Conradson Carbon on 10% Residuum, Wt.%	ASTM D189-80		0.02
Saturates, Wt.% Alpha-Olefins Internal Olefins Alcohols and Others	NMR/90 MHz		30 45 9 16
Oxygen Content, Wt.%	Elemental Analysis		3.05
Average Carbon Chain Length	GC/FID		C ₁₄
Cetane Index	ASTM D976		62
Heat of Combustion, BTU/lb	ASTM D240		19,371

Table XIV.3			
Efficiencies Taken from Description of Examples Feed 1,000,000 Std. Cubic Feet/Day			
Example	Efficiency	C ₅₊ bbl/day	CO ₂ Recycle
1	58.1	80.7	
2	50		Yes, reactor and reformer
3	36.8	51.8	No
4	43.6	61.3	Yes, from reformer inlet
5	60.5%	85.2	Yes, reformer and 1/2 FT tail gas
6	71.3%	94.6	Yes, ~ all CO ₂ and 1/2 FT tail gas hydrocarbons
7	43.7 ^a	60.0	
a. Same as example 5 except $\alpha = 0.7$.			

Table XIV.4 Stream Compositions for Case III			
Species	From Gasifer (Vol. %)	From F.T. Reactor (Vol. %)	Town Gas (Vol. %)
H ₂	55.7	56.32	56.15
CO	26.9	3.69	10.00
CO ₂	2.0	17.88	13.56
CH ₄	14.1	19.75	18.21
C ₂ H ₆	1.3	2.05	1.84
C ₂ H ₈	0.0	0.19	0.14
C ₄ H ₁₀	0.0	0.12	0.09
LHV (B/ft.3)	388.3	387.1	387.4
Volume (MMSCF)	1.0	0.572	0.786

Table XIV.5 Stream Compositions for Case IV				
Species	From Gasifer (Vol. %)	From F.T. Reactor (Vol. %)	Mixed Gas (Vol. %)	Town Gas (Vol. %)
H ₂	55.7	56.32	56.17	65.34
CO	26.9	3.69	8.59	10.00
CO ₂	2.0	17.88	14.52	0.60
CH ₄	14.1	19.75	18.57	21.57
C ₂ H ₆	1.3	2.05	1.89	2.20
C ₂ H ₈	0.0	0.19	0.16	0.18
C ₄ H ₁₀	0.0	0.12	0.10	0.11
LHV (B/ft.3)	388.3	387.1	387.7	450.9
Volume (MMSCF)	1.0	0.572	0.773	0.664

Figure XIV.1. Recycled water and alcohol.

ATTACHMENT IX

Review of Air Products Fischer-Tropsch Synthesis Work

During the 1980s, Air Products & Chemicals worked on several aspects of the Fischer-Tropsch synthesis. These included the development of novel Fischer-Tropsch slurry catalysts and process concepts, the design of a Fischer-Tropsch pilot plant, the hydrodynamics of bubble column reactors, and the development and operation of the LaPorte Fischer-Tropsch facility (IX.1-IX.7). Their patents concerning the preparation of Fischer-Tropsch catalysts contain the following: "The invention was made under DOE Contract No. [one of two contracts] and is subject to government rights arising therefrom."

The focus of the work was on the use of the low H_2/CO synthesis gas ratios expected from coal gasification. However, a limited number of runs with a H_2/CO ratio that would be typical of the gasification of natural gas were made.

The work on the preparation, characterization and performance of cobalt and ruthenium catalysts focused on the use of carbonyl clusters with the expectation that these would lead to highly dispersed supported metal catalysts. As part of this study a baseline catalyst was prepared by the "normal" procedure using a cobalt nitrate precursor and aqueous impregnation techniques.

The workers utilized a number of catalyst supports. These included: $\gamma-Al_2O_3$ (Catapal SB, 217 m^2/g , 45 μm), silica (Davison 952, 339 m^2/g , 70 μm), $MgO \cdot 3.6SiO_2$ (Florisil, 298 m^2/g , 75 μm) and titania (Degussa P-25, 50 m^2/g , 2 μm). These supports were used to prepare the catalysts shown in Table IX.1a and IX.1b.

A common impregnation procedure was used to prepare four batches of a catalyst with a formulation of $Co_2(CO)_8/Zr(OPr)_4/Al_2O_3$ in which the metal precursor to

support ratio was held constant (3.55-3.81 wt.% Co with the Co/Zr ratio 0.55). This base case catalyst, including one larger batch, exhibited similar activity and product selectivity, showing that the preparative method was reproducible.

The catalysts covered in the patents (IX.4-IX.6) are prepared using a decomposable salt or organic compound of cobalt, iron or ruthenium. One claim is (IX.5):

"1. Method of making a catalyst comprising the following steps:

- (a) treating an inert, inorganic metal oxide catalyst base material with a nonaqueous solution of a decomposable salt or organic compound of a group IVB metal and removing said nonaqueous solution;
- (b) impregnating the product of Step (a) with a nonaqueous solution of a decomposable salt or organic compound of a Fischer-Tropsch metal catalyst from the group consisting of cobalt, iron or ruthenium, and removing remaining said nonaqueous solution; and
- (c) exposing the product of Step (b) to a reducing atmosphere; all while maintaining said material and said products under conditions sufficient to avoid hydrolysis, oxidation, and calcination thereof."

A number of catalyst formulations were prepared by the patented technique. Fischer-Tropsch synthesis activity and selectivity were obtained in a fixed-bed reactor (screening test) and for those formulations exhibiting a high activity in a 1-liter continuous stirred tank reactor. The conditions used for the screening studies were 240-280°C, CO/H₂ feed = 0.55 - 2.0, 300 psig (2.0 MPa) and a space velocity of 1.0-2.0 NL/g cat/hr.

The $\text{Co}_2(\text{CO})_8/\text{Zr}(\text{OPr})_4/\text{SiO}_2$ (3.5% Co, 6.6% Zr) catalyst was found to be the most active system in the slurry reactor and also gave the best liquid fuel selectivity. The Schulz-Flory pattern was found for the products obtained using this catalyst. The bulk activity ranged from 16 to 54 mole syngas/kg cat/hr. The gasoline range ($\text{C}_5\text{-C}_{11}$) products accounted for 20 to 45% of the products and the diesel range ($\text{C}_{12}\text{-C}_{18}$) products were 17 to 32%. This catalyst was tested in an extended slurry-phase run that achieved 6 months on stream with a 10% loss in activity.

A comparison was made for 4% cobalt Zr-alumina catalysts in which the dominant difference was the cobalt compound used in the preparation of the catalyst: cobalt carbonyl in an organic solvent and cobalt nitrate in aqueous solution. The specific activity of the nitrate derived catalyst is significantly lower than the one derived from the carbonyl compound when the conversion is effected at 240°C in the CSTR (Table IX.2). However, when the conversions are compared at 260°C, there is less difference between the two conversions; one possibility to account for this is that significantly more sintering of the cobalt occurred for the carbonyl derived catalyst at this higher temperature.

The activity of the $\text{Co}_2(\text{CO})_8$ -based catalysts decreased with changing supports as follows: $\text{SiO}_2 \gg \text{TiO}_2 > \text{Al}_2\text{O}_3 > \text{MgO} \cdot \text{SiO}_2$ (figure IX.1). The Co/TiO_2 catalyst was found to exhibit an unusually high selectivity for C_{3-5} olefins. Zirconium was found to be the better promoter, compared to Ti, for enhancing activity and selectivity, with the optimum Co/Zr ratio being between 0.5 and 1.0.

As the cobalt loading was increased from 4 to 14 wt%, the catalytic activity remained constant and then eventually declined.

The supported Ru catalyst exhibited initially a high activity but the catalyst deactivated rapidly in the slurry reactor. Thus, not much data were obtained with this catalyst.

They found that the following kinetic expression best fitted the data they obtained over a wide range of conversions:

$$- (r_{CO+H_2}) = kC_{H_2}/(1 + k C_{H_2O}/C_{CO}C_{H_2}). \quad [1].$$

However, it was not possible to discriminate with great confidence among the kinetic equations tested during the study.

Catalyst Activation

The activation of supported metal carbonyl catalysts is frequently done by thermal decomposition under vacuum or inert gas atmosphere (IX.8). During the early work at Air Products, catalysts were activated in syngas. To accomplish this the catalyst precursor was heated to 180°C in a nitrogen flow at atmospheric pressure. At 180°C, the flow was switched to the synthesis gas (CO/H₂ = 1) and then heated to the reaction temperature. At the reaction temperature, the pressure was increased to the one used for the synthesis. Later in their work, they compared the impact of activation in pure H₂ or syngas (CO/H₂ = 1). For a 4%Co-zirconia promoted alumina catalyst, they found that the sample activated in hydrogen had a significantly higher activity and higher yield of liquid fuels (figure IX.2a,b; Table IX.3).

Catalyst Promoters

The Air Products work included a comparison of the promotional effects of zirconia and titania for both silica and alumina supports. The titania promoted cobalt catalyst on both alumina and silica supports showed lower catalytic activity than a

similar zirconia promoted catalyst. The bulk activity at 240°C for the alumina supported cobalt was 20 % lower with the titania promoter; with the silica supported cobalt this was 40% lower. The titania promoter also produced more methane and light hydrocarbons than the zirconia promoted cobalt catalyst. Similar activity trends were obtained in both the fixed-bed and slurry reactors; however, the differences in the selectivity were less noticeable in the slurry reactor.

Cobalt Metal to Promoter Metal Ratio

In this study the cobalt to promoter ratio for the silica support was conducted with precursors which contained the same level of cobalt but with a variable amount of promoter. Four catalysts were prepared and the compositions are shown below:

<u>Weight % Cobalt</u>	<u>Weight % zirconium</u>	<u>Co/Zr</u>
4.0	4.8	1.2
4.4	2.3	0.53
4.6	0.1	0.15
4.2	0.0	0.0

The effect of the Co/Zr ratio in the gas-phase reactor on the bulk and specific activities for this series are shown in figures IX.3 and IX.4. It appears that the optimum ratio for bulk activity occurs at about Co/Zr = 1; however, for the specific activity it occurs at about Co/Zr = 0.5, the base case catalyst ratio. The usage ratio appears to increase as the zirconium content increases. The base case catalyst provided the highest yield of liquid fuel, C₅-C₁₈.

Three of the catalysts, Zr/Co = 0, 0.53 and 1.9, that were evaluated in the fixed-bed reactor were also evaluated in the CSTR (figure IX.5). Just as in the fixed-bed

reactor, the optimum activity was obtained for the base case catalyst with a Zr/Co = 0.53 ratio.

Metal Loading

Metal loadings of 3.5, 11.0 and 14.4 wt.% Co on silica were evaluated. For the base case (3.5 wt% Co) the Zr/Co ratio was 0.53 but this ratio was not used for the catalysts with the higher cobalt loadings. One reason for using the higher Zr/Co ratio for the two higher Co loadings was to be able to make a comparison with the Co/Zr/silica catalyst that is used by Shell Oil for their Shell Middle Distillate Synthesis (SMDS). There was little change in the bulk activity in increasing Co content from 3.5 to 11.0; however, at all temperatures there was a significant decline in activity upon further increasing the Co content to 14.4 wt.% (figure IX.6). Selectivity to liquid fuels declined as the Co loading increased.

Significant increases were observed for the bulk density with increasing Co loadings: 0.394 g/cc for 3.5 % Co, 0.564 g/cc for 11.0% Co, and 0.883 g/cc for 14.4% Co. Thus, as the experiments were conducted in the fixed-bed reactors, the amount of catalyst contained in the 10 cc catalyst volume increased significantly and this may have been a major factor in determining the bulk activity shown in figure IX.6.

In the slurry reactor tests of the 3.5 and 11.0% Co catalysts, the activity at both 240 and 260°C declined as the Co content increased in contrast to the fixed-bed reactor runs (figure IX.7).

Product Selectivity

Satterfield et al. (IX.9) reviewed the literature with respect to product distributions for slurry Fischer-Tropsch reactor operation, particularly with iron catalysts. It was concluded that product hydrocarbon selectivities follow a predicted Anderson-

Schulz-Flory (ASF) distribution characterized by the chain growth probability factor, α , and that previously reported deviations are probably due to experimental artifacts. Fixed-bed temperature gradients, insufficient time to reach steady-state, volatilization of certain fractions, and condensation of high molecular weight material are some of the experimental problems that can give misleading selectivity results. These considerations are for deviations which produce chain-limiting Fischer-Tropsch product distributions; most agree that deviations which produce more high-molecular weight products than predicted by ASF are valid (IX.10). Air Products workers sought to avoid the problems previously encountered by their close attention to experimental details, and by determining product distributions over long-term slurry phase operations with good quantitative mass balances (IX.11).

With the fused iron United Catalysts, Inc. C-73 catalyst, a good fit to the ASF distribution was obtained (figure IX.8). However, for slurry catalyst A2 (later shown to be a cobalt-zirconia-silica catalyst) there was an enhanced product deviation from the ASF distribution for the C_{18} - C_{35} region when the catalyst was operated at 2.21 MPa. The effect of pressure in determining this product enhancement can be seen by comparing curves a and b in figure IX.8.

Another catalyst, B, also shows a deviation from ASF (figure IX.9). There was a significant deviation from the ASF distribution for the C_9 - C_{25} products when operating with a feed of $H_2/CO = 0.5$. The yield of 67.3 wt% product obtained in the C_9 - C_{25} products represents a 25 wt% increase over what was considered to be the limit of 54.1% imposed by the ASF distribution.

An adequate explanation for these deviations obtained early in the experimental program has not been offered. These and similar catalysts usually provided "standard"

ASF distributions based on the data reported. This implies that some experimental operational problem was responsible for this unusual, and highly desirable, deviation from ASF distribution.

Ruthenium Catalyst

A Ru/Zr/alumina ($\text{Co}_2(\text{CO})_8$) was a promising catalyst when tested in the fixed-bed reactor. The fixed-bed activity was 26.7 mol syngas/kg cat/hr (comparable to the Co base case catalyst) and a high specific activity of 0.48 mol/mol Ru/min. Methane production was high at about 20%. Slurry phase testing of this catalyst indicated a significantly lower catalytic activity (8 mol syngas/kg cat/hr).

A Ru/Zr/silica catalyst was also tested and it exhibited a much higher activity (70 mol syngas/kg cat/hr; 0.834 mol CO/mole Ru/min at 240°C; 81 mol syngas/kg cat/hr and 1.05 mol Co/mol Ru/min at 260°C) than the similar catalyst using alumina as a support. The Ru catalyst produced higher molecular weight products than a similar Co catalyst. Methane selectivity was low, never exceeding 5.3%.

The performance of the Ru/Zr/silica catalyst was poor in the CSTR. Initially showing a high activity at 240°C (43 moles syngas/kg cat/hr), it had declined to 4 moles syngas/kg cat/hr after only 280 hours on stream.

These preliminary results led the workers to concentrate their further efforts on their cobalt catalysts.

Improving Water-Gas-Shift (WGS) Activity

Since both the Ru and Co catalysts exhibited very low WGS activity, attempts were made to modify the catalyst to increase the WGS activity. A physical mixture of the base case catalyst and a commercial Cu/Zn/alumina low temperature shift catalyst was employed. The addition of the shift catalyst caused a decrease in the Fischer-

Tropsch synthesis without increasing the WGS activity. A Co/Fe/alumina catalyst was prepared using the carbonyl compound of Co and Fe. There was a 53% increase in the usage ratio indicating increased WGS; however, the bulk activity declined by 40%. A Fe/Co/Zr/silica catalyst showed only a slight increase (14%) in usage ratio and a slight decrease in bulk activity. Thus, the exploratory effort to increase the WGS activity failed.

Extended Runs in CSTRs

A run of nearly 6 months was made with a Co/Zr/silica catalyst (4.43% Co, 7.58% Zr) (IX.12). This catalyst displayed remarkable stability. During the first 1012 hours it was utilized at 240°C, 300 psig, $\text{CO}/\text{H}_2 = 0.5$ and space velocity = 1.8 l/g cat/hr, and then from 1012 to 2188 hours at 260°C, 300 psig, $\text{CO}/\text{H}_2 = 1$ and space velocity = 2.0 L/g cat/hr. The productivity declined from 52.7 to 46.9 mol syngas/kg cat/hr during 1012 hours (figures IX.10 and IX.11) and then declined slowly during operation from 1012 to 2188 hours (figures IX.12 and IX.13). During the second period the product selectivity remained nearly constant (figure IX.14).

After 2188 hours, a series of changes from the base case conditions, 260°C, 300 psig, space velocity 2.0 L/g cat/hr and $\text{CO}/\text{H}_2 = 1.0$, were made for the CO/H_2 ratio and the space velocity to generate data for kinetic studies. At intervals, the conditions were returned to the base case to obtain data to correct for the slow catalyst aging. A series of tests were made at two feed set of conditions. In one instance, the impeller speed was altered using constant feed conditions and in the other the space velocity was varied by adding a nitrogen flow, maintaining the same partial pressure of hydrogen and carbon monoxide by increasing the total pressure. Both variations show that mass transfer effects can be neglected.

At 3964 hours, the temperature was increased to 280°C to repeat the series of kinetic measurements. At this temperature the methane production was very high (up to 56.4%) and the wax production very low. At the end of the experiment, the reactor contained only solid, indicating that the operations at the higher temperature had caused the reactor to lose essentially all of the liquid through vapor pressure and/or hydrogenolysis effects.

Cobalt Dispersion

Hydrogen chemisorption was measured to obtain a measure of the metal dispersion of the cobalt and ruthenium catalysts. Air Products reports indicate that they were disappointed with the low dispersions that they obtained; however, the 10-12% dispersion values they obtained for 11 and 14% Co on silica are about as high as reported by later workers. In general, the silica supported Co exhibited a higher dispersion than the alumina supported cobalt at a similar metal loading (Table IX.4). The hydrogen chemisorption was considered to decrease along with the catalytic activity as the cobalt loading was increased for the silica supported cobalt catalysts. The dispersions obtained by the Air Products workers agree with those reported by Reul and Bartholomew (IX.13). Chemisorption was measured at higher temperatures because this led to higher surface areas.

Olefin Reincorporation

In a screening study, ethene was added to the syngas feed for runs with the $\text{Co}_2(\text{CO})_8/\text{Zr}(\text{OPr})_4/\text{Al}_2\text{O}_3$ catalyst (5.07% Co; 4.39% Zr). Under the reaction conditions employed, the CO conversion should have been 20% or less. When 10 or 20 volume percent ethene was added to the feed, the major result was the production of ethane. The oxygenate production did increase slightly (from 0.2 to 2.4 wt%) but the majority of

this fraction was propanol, the product of hydroformylation. The catalyst underwent significant (20% conversion) deactivation during the addition of ethene. The conclusion is that ethene did not undergo significant incorporation; rather it was hydrogenated to ethane.

Kinetic Study

A program was developed to obtain kinetic data from the experimental data (figure IX.15). Experimental data from two runs were made with a catalyst formulation that was essentially the same as the base case catalyst but a more active $\text{Co}_2(\text{CO})_8/\text{Zr}/\text{SiO}_2$ catalyst (4.9% Co; 9.3% Zr). Henry's Law was assumed to apply and to allow for calculation of vapor partial pressures. Henry's Law data was taken from Peter and Weinert (IX.14) and liquid densities were calculated using correlations proposed by Deckwer (IX.15). Mass transfer from bulk liquid to catalyst surface was considered to negligible, based upon the experimental data.

The authors fit the data to five kinetic expressions (to correlate with equations in reference 13, A=2, B=1, C=3, D=4):

$$- r_{\text{CO}+\text{H}_2} = k C_{\text{H}_2} / (1 + K C_{\text{CO}_2} / C_{\text{CO}}) \quad [2]$$

$$- r_{\text{CO}+\text{H}_2} = k C_{\text{H}_2} / (1 + K C_{\text{H}_2\text{O}} / C_{\text{CO}}) \quad [3]$$

$$- r_{\text{CO}+\text{H}_2} = k C_{\text{H}_2} / (1 + K_1 C_{\text{CO}_2} / C_{\text{CO}} + K_2 C_{\text{H}_2\text{O}} / C_{\text{CO}}) \quad [4]$$

$$- r_{\text{CO}+\text{H}_2} = k C_{\text{H}_2} / (1 + K C_{\text{H}_2\text{O}} / C_{\text{CO}} C_{\text{H}_2}) \quad [5]$$

$$- r_{\text{CO}+\text{H}_2} = k C_{\text{H}_2}^a C_{\text{CO}}^b \quad [6]$$

For the run with the catalyst similar to the baseline catalyst, the data at high H_2/CO feed ratios and at high space velocities were best described by the first order rate equation:

$$-r_{CO+H_2} = kC_{H_2}^a C_{CO}^b \quad [7]$$

where $a = 1.1$ and $b = 0$. For low H_2/CO data, equation 3 fits the data better:

$$-r_{CO+H_2} = k C_{H_2} / (1 + KC_{H_2O}/C_{CO}) \quad [8]$$

where $k = 0.349$ and $K = 0.425$. The activation energy was in the range of 33-44 kJ/mole.

For the more active catalyst, none of the five equations were able to be used to fully describe the data. They concluded that equation 3 provided the better fit to the data and transformed the equation to a linear form:

$$C_{H_2} / -r_{CO+H_2} = (K/k) C_{H_2O}/C_{CO} + (1/k). \quad [9]$$

The data are plotted using equation 7 and is shown in figure IX.16 for 240, 260 and 280°C. From the intercept, the rate constant, k , is derived with values ranging from 0.328 to 0.775 cc/g cat/sec. This allows K to be determined from the slope and values ranging from 0.466 to 0.302 are obtained. An activation energy of 51 kJ/mole was obtained from the Arrhenius plot.

The authors write that, at that time, relatively few kinetic studies of the Fischer-Tropsch reaction using cobalt catalysts have been made (IX.17-IX.22). From the available literature, activation energies for cobalt catalysts are in the range of 67-117 kJ/mole; for iron catalysts they range from 37 to 105 kJ/mole. The activation energies obtained by the Air Products workers for these catalysts are surprisingly low.

The Air Product workers analyzed the kinetic data obtained during run hours 2188 and 3964 in the extended run described above. It was assumed that the deactivation led to a linear decrease in conversion during the kinetic measurements. They concluded that Equation 5, which included water inhibition, fit the data better than the other equations; a plot of the data using the linearized form of Equation 5 is shown in figure IX.17. It had been reported by Huff and Saterfield (IX.23) that this equation describes data with high water concentration quite well. After Equation 5, the data was best fit by equation 6. The rate constant obtained using Equation 5, based upon fresh catalyst activity, are $K = 5.24 \times 10^9 \exp(-23,254/RT)$ cc/g cat/sec and $K = 1.55 \times 10^{-3} \exp(-6,250/RT)$ mol/cc. The Arrhenius plot returned an activation energy of 97 kJ/mole, and this value agrees much better with those reported earlier for cobalt catalysts.

Slurry Reactor Hydrodynamics Studies

The final report (IX.24) provides a detailed summary of the literature to that date (about 1983) and experimental data obtained in cold flow simulators of 12.7 and 30.5 cm diameter (1.52 and 4.75 m height, respectively) that was conducted at Air Products. With the simulator, phase holdups, phase dispersion coefficients, and interphase heat and mass transfer coefficients were measured. The measured heat and mass transfer and phase dispersion correlations were found to conform to the literature, while the phase holdup correlations were different from the literature. The product distributions from Air Products' catalyst testing program were combined with the hydrodynamic studies to make predictions of space-time yields of product fuel fractions in large-scale bubble column reactors.

Based upon the study, they concluded:

1. Both hydrodynamic and kinetic effects are important to the proper design of the bubble column reactor.
2. For solid particles below 60 μm , the slurry can be modeled as a pseudo-single phase. Larger size solid particles were distributed in accordance with Cova's sedimentation-diffusion model (IX.25).
3. Of those studied, the most important independent variable affecting the reactor performance was the superficial gas velocity, followed by solid particle loading. The type of liquid had a small effect on the column hydrodynamics. The parameters that had little or no effect in the range studied included the presence of heat transfer internals, solid type, distributor hole size, and superficial slurry velocity.
4. Staging the bubble column system to provide more plug flow behavior of the gas was predicted to result in a 5% increase in conversion rates, assuming the same bubble size, about 0.23 cm, as in the unstaged column. On the other, if the average bubble diameter is decreased to 0.07 cm, the conversion rates are expected to increase by 25%.
5. The gas holdup obtained in the cold flow systems was lower than measured by Deckwer (IX.26) and Mobil (IX.27) but in agreement with results of Satterfield (IX.28) and with the correlations from Air Products' slurry phase methanol project (IX.29).
6. Adding seven, 5.7 cm o.d. x 1.42 m heat transfer internals to the 30.5 cm column had no effect on column hydrodynamics.

7. The heat transfer results agreed with Deckwer's correlation (IX.30) but, unlike Deckwer, the heat transfer rates continued to increase beyond a 10 cm/s superficial gas velocity. Heat transfer tubes would therefore take only a small fraction of the internal volume of a Fischer-Tropsch slurry bubble column reactor.
8. Mass transfer results agreed with Akita and Yoshida (IX.31) and Hikita et al. (IX.30-IX.33).
9. Liquid dispersion results agreed with Kato et al. (IX.34), indicating that above a superficial gas velocity of 3 cm/s, the slurry was well-mixed.

The Air Products workers wrote, "One of the more important aspects of gas flowing through a tubular reactor is its availability at the reaction site. This is ultimately related to the interfacial area between the liquid and gaseous phases. In a two-phase, gas-liquid system, the interfacial area, a , is related to the gas volume fraction, ϵ_G , and mean bubble size, d_{SB} , by

$$a = 6 \epsilon_G / d_{SB} \quad [10]$$

Both the mean bubble size, also known as the Sauter mean diameter, and the volume fraction, which is typically referred to as gas holdup or void fraction, are values which are extremely important to optimum reactor design."

The Air Products work followed three steps:

1. Hydrodynamic data were obtained in a 5" ID x 5' (12.7 cm ID x 1.52 m) cold flow simulator.
2. Scale hydrodynamic study to 12" ID x 15.5' (30.5 cm ID x 4.75 m) column.
3. Incorporate kinetic data from catalyst studies with hydrodynamic correlations into a computer model and use this to predict the conversion rates and space-time yields that would be obtained in actual Fischer-Tropsch slurry reactor operation.

Using the model, the heat, mass and momentum transfer parameters which most affect the bubble column design were better quantified.

In the slurry reactor, either mass transfer resistance or kinetic resistance is expected to dominate. Gas holdup, average bubble size and mass transfer coefficient are the important dependent variables that impact mass transfer resistance. Two important factors for kinetic resistance are solids dispersion and liquid dispersion, both affecting catalyst loading, and thereby reactor productivity. Heat transfer rate is also important since this will determine the fraction of the reactor volume required for heat exchangers, and not available for production. The Air Products work attempted to quantify the above mentioned parameters (Table IX.5).

The workers reviewed work prior to 1982 concerning gas-liquid-solid systems. They indicate that Kara (IX.35) found that solid particles promote bubble coalescence and hence the onset of the churn-turbulent regime. However, reports of solids decreasing or increasing gas-holdup can be found in the literature. Kurten and Zehner (IX.36) report Sittig's work on bubble breakup caused by solids. It was shown that bubble breakup occurs when the inertia forces of the solid particle exceed the bubble surface tension forces:

$$(\pi/6)(\rho_s/2) d_s^3 u_{SG}^2 > (\pi/4) \sigma d_s^2 \quad [11]$$

which, when rearranged, shows that bubble breakup can occur when the Weber number is greater than 3:

$$We = (\rho_s d_s u_{SG}) / \sigma \geq 3 . \quad [12]$$

This indicates that below the critical Weber number the solid will not cause bubble breakup.

Since for a particle of about 4 or about 100 μm , a bubble rise velocity > 0.1 or 0.65 m/sec , respectively, is needed for the particle to induce bubble breakup, it is not anticipated that Fischer-Tropsch slurry column will experience bubble breakup due to the presence of solid catalyst particles. In fact, it is expected that bubble coalescence will occur, decreasing gas holdups.

Deckwer et al. (IX.15) studied gas holdup in 4.1 and 10 cm ID columns in the bubbly flow regime (1 to 4 cm/sec) using a hydrogenated Fischer-Tropsch liquid and up to 16 wt.% of > 5 micron alumina particles and obtained the empirical correlation:

$$\epsilon_G = 0.053 j_G^{1.1} \quad [13]$$

where j_G is the superficial velocity of the gas. It was suspected that foaming occurred in the measurements reported by Deckwer et al. (IX.15). Kuo (IX.27) obtained data for the same system showed that with a sintered plate gas distributor he obtained foaming but that no foaming and a much smaller gas holdup was obtained with a distributor with larger openings. Bukur (IX.37) used the same wax as Deckwer and Kuo and obtained a means of eliminating the formation of a foam region. In the absence of a foam region, Bukur obtained a gas holdup that was comparable to those of Pilhofer and Bach (IX.38) and the results obtained by Air Products.

It was concluded that gas holdup was mostly a function of gas velocity and varies to the first power. Slurry density, or weight loading, has the second largest impact on gas holdup. The larger column (30.5 cm) had a lower gas holdup than the 12.7 cm column at the higher gas velocities. It was considered that this was due to more bubble coalescence in the taller column and that the data obtained in the larger diameter column, being more reliable, would be used in the computer simulation of an operating commercial Fischer-Tropsch reactor.

The gas bubble diameter was obtained over a wide range of conditions. The bubble diameter, d_{SB} , relationship with the gas holdup, the gas liquid interfacial area is related to the Sauter mean bubble diameter and gas holdup by

$$a = 6 \epsilon_G / d_{SB} . \quad [14]$$

The uncorrected bubble chord lengths were in the range from 0.28 to 0.44 cm. The measured values are slightly larger than the true values because the experimental approaches caused bubble acceleration/elongation during the measurement. The corrected bubble diameters ranged from 0.22 to 0.35 cm and the bubble velocity ranged from 26.3 to 32.7 cm/sec, both range over fairly narrow values. Since the bubble size should be smaller in Fischer-Tropsch liquids than in water, they concluded that the Calderbank (IX.39) correlation suggested a Sauter diameter size of 0.23 cm for a Fischer-Tropsch type system and this produces

$$a = 6 \epsilon_G / 0.23 = 26.09 \epsilon_G \quad [15]$$

which was used in the computer model.

The overall mass transfer coefficient, $K_L a$, is the product of the mass transfer rate per unit area, K_L , and the interfacial area, a . Air Products workers measured $K_L a$ because of the variation in the reported values. This variation was primarily due to variation in the reported gas holdup and average bubble size; however, there is also variation in the reported values of K_L . They obtained an empirical correlation for $K_L a$:

$$K_L a = (0.30 \epsilon_G^{1.06} d_p^{0.05}) / W^{0.08} \quad [16]$$

where W = weight fraction of solids. Gas velocity was considered to be the primary factor in estimating $K_L a$.

Liquid dispersion relates to how well mixed the liquid phase is and how much solid can be suspended. The Air Products workers discussed this in terms of two extremes:

1. Ideal mixing, continuous stirred tank reactor (CSTR) behavior where any liquid molecule can move to any other part of the column from one instant to the next, and
2. Plug flow reactor (PFR), where any molecule will move in concert with the other neighboring molecules, entering and leaving the column at the same time.

The axial liquid dispersion coefficient, E_z , provides one way to quantify where a particular reactor lies between these two extremes (CSTR and PFR). E_z will be zero for PFR and infinity for CSTR behavior. In practice, when E_z is greater than $10^{-2} \text{ m}^2/\text{sec}$, a well-mixed behavior exists. Knowing E_z , one can plot a sample's concentration as a function of time at a fixed point within the column; such a plot is a residence time distribution (RTD) curve.

A model that is used to describe the sample concentration at any time is Fick's Law:

$$dC/dt = E_z d^2C/dZ^2 . \quad [17]$$

Using the appropriate boundary conditions, an approximate analytical solution which describes the RTD curve at any point within the column was given by Ohki and Inoue (IX.40):

$$dC/dt = E_L d^2C / dZ^2 . \quad [18]$$

For the boundary conditions where a tracer impulse is inserted at any longitudinal location:

$$dC/dt)_{0,T} = dC/dZ)_{L,T} = 0 \quad [19]$$

where L = extended bed height and

$$C(Z,0) = \begin{cases} 0, & 0 \leq Z < Z_1 \\ C_0, & Z_1 \leq Z \leq Z_2 \\ 0, & Z_2 \leq Z \end{cases} \quad [20]$$

$$C/C_0 = 1 + 2 \sum_{n=1}^{100} [\cos(n\pi Z/L) \exp(-n^2 \pi^2 E_L t/L^2)] \quad [21]$$

Little difference is obtained if the summation is to infinity, the exact solution, or stops at 100.

The experimental program to address the dispersion issue and to obtain the RTD curve utilized the injection of a sodium chloride solution into water, detecting the movement of the sodium chloride, the tracer, by conductivity measurements at various heights in the column.

The energy dispersion is greatest at the gas distributor inlet and least at the gas disengagement zone at the top of the reactor. However, E_z was not height dependent was not evident since one dispersion coefficient was sufficient to characterize the entire column. The results of the liquid dispersion runs at Air Products were in agreement with the work of Kato and Nishiwaki (IX.41):

$$Pe = (13 Fr) / (1 + 6.5 Fr^{0.8}) \quad [22]$$

where Pe is the Peclet number $((V_G d_c) / E_z)$ and Fr is the Fraud Number $(V_G / g d_s)^{1/2}$.

From their experimental work, they obtained data to show that a uniform distribution of 0.5-5 micron sized particles was obtained. With larger particles there was, as expected a distribution of particles along the column height, with more at the bottom than the top. They concluded that nonagglomerating catalyst particles less than 60 microns should be suitable for Fischer-Tropsch bubble column batch operation, as no unsuspended solids were observed.

Heat transfer was studied by placing tubes with heaters in the bubble column. It was noted that the agitation produced by the gas phase within the reactor produces heat transfer coefficients that are higher than those produced by gas or slurry alone. The heat transfer surface needed for internal use is less than required for an external exchanger.

The report ends with an engineering evaluation that utilizes the model proposed by Deckwer et al. (IX.42). The substitution of the Air Products correlations for those in Deckwer's model showed little effect at low gas velocities. At 9 cm/sec the space-time yield was doubled (Tables IX.6 and IX.7). A major reason for this was that the lower gas holdup allowed for more catalyst per unit volume. In the bubble column operation there exists an optimum gas holdup which will maximize column space-time yield. Gas holdups higher than this optimum will be reaction rate-limited while those lower than this will be mass transfer-limited. The optimum gas holdup will be affected by the bubble size (b_{SB}), intrinsic kinetic rate (K_o), catalyst weight loading (W), the rate of mass transfer across the gas-liquid interface (K_L), and the usage ratio (U). The optimum gas holdup is given by the expression:

$$\alpha_{opt} = 1 / [1 + (6 K_L (1 + U) / K_o W d_{SB})^{1/2}]. \quad [23]$$

Using this equation allows one to calculate the relative space-time yields for a variety of K_o , W and D_{SB} (Table IX.8).

The Air Products workers compared the space-time yield for a bubble column reactor and for a series of staged reactors. In the first method of calculating the space-time yield, a number of idealized CSTRs are simulated with almost complete recycle of the liquid and catalyst but no recycle of the gas phase. This model would be equivalent to the recirculating cell model used in the literature. In the second method, the extent of backmixing of the gas phase was modeled by applying an axial dispersion model (IX.43).

In this model, a low dispersion coefficient refers to many CSTRs in series, while a high dispersion coefficient refers to very few CSTRs in series. Carberry (IX.44) showed that the two methods are related so that:

$$N = V_G L / 2D \quad [24]$$

Since the Deckwer computer model incorporates the axial dispersion model for the gas, liquid and catalyst phases, this approach was chosen.

Results of simulating the Rheinpreussen-size column as several stages as having the same total volume as the original single-stage column (figure IX.18) are shown in Table IX.9. Thus, a 5% increase in space-time yield is obtained by using 5 CSTRs but a further increase does not lead to a further increase in yield (figure IX.19).

Design of LaPorte Plant

As part of the work, a design for a pilot plant to be located at La Porte, Texas adjacent to an Air Products plant was completed (IX.45). The bubble Fischer-Tropsch reactor was sized to operate in the churn-turbulent flow regime, in which commercial-scale reactors will operate. The study indicated that this flow regime could be achieved

with an effective reactor diameter of five inches. However, it was recognized that the exact diameter of the transition from the quiescent to churn turbulent regime is an unknown function of the slurry viscosity and surface tension. To achieve a 40-50% conversion of the synthesis gas in a single pass at a superficial gas velocity of 0.3 ft/sec would require a 30 foot expanded slurry height.

The reasons for the choice of flow regime were described. Concurrent up-flow bubble columns can operate in any one of three flow regimes (IX.15) and these are illustrated in figure (IX.20) together with an indication of the Air Products cold flow work, the LaPorte design and the Rheinpruessen work. The bubbly flow or quiescent regime occurs at velocities less than typically 0.15 ft/sec. Bubbles are of uniform size and do not interact or coalesce to any substantial degree. At higher velocities, the bubbles do not rise uninfluenced by neighboring bubbles and the churn turbulent regime is entered. Coalescence occurs, yielding larger bubbles and faster rise velocities. Because of coalescence, gas holdup does not increase as quickly with gas flow rate in the churn turbulent regime as in the bubbly flow regime. Where the coalesced bubble would be larger than the diameter of the column, the slug flow regime is reached. Slug flow is undesired because of the low gas/liquid interfacial area and the tendency for the slurry to be lifted out of the reactor along with the gas.

The choice of flow regime was dictated by two economic factors. For a given reactor volume:

1. The highest space time yield or production rate per unit volume is optimal.
2. A tall column is preferred to a short one.

The higher the space-time yield, the smaller the reactor volume required for a given production. The simulations with the Deckwer model and the Air Products

hydrodynamic and catalytic data showed that, in every case, the optimum gas velocity for a maximum space-time yield falls within the churn turbulent regime. It was concluded that the value of 9.1 cm/sec (0.3 ft/sec), although slightly below the optimum, would still allow a reasonable conversion for the reactor height chosen.

Air Products workers wrote, "For a commercial plant with multiple trains, it is advantageous to have as few reactor vessels as possible. In the quiescent regime only about 15' of reactor height is required to achieve 90+% conversion of syngas. By increasing the gas velocity into the churn turbulent regime, 90+% conversion of syngas is not achieved until a height of 60'. For equivalent STY's, it is more economical to have N vessels at 60' than to have four times that number of vessels, each with a height of 15'." (IX.45).

The slurry reactor was designed to operate in a fluidized-bed mode. Once charged, the slurry will not be added or removed except for removal of high molecular weight products that form during reactor operation. Gas will flow up the column and exit out the column top.

The design was implemented at the La Porte location and the plant has been modified during the years of operation. To date, four runs, two with an iron catalyst and two with cobalt catalyst, have been conducted.

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Table IX.1a.

Compositions (wt.% of catalyst) and specific catalytic activity (mol CO/mol metal/min) for catalysts prepared using an alumina support during the Last Three-Year DOE Contract (reference IX.1).

Co	Zr	Ti	K	Fe	Mn	Act.
3.6	6.6					0.25
4.4	1.8					0.31
3.4	6.6				1.6	0.31
2.8	4.9					0.48
1.4				0.51		0.40
1.2			0.3	0.4		
4.7 ^a						0.25
3.5		8.6				0.23
2.6				0.85		0.34
2.4			0.02	0.79		0.27
3.9	5.0					0.24
5.1 ^a	4.4					0.20
4.2 ^a	7.1					0.20
4.0	6.4					0.21
10.8	8.5					0.26
3.5	6.6					0.51
3.7	7.3			0.72		0.26

a. Cobalt added as cobalt nitrate.

Table IX.1b.

Compositions (wt.% of catalyst) and specific catalytic activity (mol CO/mol metal/min) for catalysts prepared using an silica support during the Last Three-Year DOE Contract (reference IX.1).

Co	Zr	Ti	K	Fe	Mn	Act.
4.4		4.0				0.24
3.7	7.2					0.23
4.6	7.5					0.43
4.0	3.3					0.83
3.5						0.31
	7.3			2.4		n.d.
4.0	4.8					0.44
4.4	2.3					0.32
4.6	2.3					0.32
4.2						0.14
4.1	6.8					0.31
11.0	7.4					0.15
14.4	10					0.07

Table IX.2				
Effect of Co source on activity and selectivity of 4% Co on Zr/alumina catalyst tested in the slurry phase using a CSTR at 300 psig, CO/H ₂ = 1.0 and 2.0 NL/g cat-hr. (from reference IX.1)				
Cobalt Source	Carbonyl	Carbonyl	Nitrate	Nitrate
	240°C	260°C	240°C	260°C
Bulk activity, mol syngas/kg cat/hr	35.3	38.5	15.8	29.9
Specific activity, mol CO/mol Co/min	0.29	0.32	0.09	0.21
Selectivity, Wt. %				
C ₁	7.9	10.4	10.9	16.5
C ₂₋₄	13.7	15.0	6.5	11.1
C ₅₋₁₁	37.0	44.5	12.9	26.5
C ₁₂₋₁₈	23.4	25.8	19.8	23.8
C ₁₉₋₂₃	8.9	2.0	21.9	10.6
C ₂₄₊	9.1	2.3	28.0	11.5
TOTAL FUELS, C ₅₋₂₃	69.3	72.3	54.6	60.9

Table IX.3		
Effect of syngas vs. hydrogenation activation on the activity and hydrocarbon selectivity using a 4% Co on Zr/Al ₂ O ₃ catalyst in a slurry CSTR (from reference IX.1)		
	Syngas	H ₂
Space velocity, NL/gcat/hr	1.6	2.0
CO/H ₂	1.6	1.5
Pressure, psig	300	300
Temperature, °C	250	258
Hydrocarbon, wt. %		
C ₁	11.5	7.2
C ₂₋₄	10.4	10.8
C ₅₋₁₁	29.2	34.1
C ₁₂₋₁₈	15.3	27.9
C ₁₉₋₂₃	12.5	8.6
C ₂₄₊	21.1	11.4
C ₅₋₂₃	57.0	70.6

Table IX.4			
Metal dispersion for Co and Ru Catalysts (from reference IX.1)			
Catalyst	BET Surface Area, m ² /g	Metal Surface Area, m ² /g	Dispersion, %
3.5%Co/Zr/SiO ₂	316	1.9 (a)	6
4.0%Co/Zr/Al ₂ O ₃	209	0.3 (b)	1
4.1%Co/Zr/SiO ₂	210	1.9 (a)	7
11.0%Co/Zr/SiO ₂	302	8.1 (a)	12
10.8%Co/Zr/Al ₂ O ₃	n.d.	5.4 (a)	7
14.4%Co/Zr/SiO ₂	145	9.3 (a)	10
4.0%Ru/Zr/SiO ₂	325	1.6 (b)	8
(a) Hydrogen chemisorption performed at 100°C			
(b) Hydrogen chemisorption performed at 35°C.			

Table IX.5	
Slurry Reactor Design Variables Considered in the Air Products Study (reference IX.21)	
DEPENDENT VARIABLES	
Gas Hold-Up	Mass Transfer
Bubble Size	Liquid Dispersion
Solids	Heat Transfer
INDEPENDENT VARIABLES	
Slurry Medium: Paraffin, water	
Superficial Gas Velocity: 1.52 - 15.2 cm/sec	
Superficial Slurry Velocity: 0 - 3.0 cm/sec	
Solid: Silica, Iron Oxide	
Solid Size: 1 - 5 μm , 45 - 53 μm , 90 - 106 μm	
Solid Concentration: 0, 10, 20, 30 Wt.%	
Distributor Hole Size: 0.9, 3.2, 12.8 mm	
Heat Transfer Internals: None, Plain	

Table IX.6			
Rheinpreussen Simulation using Deckwer Correlations (from reference IX.1)			
REGIME	CHURN TURBULENT		
CATALYST	Base Case	Cat. A	Cat. B
Inlet gas velocity, cm/sec	9.00	9.00	9.00
Gas holdup	0.385	0.512	0.526
Interfacial area, cm ² /cm ³	32.66	43.44	44.66
Temperature, °C	260.2	259.7	260.2
Rate Constants			
Preexponential factor (sec wt.% in slurry) x 10 ⁵	1.12	90.3	115
Activation energy, kJ/mol	70	94.7	94.7
Inlet ratio, mol CO/mol H ₂	1.5	1.5	1.98
Usage ratio, mol CO/mol H ₂	1.5	1.5	0.65
Hydrogen conversion, %	80.4	34.9	49.8
Relative mass transfer resistance	0.106	0.021	0.035
Space-time yield, mol CH ₂ /hr	2937	1065	1022
Constants in Case Study			
Reactor length, ft (cm): 26.25 (800)			
Reactor diameter, in (cm): 59 (150)			
Contraction factor: -0.5			
Particle diameter, μm: 50			
Reactor pressure, psig (bar): 174 (12)			
Weight fraction catalyst in slurry: 0.20			
Specific heat transfer area, cm ² /cm ³ : 0.10			

Table IX.7				
Rheinpreussen Simulation using Air Products Correlations (from reference IX.1)				
REGIME	CHURN TURBULENT			
CATALYST	Base Case*	Cat. A	Cat. B#	Cat. B with Shift
Inlet gas velocity, cm/sec	9.00	9.00	9.00	9.0
Gas holdup	0.385	0.149	0.171	0.146
Interfacial area, cm ² /cm ³	32.66	36.06	41.43	35.39
Temperature, °C	260.2	260.4	260.4	261.1
Rate Constants				
Preexponential factor (sec wt.% in slurry) x 10 ⁵	1.12	90.3	115	115
Activation energy, kJ/mol	70	94.7	94.7	94.7
Inlet ratio, mol CO/mol H ₂	1.5	1.5	1.98	1.98
Usage ratio, mol CO/mol H ₂	1.5	1.5	0.65	1.98
Hydrogen conversion, %	80.4	55.9	62.9	58.5
Relative mass transfer resistance	0.106	0.043	0.069	0.048
Space-time yield, mol CH ₂ /hr	2937	2042	1273	2135
Constants in Case Study				
Reactor length, ft (cm): 26.25 (800)				
Reactor diameter, in (cm): 59 (150)				
Contraction factor: -0.5				
Particle diameter, μm: 50				
Reactor pressure, psig (bar): 174 (12)				
Weight fraction catalyst in slurry: 0.20				
Specific heat transfer area, cm ² /cm ³ : 0.10				
*Operating conditions at Rheinpreussen #Cold flow model gas holdup correlation				

Table IX.8						
Optimum gas holdup, gas velocity*, and space-time yield (STY) ($K_L = 0.0205$ cm/s; $U = 2$) (from reference IX.1)						
CASE	$K_o, \text{sec}^{-1} \text{wt}\%^{-1}$	W, %	d_B, cm	$\alpha \text{ opt, vol \%}$	$V_G \text{ cm/sec}$	STY
1	1.4×10^{-3}	20	0.07	6.8	2.13	1.00
2	1.4×10^{-3}	60	0.07	11.2	12.75	2.72
3	6.1×10^{-3}	60	0.07	20.9	36.43	9.42
4	1.4×10^{-3}	20	0.30	13.1	5.29	0.87
5	1.4×10^{-3}	60	0.30	20.7	36.00	2.17
*Using Air Products cold flow gas holdup correlation						

Table IX.9				
Rheinpreussen simulation for staged reaction systems (from reference IX.1)				
NUMBER OF STAGES	1	20	5	20
DISPERSION COEFF., cm ² /s	72.130	128.8	572.5	143.8
Gas Holdup	0.145	0.148	0.158	0.158
Interfacial area, cm ² /cm ³	4.148	12.717	4.514	4.527
Hydrogen Conv., %	66.1	85.1	69.2	69.2
Rel. Mass Transfer Resistance	0.556	0.310	0.542	0.541
Space-Time Yield, mol CH ₂	2,417	3,128	2,529	2,530
Improvement Ratio	1.000	1.294	1.046	1.047
CONSTANTS IN CASE STUDY				
Reactor Length, ft (cm): 26.25 (800)				
Reactor Diameter, in (cm): 59 (150)				
Contraction Factor: -0.5				
Particle diameter, m: 50				
Reactor Pressure, psig (bar): 174 (12)				
Weight Fraction Catalyst in Slurry: 0.20				
Specific Heat Transfer Area, cm ² /cm ³ : 0.30				
Inlet Gas Velocity, cm/sec: 9				
Temperature, C: 260.0				
Preexponential Factor (see wt% in slurry): 3.45 x 10 ⁷				
Activation Energy, kJ/mol: 9417				
Inlet Ratio, mol CO/mol H ₂ : 1.98				
Usage Ratio, mol CO/mol H ₂ : 1.98				

Figure IX.1. Activity of CO₂(CO)₈-based catalysts, fixed bed reactor (240°C, CO/H₂ = 1.0, GHSV = 1000 hr⁻¹, 300 psig).

Figure IX.2a. Effect of syngas versus hydrogen activation on conversion.

Figure IX. 2b. CO/Zr ratio effect on activity.

Figure IX.3. Effect of Co/Zr ratio on bulk activity (gas phase, $\text{CO}/\text{H}_2 = 1$, $\text{SV} = 1000 \text{ hr}^{-1}$, 300 psig).

Figure IX.4. Effect of Co/Zr ratio on specific activity (gas phase, CO/H₂ = 1, SV = 1000 hr⁻¹, 300 psig).

Figure IX.5. Effect of Co/Zr weight ratio on slurry-phase activity of Co/Zr/silica catalysts.

Figure IX.6. Effect of cobalt loading on bulk activity of Co/Zr/SiO₂ Catalyst (fixed bed reactor, CO/H₂ = 1, 1000 hr⁻¹, 300 psig).

Figure IX.7. Effect of Co loading on Co/Zr/SiO₂ performance.

Figure IX.8. Hydrocarbon Schulz-Flory distribution of slurry catalyst A2.

Figure IX.9. Hydrocarbon Schulz-Flory distribution of slurry catalyst B.

Figure IX.10. Bulk activity maintenance - extended slurry test 8862-1-31 Co/Zr/SiO₂, 240°C, CO/H₂ = 0.5, 1.8 L/g/hr, 300 psig.

Figure IX.11. Conversion maintenance - extended slurry test 8862-1-31 Co/Zr/SiO₂, 240°C, CO/H₂ = 0.5, 1.8 L/g/hr, 300 psig.

Figure IX.12. Bulk activity maintenance - extended slurry test 8862-1-31 (Co/Zr/SiO₂, 260°C, CO/H₂ = 1.0, 2.0 NL/g/hr, 300 psig).

Figure IX.13. Conversion maintenance - extended slurry test 8862-1-31 (Co/Zr/SiO₂, 260°C, CO/H₂ = 1.0, 2.0 NL/g/hr, 300 psig).

Figure IX.14. Hydrocarbon selectivity — extended slurry test 8862-1-31 (Co/Zr/SiO₂, 260°C, CO/H₂ = 1.0, 2.0 NL/g/hr, 300 psig).

Figure IX.15. Kinetic data analysis program ($\rho = 0.758 - 0.555 \cdot (T_k - 373)$ (ref. 12); $He_{H_2} = 34.162 \cdot \exp(739.485/T_k) \cdot 14.23$ psia/mol/kg oil (ref. 11); $He_{CO} = 44.583/T_k \cdot \exp(433.391/T_k) \cdot 14.23$; $He_{CO_2} = 119.925 \cdot \exp(-438.926/T_k) \cdot 14.23$; $He_{H_2O} = 275.113 \cdot \exp(-1122.92/T_k) \cdot 14.23$).

Figure IX.16. Fitting $\text{Co}_2(\text{CO})_8/\text{Zr}(\text{OP}_R)_4/\text{SiO}_2$ data.

Figure IX.17. $\text{Co}_2(\text{CO})_8/\text{Zr}(\text{OP}_R)_4/\text{SiO}_2$ activation energy.

Figure IX.18. Staged reaction systems.

Figure IX.19. Hydrogen conversion vs. column height.

Figure IX.20. Bubble column flow regimes.

ATTACHMENT X

Review of Exxon Patents

Edwin N. Givens

and

Burtron H. Davis

ATTACHMENT X

Review of Exxon Patents

INTRODUCTION

It is quite apparent from searching the patent literature that Exxon has been actively involved in conducting research on conversion of synthesis gas to fuels and chemical products for many years. They have used CO as a chemical reactant for producing olefins and alcohols in addition to preparing liquid fuels. Since the mid 1970s the number of patents that have been assigned to Exxon and the types of examples contained in those patents reflect an increasing interest in converting synthesis gas to hydrocarbons. The earlier patents that were obtained during this period contain numerous examples of synthesis gas conversion at ambient pressures that gave very small CO conversions, typically less than 10%. More recently, the data reflect a more sophisticated evaluation of catalysts and the beginning of a string of patents that relate to improvements in equipment and operation. The latter are a result of the operation of a sizable pilot facility at their Baton Rouge Laboratory. These patents have addressed many of the finer points of reactor design.

The search was focused on synthesis gas conversion, i.e. the Fischer-Tropsch reaction, and limited to U. S. patents that were assigned to Exxon that were abstracted by Derwent through mid-1995. There are apparently numerous other patents that were issued to Exxon that relate to CO conversion which are not included, such as those related to conversion of CO to hydrocarbons or alcohols. Exxon's approach to developing a patent portfolio in this technology area is unlike most of their competitors, in that they have obtained an extensive number of composition of matter patents. Supplementing these patents are a large number of process related patents that apply

to either methods for preparing these materials or the use of these compositions in the conversion of synthesis gas. In some of the composition of matter patents that are of interest for synthesis gas conversion, the claimed materials are used for hydrocarbon conversion without mention of their use as catalysts for the FT reaction. Based upon the addresses of the inventors in these various patents, it is clear that significant work on the FT reaction has been going on at Exxon's New Jersey and Baton Rouge laboratories. Although there is overlap in the type of work that was being done in these laboratories, it appears from the timing of the patents that the approaches that were being taken were quite independent. Those differences were apparent from the discussion in the patents regarding various elements of catalyst composition and the claims that are made regarding those compositions.

The Exxon patent portfolio includes a large number of patents on iron and iron-containing catalysts. The majority of these cases relate to compositions that have spinel structures that are isostructural with Fe_3O_4 but contain one or two additional metal atoms, with iron usually being the dominant metal. In these patents, the spinel structures are expressed interchangeably either as $\text{M}_x\text{N}_{3-x}\text{O}_4$ or as $\text{M}_{3-x}\text{N}_x\text{O}_4$, where M is almost exclusively Fe. For consistency, the first format is used exclusively throughout this discussion. Other iron-related catalysts are also covered including catalysts in which the iron, as the oxide, is used as a substrate, and others in which the iron is deposited on other substrates.

There is extensive coverage for catalysts in which titania and titania containing materials are used as metal supports. These include combinations of titania with vanadium, tantalum and niobium oxides (Group Vb) which are used either as intimate mixtures or as coatings on the surface of titania. All of these supports apparently give

rise to unique metal-support interactions that had not hitherto been reported. Other coverage was obtained for titanias that are coated with silica. Some of these patents specify titanias having rutile as the dominant crystalline phase which is favored at high temperatures. One case claims an anatase based catalyst that was stabilized through addition of silicon, zirconium and tantalum. In many of these cases, the catalyst is formed by impregnating the oxides with metals from Group VIII, of which cobalt or ruthenium are the most common. In other cases, addition of rhenium, thorium, cerium, copper, hafnium, zirconium, and uranium is claimed. Although many of the catalysts that are covered in these patents fall into one of the above categories, they have also obtained coverage in several related areas. Catalysts comprising ruthenium or combinations of several Group VIII metals on manganese oxide are covered as are cobalt-manganese spinels. Coverage of catalysts comprising Group VIII metals supported on various oxide supports was obtained which specifically apply to FT type processes.

In almost all of these cases the use of an alkali promoter is also covered, either in the main claim or a dependent claim. Almost without exception, potassium is specified as the alkali metal of choice, although in a few rubidium has been specifically mentioned. Most of the patents specify that the catalysts can be used in either a fixed-bed or a slurry type process, although in some cases they can be applied to both. Generally, powder catalysts are specified for slurry operations while sintered spinel type catalysts apply to fixed-bed type operations. There are, however, cases which claim that the catalysts are useful for either slurry or fixed-bed type operations.

The third area of significant coverage includes various process improvement patents that relate to process equipment or operation, most of which have been

obtained in recent years. These include 2-stage processes, modified feeds, modified reactor designs, methods of reactor operation and methods of catalyst pretreatment. Many of these patents contain data that were taken from highly sophisticated pilot plant operations, some of which were quite large in size.

Iron

A number of patents were issued to Exxon related to the use of iron in FT synthesis. Most apply to catalysts in which the iron is in combination with other metals. However, two patents were issued that apply to the use of iron alone. These were catalysts that were prepared using a laser technique in which volatile iron compounds were thermally decomposed to form iron carbides having particle diameters of less than 0.1 μm . Most of the iron containing catalysts that are covered in these patents relate to spinels in which Fe is combined with different metals in the spinel structure, including cobalt, manganese, zinc, and titanium. Various promoters are also added, including cerium, copper and potassium. Two patents covered catalysts in which thallium was deposited on an iron support, while others covered catalysts prepared by depositing Fe salts onto supports. One covers an Fe/TiO₂ catalyst that was prepared by converting an impregnated Fe salt to the carbided form. Another covered catalyst prepared by decomposing Fe and Co carbonyl compounds in the presence of CO which deposited them onto finely divided supports which were then reduced in H₂.

Particulate Iron Catalysts

A patent issued to Rice et al. (X.99) claims compositions comprising finely divided particles of iron and carbon in absence of Si produced in a reaction zone in the presence of laser radiation under such conditions of laser flux density, power adsorption, concentration of iron reactants, and pressure sufficient to give non-

pyrophoric particles having diameters from 1-100 nm. The iron reactants are selected from iron carbonyls, iron acetylacetonate and ferrocene. A related patent issued to Rice et al. (X.100) claims the same compositions which are subsequently impregnated with $\geq 2\%$ of a promoter selected from a group of salts and oxides of alkali and alkaline earth metals. These patents specify these compositions can be used in either slurry or fixed bed FT reactions. Data were presented in the examples for a fixed-bed catalyst in which the claimed composition was deposited on a refractory MgO support. Laser generated Fe carbide, either with or without K, was found to be considerably more active than Fe carbides generated from either Fe_3O_4 or from mixtures of $\text{Fe}(\text{CO})_5$ and C_2H_4 in the presence of $\text{SiH}_2(\text{CH}_3)_2$ (see Table X.1). The Fe_3O_4 and silane generated carbides have lower CO conversions and higher methane yields while the catalysts of these inventions produce more olefins in the $\text{C}_2\text{-C}_4$ fraction.

A catalyst was illustrated which was prepared by reacting Fe_3O_4 until all of the iron was converted to a carbide phase which was predominantly Fe_5C_2 and Fe_3C . The iron carbide phase was dispersed in a matrix of 40 to 70 wt.% of amorphous carbon. The comparison of the activated Fe_3O_4 catalyst and the laser generated catalyst is for activity for CO conversion on a volume of gas/volume of catalyst basis. The laser generated sample contained 5-15 wt.% of amorphous carbon phase. If we take into account (1) the difference in density of amorphous carbon and iron carbide (factor of 2) and (2) the difference in the amount of amorphous carbon (factor of about 5-8), we calculate that the material produced by the laser technique will contain 10 to 20 times as much iron as the material prepared from Fe_3O_4 . Thus, while the material prepared using the laser technique is about two times as active as the material derived from Fe_3O_4 when the comparison is based on volume of catalyst, it is estimated by us to be 5

to 10 times less active on the basis of the iron content. Furthermore, it has been shown that, under reaction conditions utilized for slurry phase synthesis, a significant fraction of the iron carbide is gradually converted to Fe_3O_4 (X.101) during synthesis. Thus, the relative advantage of the catalyst generated by the laser technique depends upon how it is compared to the precipitated catalyst.

Spinels Containing Fe

The first patents assigned to Exxon that apply to the use of spinel or spinel-derived compositions for converting synthesis gas appeared in 1985. These materials were generally prepared by one of two methods and they had distinctly different morphological features. In one case, high surface area materials were prepared by co-precipitation of salts coupled with moderate heating. These materials have been used directly as slurry catalysts. The second method of preparation involves sintering of metal/metal oxide mixtures at much higher temperatures to give low-surface-area, fused materials, which after grinding and sizing are used directly in fixed bed applications. Hydrogen reduction of either of these products at temperatures of 400°C leads to alloys, which when treated with CO, give high surface area carbides containing considerable carbon inclusion. The reduced and carbided spinels are then used as catalysts in either slurry or fixed-bed applications.

A number of different combination of metal spinels have been patented in this series, all of which, except one, contain iron. In all the Fe cases, the claims cover spinel compositions that allow the use of high concentrations of Fe. From an economical standpoint, this is favorable since the cost of co-metals is generally greater than for Fe. The different Fe-containing combinations that are covered, most of which are promoted with potassium, are:

- ! Fe-Co, either with or without added Cu,
- ! Fe-Mn containing Cu,
- ! Fe-Zn containing Ce or Cu,
- ! Fe-Zn-Ti and/or Mn with Ce and
- ! Co-Mn with Cu.

The only non-Fe containing spinel that was covered was a Co-Mn spinel that is promoted with Cu. This catalyst is discussed with the manganese supported catalysts.

Fe-Co Spinels. Both high and low surface area spinels are covered. High surface area spinel compositions and reduced and carbided iron-cobalt alloy compositions derived from the spinels that are isostructural with Fe_3C and $\chi\text{-Fe}_5\text{C}_2$ are covered in a patent issued to Soled and Fiato (X.102). Because of their fine particle size, the preferred use of these materials is in a slurry process which is covered in a patent issued to Soled and Fiato (X.103). High surface area copper promoted Fe-Co spinel compositions are covered in a patent issued to Soled and Fiato (X.104) while their use as a catalyst in a slurry process is covered in Soled and Fiato (X.105). Low-surface area Fe-Co spinel compositions are claimed by Fiato et al. (X.106) and their use as catalysts in a fixed-bed process is claimed by Fiato et al. (X.107). The use of the carbided and reduced form of these low-surface area Fe-Co spinels in a slurry phase process is claimed by Fiato and Soled (X.108). No patents were found that contain claims related to low-surface area Cu-promoted Fe-Co spinels.

Fe-Mn Spinels. High surface area K and Cu promoted Fe-Mn spinels are covered in a patent issued to Fiato and Soled (X.109). The use of this spinel as catalyst in a slurry process is covered in Fiato and Soled (X.110) and in a fixed-bed process in Iglesia et al. (X.111). The corresponding low surface area spinels derived from sintering

mixed oxides was covered in a prior patent issued to McGrath and Rubin (X.112) and assigned to Kellogg. An alternative method for forming Fe-Mn alloys directly at low temperature without going through the spinel is covered by Soled et al. (X.113).

Fe-Zn Spinels. Two patents comprising compositions of Fe and Zn using different promoters were issued. In one patent compositions comprising sintered combinations of metal oxides of Fe and Zn promoted with Ce and K are covered in Gates and Fiato (X.114). In the other, compositions containing Fe and Zn promoted with Cu and K are covered in Soled et al. (X.115).

Fe-Zn Spinels with Ti and/or Mn. Compositions comprising sintered combinations of metal oxides of Fe, Zn, Ti, and/or Mn promoted with K and Ce are claimed in Fiato et al. (X.116).

Fe-Co Spinels

Seven patents assigned to Exxon relate to Fe-Co spinels, five of which were issued either from applications filed on December 14, 1983, or were continuations-in-part of applications filed on that day. Cross reference was also made to applications which apparently never issued as patents. The series of seven patents that did issue fit into three different groups with at least two patents being in each group. One of the groups relates to Cu promoted Fe-Co spinels while the other two groups relate to Fe-Co spinels that are prepared by two different methods. In one group the spinels are prepared by sintering mixtures of metal-metal oxides while in the other, spinels are prepared by precipitating metal oxides from the respective metal salt solutions. In each of these three groups, two of the patent specifications are identical differing only in their claims. In the one group that includes a third patent, the specification differs only slightly from the other two. For each of the three groups, one patent is a composition of

matter case for a specific Fe-Co containing spinel and the other(s) claims either a fixed-bed or slurry process that employs the claimed catalyst composition.

The empirical formula of the spinels claimed in these cases can be written as $\text{Fe}_x\text{Co}_{3-x}\text{O}_4$ where compositions having x-values ≥ 2.4 or 2.7 are claimed. Prior art existed for structures having x values of 2, i.e. Fe_2CoO_4 (X.117). Among the various spinel compositions that were patented, there appears to be a pattern of obtaining coverage for both slurry and fixed-bed type FT processes. In the case of the Fe-Co spinels, specific claims are made to fixed-bed processes using catalysts derived from spinels prepared by sintering metal-metal oxide mixtures. These are classified as having low surface areas (less than $5 \text{ m}^2/\text{g}$). For slurry processes, patents were issued that claim use of catalysts derived from both low surface area spinels as well as those prepared by precipitating metal oxides from the respective metal salt solutions. This latter group is classified as high surface area spinels having surface areas greater than $5 \text{ m}^2/\text{g}$. In these Fe-Co spinel cases, patents were not found that claim the use of high surface area spinels in a fixed-bed process, although such claims were obtained for Fe-Mn spinels, which are discussed below.

High surface area spinel compositions are covered in a patent issued to Soled and Fiato (X.4) that claims Group 1A or IIA promoted high surface area spinels having compositions $\text{Fe}_x\text{Co}_{3-x}\text{O}_4$ with x-values ≥ 2.4 and BET surface areas $>5 \text{ m}^2/\text{g}$. A second composition in this same patent, given in claim 20, comprises reduced and carbided iron-cobalt alloy that is isostructural with Fe_3C and has a BET surface area $>5 \text{ m}^2/\text{g}$. A third independent claim covers compositions that are isostructural with $\chi\text{-Fe}_5\text{C}_2$ having surface areas $>5 \text{ m}^2/\text{g}$ that are produced by carbiding iron-cobalt alloy which is isostructural with alpha Fe and has a BET surface area $>5 \text{ m}^2/\text{g}$, which is produced by

reducing the high surface area spinel composition. Therefore, compositions are claimed that include the spinel, the reduced alloy and the resulting carbided alloy. The specification is even broader in that it anticipates the application of the spinel, the alloy and the reduced-carbided spinel in either a fixed-bed or slurry-type process. The corresponding process related patent issued to Soled and Fiato (X.5) claims a slurry process that uses the catalyst that is claimed by Soled and Fiato (X.4). The two specifications are identical except for the claims. Although there is a slight difference in the spinel compositions that are claimed in these two cases, in that Soled and Fiato (X.4) claim spinels having Fe/Co ratios $\geq 4/1$ while Soled and Fiato (X.5) claims Fe/Co ratios $\geq 7/1$, this would not likely have any real impact on the application of the invention.

Low surface area Fe-Co spinel compositions are covered in a patent issued to Fiato et al. (X.8) that claims hydrocarbon synthesis catalyst compositions comprising an unsupported, Group Ia or IIa metal salt promoted low-surface area iron-cobalt spinel, an initial empirical formula $\text{Fe}_x\text{Co}_{3-x}\text{O}_4$, where x is ≥ 2.625 , a powder X-ray diffraction pattern isostructural with Fe_3O_4 and having an initial BET surface area $< 5 \text{ m}^2/\text{g}$. Various dependent claims are included such as the use of diluents like silicas, aluminas, titanias, oxides of La, Ce, Cr, and Mn and mixtures including zeolites, glasses, etc. K_2CO_3 is claimed as a promoter and potassium promoted compositions are claimed that are substantially carbided by contact with CO/H_2 at elevated temperatures. Two process patents were issued that are related to use of low-surface area spinel compositions in synthesis gas conversion reactions. One patent, issued to Fiato et al. (X.9), claims a process for synthesizing hydrocarbons containing C_2 - C_6 olefins by contacting a fixed-bed of catalyst, having the initial spinel composition specified in Fiato et al. (X.8), with

synthesis gas. The specifications of Fiato et al. (X.8) and Fiato et al. (X.9) are identical, except for different claims. The second process patent issued to Fiato and Soled (X.10) claims a slurry process utilizing the carbided and reduced unsupported spinel of Fiato et al. (X.8), which reflects the need to *ex situ* pretreat the spinel before placing it in the slurry reactor.

Catalyst preparation

The following method was used to illustrate the preparation of several of the high surface area spinels. A solution containing Fe and Co nitrate salts and an ammonium α -hydroxy carboxylic (glycolic) acid was evaporated and the recovered solid was heated at 350°C for 2 hours and then impregnated with K_2CO_3 and dried. The material, prior to impregnation with potassium, had a very small particle size, an x-ray diffraction pattern isostructural with Fe_3O_4 , and surface area $>100\text{ m}^2/\text{g}$. The specification refers to prior art for the preparing of Fe_2CoO_4 ¹⁹ that involved evaporating aqueous solutions of metal glycolates, lactates, and tartarates to dryness. The prior art apparently limited claims to Fe/Co ratios > 4 .

The invention was illustrated for various low-surface area spinels prepared by sintering mixtures of metal oxides and metals in combinations having the stoichiometric composition necessary to provide the correct empirical formula. Sintering is done first in an inert or vacuum atmosphere at temperatures preferably from about 800 to 900°C for about 8 to 24 hours. The material is then exposed to air and heated an additional 24 hours until the x-ray diffraction pattern of the material is isostructural with Fe_3O_4 . Sintered pellets are crushed, sieved and then impregnated with aqueous potassium carbonate to a 1% K loading providing a material having a surface area of 0.25-0.30 m^2/g .

Reduced and carbided slurry catalysts are prepared starting with both high and low-surface area spinels. The preparation starting with low-surface area spinel is described in Fiato and Soled (X.10) and the preparation from high-surface area spinel is described in Soled and Fiato (X.4). In both cases, the respective spinel powders were reduced at 400°C in H₂ for 4 hours to produce an alloy, which was passivated with dilute oxygen. These materials had surface areas of 3 and 8 m²/g and x-ray diffraction patterns isostructural with alpha iron. The active catalyst was produced by carbiding the alloys in dilute synthesis gas and passivating with dilute oxygen to give products having x-ray diffraction patterns isostructural with chi Fe₅C₂ and BET nitrogen surface areas of 118 and 173 m²/g. The resulting catalysts contained 60-70% carbon and had the composition Fe_{2.85}Co_{0.15}O₄/1 wt.% K.

The form of the active catalyst generated by these two different preparative methods was not differentiated from each other. Both, after reducing and carbiding, give materials that are isostructural with chi-Fe₅C₂ or Fe₃C, apparently contain sizable amounts of carbon, and have surface areas >100 m²/g.

Slurry Catalysts. A number of examples were provided in the five cases which illustrate the use of catalysts derived from spinels for converting synthesis gas.

Catalysts to be used in slurry reactors were pretreated in various ways before being placed in the slurry reactor and exposing them to synthesis gas at reaction condition.

The methods of pretreatment included:

- ! Adding the spinel to the slurry reactor and reducing in H₂ before exposure to synthesis gas;
- ! Reducing and carbiding the spinel *ex situ* before introducing into the reactor;

! Reducing the spinel in H₂ to form the alloy before introducing into the reactor.

Conversion and product distribution data were provided for each of the respective catalysts and compared with data obtained on a high surface area Fe₃O₄/1%K catalyst that was prepared in the same manner as the high surface area spinel.

There was a big difference in the activities of the *in situ* treated spinel slurry catalysts. The high surface area Fe-Co spinel oxide that was reduced *in situ* with flowing H₂ (1 atm) for 1 hour at 200°C gave 60% CO conversion, whereas both the high surface area Fe spinel and the low-surface area Fe-Co spinel that were pretreated in the same way were inoperable. They gave CO conversions of only 8 and <4%, respectively (see Table X.2). *Ex situ* treatment had little effect on CO conversion of the high surface area spinel derived catalyst which gave essentially the same CO conversion as the *in situ* treated spinel, namely 64 and 60%, respectively. By contrast, *ex situ* treatment of both the low-surface area Fe-Co spinel and Fe spinel catalysts improved their activity, giving 42 and 65% CO conversion, respectively. Apparently insufficient carbided catalyst was formed in the *in situ* pretreatment of the low-surface area spinel, whereas the *ex situ* treatment was sufficiently severe to convert the low-surface area spinel to the carbided form. In the comparisons that were provided, the Fe-Co spinels produced more C₅+ hydrocarbons and less C₂-C₄ olefins than the Fe spinel catalysts. Although data with a 2/1 H₂/CO synthesis gas mixture in Table X.2 on *ex situ* treated catalysts indicate a difference between the CO conversion of the reduced-carbided low- and high-surface-area Fe-Co spinel derived catalysts, i.e. 42 and 64% conversion, respectively, other data with a 1/1 H₂/CO synthesis gas mixture showed no difference in activity (see Table X.3). The latter data indicate that the *ex situ*

reduced and carbided high- and low-surface-area Fe-Co spinel derived catalysts, as well as the activity of the *ex situ* reduced and carbided high-surface-area Fe spinel catalysts, have essentially the same activity. The activity of the *ex situ* low-surface-area Fe-Co spinel and the lack of activity for the *in situ* treated low-surface-area spinel appears to be one reason why Fiato and Soled (X.10) claim a slurry process utilizing only the carbided and reduced low-surface area spinel.

Alloys active for CO conversion are formed by reducing the high-surface-area Fe-Co spinel *ex situ* with H₂ at 350°C for 12 hrs followed by further reduction with H₂ at 400°C for 24 hrs. CO conversions with either 1/1 and 2/1 H₂/CO synthesis gas mixtures were higher than the correspondingly reduced Fe-only spinel, as shown in Table X.4. Although the correspondingly reduced high surface area Fe-only spinel was not quite as active as the Fe-Co alloy, its selectivity for CO₂ production was much smaller. The hydrocarbon selectivity of the Fe-Co spinel was greater and its methane and C₅+ selectivities were less than for the Fe-only spinel. In this series of patents, no claims were made nor information provided on alloys produced from reduced low-surface area Fe-Co spinels.

Fixed-Bed Catalysts. Only catalysts prepared from low surface area Fe-Co spinels were used as fixed-bed catalysts. Although high-surface area spinel derived catalysts were anticipated for use in fixed-bed reactors, no claims nor examples were found that relate to such usage. An example was provided in which low-surface area Fe_{2.85}Co_{0.15}O₄ spinel was reduced at 500°C with a mixture of 90% H₂ in N₂ at 100 psig for 5-7 hrs before exposing to synthesis gas. It was more active for CO conversion than a comparably prepared and treated Fe₃O₄/1%K spinel, as shown in Table X.5. At a run temperature that was 35°C lower than the control sample, the Fe-Co conversion of

CO was higher than for the Fe-only catalyst at the same space velocity. Both CO₂, hydrocarbon yields and olefin content in the C₂-C₄ fraction were higher for the Fe-Co catalyst while the C₅+ and C₆+ products were greater for the control.

In all the Fe-Co spinel patents, there was only one example of a spinel having an Fe-Co concentration that did not fall within the claimed limits. That spinel, having an x value of 2.20, falls below the 2.4 value specified in the claims. The CO conversions and hydrocarbon yields were essentially the same for this catalyst as for those that fell within the claimed limits, i.e. x values either ≥ 2.4 or > 2.625 , both of which were used in different patents (see Table X.6). Regardless, all of these catalysts had Fe/Co ratios that were greater than 2 (x value 2.0), which was consistent with the prior art value discussed above.

In almost all of the patents regarding the FT reaction that are assigned to Exxon, only a few discuss the exotherm that is observed in any of the experimental reactors. In one of the patents, assigned to Fiato et al. (X.8) claiming Fe-Co spinel derived materials as catalysts for fixed-bed FT reactors, the exotherms observed in those reactors are discussed. Actual maximum bed temperatures are given for runs in which furnace temperatures were from 225 to 290°C. In these runs made with a cobalt spinel having an x value of 2.625 (Fe_{2.625}Co_{0.375}O₄/1 wt.% K), exotherms of 8 to 44°C were observed at 240°C and 290°C, respectively (see Table X.7). Over this range the corresponding CO conversion increased from 31% to 97%. The CO conversion follows the same trend as does the difference between the furnace and bed temperatures. At the higher temperature, the hydrocarbon selectivity deteriorated resulting in increased conversion to methane, whereas at the lower temperature the olefin selectivity was higher, i.e. 55.3% versus 37.1%, and the C₆+ yield was also higher. The effect of furnace

temperature at 235 and 270°C for a $\text{Fe}_{2.85}\text{Co}_{0.15}\text{O}_4$ /1 wt.% K spinel, where $x = 2.85$, is also shown in Table X.7. In this case the actual bed temperatures were not reported but can be assumed to be about the same as for runs made at the same temperature. The CO conversion and CO_2 and hydrocarbon yields for the $x = 2.85$ spinel were essentially the same as for the $x = 2.625$ spinel. At high conversion, hydrocarbon selectivity of the $x = 2.85$ spinel was better giving less methane, more C_6+ , and more C_2 - C_5 olefin yields. This provides further evidence that lower cobalt concentration provides better yields.

Copper promoted Fe-Co spinels. Two patents claim Cu promoted Fe-Co spinels as slurry phase catalysts. A patent issued to Soled and Fiato (X.6) claims compositions comprising a reduced-carbided Cu-promoted Fe-Co alloy, produced by contacting a Cu-promoted Fe-Co alloy with a carbiding atmosphere, which was prepared by reduction of a Group Ia or Group IIa metal salt promoted Fe-Co spinel possessing a BET surface area greater than $5 \text{ m}^2/\text{gm}$. The spinels correspond to high surface area spinels prepared by precipitating the Fe and Co nitrate salts, as presented in Soled and Fiato (X.4). A corresponding patent issued to Soled and Fiato (X.7) which, except for the claims, is identical to Soled and Fiato (X.6) claims a slurry process using a catalyst comprising an unsupported Cu-promoted Fe-Co spinel having an initial BET surface area $>5 \text{ m}^2/\text{g}$ and a Fe/Co ratio $\geq 4/1$.

Copper promoted spinels are prepared by impregnating Fe-Co spinel with an aqueous solution of cupric nitrate, drying, and then impregnating with an aqueous solution of K_2CO_3 followed by a final drying to give a composition of $\text{Fe}_{2.85}\text{Co}_{0.15}\text{O}_4$ /(1 wt.% K, 1 wt% Cu). *Ex situ* carbided catalysts were prepared by reducing the spinel in a 40% H_2 , 20% CO and 40% He containing stream at 400°C for 24 hrs. After cooling to

room temperature, the oxygen (1%) passivated sample gave an X-ray diffraction pattern isostructural with Fe_5C_2 , had a BET surface area of $150 \text{ m}^2/\text{g}$, and contained 40-50% carbon. Corresponding Co-free and carbided spinels were also prepared by the same method.

Examples were included which illustrate the use of these spinels as catalysts in a slurry reactor both in *in situ* unreduced as well as *ex situ* carbided forms. CO conversion for the *in situ* reduced catalysts followed the sequence Cu/K-promoted Fe-Co spinel > K-promoted Fe-Co spinel > Cu-free Fe spinel (see Table X.8). However, data were not provided that showed relative selectivities for hydrocarbon versus CO_2 formation. The CO conversion activities of the *ex situ* carbided-reduced Fe and Fe-Co spinels were quite similar as were the methane and $\text{C}_2\text{-C}_4$ olefin selectivities. The olefin concentrations (52-59%) in the C_{10} fractions from these catalysts were quite high.

Iron - Manganese Spinels

A composition of matter and three process related patents assigned to Exxon cover iron-manganese spinels. Two cases that were originally filed on December 20, 1983 were abandoned and refiled in December 1985. Both applications resulted in patents that issued in 1986. Apparently at some time during the application process, claims for a fixed-bed process were split from the slurry bed process application and refiled as a separate application. The latter fixed-bed application was subsequently abandoned, refiled and again abandoned before being refiled in 1990, which apparently resulted in a patent covering a fixed-bed process. Unlike the Fe-Co spinel cases, only high-surface-area Fe-Mn spinels were covered, since prior art appears to preclude coverage for Fe-Mn spinels prepared by sintering mixtures of iron oxide and manganese oxide.

The first patent in this series, issued to Fiato and Soled (X.11), claims compositions comprising an unsupported Group Ia or Group IIa metal and copper promoted Fe-Mn spinel having a BET surface area $>30 \text{ m}^2/\text{g}$, an Fe/Mn ratio >2 , and an empirical formula of $\text{Fe}_x\text{Mn}_{3-x}\text{O}_4$, where x is >2 . The second patent issued to Fiato and Soled (X.12) is identical to Fiato and Soled (X.11), except for the claims, and claims a slurry FT process using a catalyst comprising the composition of Fiato and Soled (X.11). The third patent issued to Iglesia et al. (X.13) claims a fixed-bed FT process using a catalyst comprising the composition of Fiato and Soled (X.11) in a pelletized form.

In the examples, a high-surface area Cu-K promoted $\text{Fe}_{2.25}\text{Mn}_{0.75}\text{O}_4$ spinel was prepared by combining Fe and Mn nitrate, in a molar ratio of 3/1, with a solution of ammonium glycolate having a pH of 6.5 in a ratio to give a total metal ion to glycolate ion ratio of 1/1. Water was removed at room temperature and the solid was air calcined at 175°C for 2 hours to produce the spinel having a surface area $>50 \text{ m}^2/\text{g}$. Promoter was added by impregnating the spinel with 2 atomic % K and 1 atomic % Cu. Interestingly, a paper that appeared in 1985 by Maiti et al., (X.118) at about the same time that the final application was filed, also reported preparing Fe-Mn spinels by base precipitation of Fe and Mn nitrate salt solutions. The reduced and carbided form of the resulting solids, none of which contained promoters, was active for FT synthesis gas conversion. Even though the Maiti paper disclosed materials related to the claimed compositions, it apparently did not preclude the issuing of a patent for these compositions.

Under slurry conditions, the high surface area K-Cu dual-promoted Fe-Mn spinel gave higher CO conversions than either the comparable K or Cu promoted spinels, as shown in X.Table 9. At half the catalyst loading, CO conversion for the Cu promoted

catalyst was higher at 69% than the 34% and 36% conversion for the K-promoted catalyst. The methane selectivity was also favorable in that it was lower for the dual promoted catalyst. The effect of Fe-Mn ratio is shown in Table X.10. CO conversions for Cu-K promoted spinels having Mn concentrations with x values >2, as claimed in this patent, were higher than for two spinels having x values of 0.25 and 1.5, which were below the Mn concentrations in the compositions claimed in this patent.

Unlike patent coverage for the Fe-Co spinels, which claimed both high and low-surface area compositions, none of the patents assigned to Exxon claimed compositions or processes comprising low-surface area Fe-Mn spinels as catalysts or precursors to catalysts for synthesis gas reactions. Such catalysts are apparently covered by a previous patent issued to McGrath and Rubin (X.14), and assigned to Kellogg, which claims a process for converting synthesis gas using a catalyst comprising elementary Fe with manganese oxide and alkali compound as promoters. Fiato and Soled (X.11) showed that a reduced low-surface area Fe-Mn composition reported by McGrath and Rubin (X.14) was inactive for CO conversion in the slurry process. This composition had an empirical formula of $\text{Fe}_{2.86}\text{Mn}_{0.14}\text{O}_4/0.7$ atomic % K and was prepared by sintering a paste of $\text{Mn}(\text{NO}_3)_2$ and Fe_3O_4 containing K_2CO_3 at 1400°C for 6 hrs and reducing with H_2 at 371°C for 48 hrs. For comparison, two low-surface area ($<5 \text{ m}^2/\text{g}$) K and K-Cu promoted Fe-Mn spinels were evaluated. They were prepared by fusing a mixture of Fe_2O_3 , Fe and Mn_3O_4 at $800\text{-}1000^\circ\text{C}$ for 48-72 hours and impregnating with K or with K and Cu to give spinels having a composition of $\text{Fe}_{2.25}\text{Mn}_{0.75}\text{O}_4$ and containing 2 atom % K or 2 atom % K/1 atom % Cu. Both of these materials were inactive for CO conversion in the slurry process (see Table X.9). However, based upon the fact that reduced and carbided low-surface area Fe-Co

spinel is quite active for CO conversion in the slurry process (see Table X.3), similarly pretreated Fe-Mn spinels may also be active; however, such information was not provided.

The use of glycolate in the production of the $\text{Fe}_x\text{Mn}_{3-x}\text{O}_4$ spinel is covered in an independent claim that specifies the use of α -hydroxy aliphatic carboxylic acid. The spinel prepared in the examples using glycolate, as the carboxylic acid, was more active than spinel prepared by precipitating a solution of the salts using ammonium hydroxide. The latter spinel was prepared by calcining at 500°C. The CO conversion for the glycolate spinel was 68.9% versus 20.5% for the ammonium hydroxide prepared spinel.

Another related patent issued to Soled et al. (X.15) claims a process for producing powdered metal-based iron alloys which are structurally the same as prepared by reducing $\text{Fe}_{2.25}\text{Mn}_{0.75}\text{O}_4$. This method comprises heating a mixture of powdered mixed metal oxide with a stoichiometric amount of calcium metal in an inert atmosphere at 850°C for 72 hours, leaching out the Ca and calcium products with an aqueous acid and recovering the metal-based alloy. The other method used by Fiato and Soled (X.11) involves sintering the metal oxides at 1000°C to form the alloy.

The patent issued to Iglesia et al. (X.13) claims a fixed-bed FT process using a catalyst comprising the Cu-K-promoted Fe-Mn spinel composition in a pelletized form. Comparison between a fixed bed and slurry operation for this catalyst indicates the slurry catalyst gives higher conversion, similar CO_2 selectivity, and lower methane and higher C_5+ olefin yields (see Table X.11).

Fe - Zn Spinels

A patent issued to Gates and Fiato (X.16) claims a sintered combination of metal oxides having the following components (preferred metals) from Group VIII (Fe), Group

IIB (Zn), Group IA (K), and the Lanthanum Group (Ce). Although there are no limits on the claimed composition, the only catalyst prepared in the examples had an empirical formula of $\text{Fe}_{2.81}\text{Zn}_{0.19}\text{O}_4\cdot\text{Ce}_{0.08}\text{K}_{0.08}$ (atom ratio of 1.0/0.065/0.03/0.03). This corresponds to an Fe_2O_3 concentration of 87 wt.%, which, surprisingly, falls outside the 5-80 wt.% range specified in the independent claim 7. The spinel catalyst was prepared by sintering a mixture of Fe_2O_3 , ZnO, and CeO_2 at $\sim 1050^\circ\text{C}$ in air for 24 hours. It had a BET surface area $< 2 \text{ m}^2/\text{g}$ and XRD indicated it was a highly crystalline mixture of mixed spinels and iron oxides in a CeO_2 phase. The composition is very similar to the Fe/Zn/Ti-Mn spinels that are discussed below. The spinels were reduced in H_2 at 500°C for 7 hours, after which they were passivated by exposure to oxygen at 25°C . The reduced form still contained unreduced metal oxides as shown by X-ray diffraction analysis. The passivated reduced catalysts, after preheating in H_2 in a fixed bed reactor at 500°C , gave the same level of CO conversion as a Zn and Ce-free 1% K/ Fe_2O_3 that was prepared in the same way. The Zn-Ce containing catalyst gave lower methane and higher C_7+ liquid selectivity in addition to producing a higher yield of CO_2 , as shown in Table X.12.

Another patent issued to Soled et al. (X.17) claims compositions comprising Fe, Zn, and Cu and one member chosen from the group of K, Rb, or Cs wherein the Fe/Zn atomic ratio is ≥ 5 and the alkali metal/Cu atomic ratio is ≥ 2 . The claim specifies spinel compositions having empirical formulas of $\text{Fe}_x\text{Zn}_{1-x}\text{O}_4$ with x values ≥ 2.5 . Although compositions having single phase spinel structures are preferred, the compositions claimed in the patent are not limited to a method of preparation, specific structures or any morphological feature. A corresponding patent, having an identical specification, issued to Soled et al. (X.119) claims a FT process utilizing these catalyst compositions.

Only methods that generate high surface area materials were used in the examples to demonstrate the preparation of three different spinel compositions, i.e. $\text{Fe}_{2.8}\text{Zn}_{0.2}\text{O}_4$, $\text{Fe}_{2.45}\text{Zn}_{0.55}\text{O}_4$ and $\text{Fe}_{2.3}\text{Zn}_{0.7}\text{O}_4$. Only the first catalyst, which was prepared by two different methods, fell within the range specified in the claims. All three catalysts were prepared by mixing a solution of iron nitrate and zinc nitrate with an ammonium glycolate solution having a pH of 6.5, forming a precipitate, and drying and heating in air at 350°C/1 hr. The resulting spinels were impregnated with K_2CO_3 and $\text{Cu}(\text{NO}_3)_2$ and dried in a similar fashion. The second $\text{Fe}_{2.8}\text{Zn}_{0.2}\text{O}_4$ spinel was prepared by adding ammonium hydroxide to a solution of iron nitrate and zinc nitrate to a final pH of 9. The washing, drying and impregnation steps were the same.

Although the catalysts were claimed to be useful in either fixed-bed or slurry FT reactors, the examples included only slurry reactor applications. The effect of promoter on synthesis gas conversion of Cu, K and Cu-K promoted $\text{Fe}_{2.8}\text{Zn}_{0.2}\text{O}_4$ showed that the K/Cu promoted catalyst gave higher CO conversion and methane selectivity, as shown in Table X.13. Surprisingly, the highest CO conversion was observed for a spinel having a Fe/Zn ratio less than 5 which falls outside the claimed composition range. It is not clear why this composition was not included in the claimed range of compositions.

Comparative performance tests of the zinc ferrite based catalysts were conducted with 2g samples of catalyst and 72g of octacosane in a 300 cc Parr CSTR. The synthesis gas ($\text{H}_2:\text{CO} = 2:1$) feed rate was 180 cc/min at 75 psig and 270°C. Activation was accomplished by heating up to and at 270°C in synthesis gas. Nitrogen (20 cc/min) was added as an internal standard. The superficial space-velocity (V/V/hr) based on an initial catalyst density of 1.8 g/cc was approximately 15,000 V/V/hr. CO conversions in excess of 60% were maintained during initial 80 hr test. Methane

selectivity of 4.5% (CO₂ free) was obtained. C₅₊ selectivities were >75% on a CO₂ free basis. On this basis, the space velocity (including 20% inert gas) was about 6 NL/hr-g catalyst (Table X.14); this compares favorably with the activity of cobalt catalysts discussed later. The Exxon workers report that the pressure useful in the process will range between 150 and 450 psig and preferably 250 and 400 psig. They state that higher pressures can be used but these can lead to high levels of condensed water which can retard activity. This statement implies that the catalyst either has low water-gas shift activity or is being operated under conditions where the fraction of CO converted to hydrocarbons, and not CO₂, is very high.

Fe-Zn-Ti and Fe-Zn-Mn Spinels

A patent issued to Fiato et al. (X.18) claims compositions comprising sintered combinations of metal oxides taken from Group VIII (Fe), Group IIb (Zn), Group IVb (Ti) and/or Group VIIb (Mn), Group Ia (K), and the Lanthanum Group (Ce) such that the sintered combinations comprise a series of spinels of Group VIII (Fe), Group IIb (Zn), Group IVb (Ti) and/or Group VIIb (Mn) and a Group Ia metal oxide in a lanthanum group oxide matrix. The preferred metals are shown in parenthesis. There were specific limits on concentration of the metal oxides in the mixture which are quite similar to the sintered combination in Gates and Fiato (X.16) which included Fe, Zn, Ce and K. In that case, the only limits on concentrations of the metals were in a subordinate claim. The sintered catalysts are red-brown or red-purple, have BET surface areas ≤ 2 m²/g and are highly crystalline. The crystalline phase comprise hematite, magnetite, ilmenite, a series of mixed spinels and CeO₂. A corresponding identical patent issued to Fiato et al. (X.120) claims a FT process utilizing this catalyst.

The catalysts are prepared, as in Gates and Fiato (X.16) by sintering a mixture of oxides having the correct atomic ratio and reducing in H_2 at $500^\circ C$ for 6 hrs. The K, Ce, and K/Ce catalysts in a fixed-bed reactor configuration had CO conversion activities that varied with the promoter following the order $K/Ce > Ce > K$, as shown in Table X.15. At a reasonable CO conversion level the C_2 - C_3 olefin selectivity was high and the methane selectivity was lower for the K/Ce spinel. Data were also given at higher reactor temperature, i.e. $305^\circ C$, as well as at lower space velocity, which resulted in excess of 80% CO conversion with high olefin concentrations in the C_2 - C_4 fraction plus a sizable yield of C_5+ product.

K, Ce and K/Ce catalysts having compositions in which Ti was replaced with Mn were also included. The atomic ratio of the metallic components in the catalyst containing both K and Ce was 1.0 Fe/1.0 Mn/0.07 Zn/0.05 K/0.04 Ce. On a weight basis, this composition (43.6% Fe_2O_3 /48.2% MnO_2 /3.1% ZnO/1.2% K/3.8% Ce) is excluded from being a covered composition since it fell outside the specified composition in the main claim. Specifically, the MnO_2 composition of 48.2 wt.% of the total oxides is excluded, unless there is an error in the composition as stated in Example 6, since the claims specify a range for MnO_2 of 10 to 40 wt.% of the combination. The performance of the K, Ce and K/Ce promoted Fe/Mn/Zn spinels in a fixed-bed reactor configuration are shown in Table X.16. The K/Ce dual promoted spinel provides high activity, low methane selectivity and high C_2 - C_3 olefin selectivity.

Thallium Impregnated Iron Supports

Two patents were issued regarding thallium and iron catalysts. One is a composition of matter case issued to Wright (X.121) and the second, a process patent issued to Wright et al. (X.122). Both cases involved several filings and abandonments;

there is also a difference in the inventors for the two cases. Overall, the texts in these two are very similar, though not identical. The main claims cover all Fe-Tl compositions wherein the thallium compound, being supported or unsupported, is substantially deposited on the surface of the iron compound, with the iron compound in the trivalent state. Included in a dependent claim is incorporation of promoters including Co, Zn, Cr, Mn, Ba and Group I metals.

The main claim appears confusing since it states that the thallium may be both supported and unsupported but is also substantially supported on the surface of the iron. The examples contain numerous examples in which the thallium was impregnated onto the surface of the iron, however one catalyst was prepared by impregnating a melt of ferric nitrate and thallium nitrate onto a magnesium-alumina spinel. This presumably is a supported example. Also, there is nothing in the claims regarding pretreatment of the catalyst to reduce the Tl and Fe to the metallic or carbided forms, although a number of different methods for preparing the catalysts are included in the examples.

Several techniques for preparing Fe/Tl catalysts were presented in the examples. Several Fe-Tl catalysts were produced having Fe/Tl ratios from 10/1 to 2.5/1 by precipitating solutions of ferric nitrate with ammonium carbonate and impregnating the washed and dried solids (110°C for 12 hrs in air) by an incipient wetness method with solutions of thallium nitrate or thallium chloride. Examples were also given for preparation of other Fe/Tl catalysts supported on alumina, cesium-doped and magnesia-doped aluminas, and commercially available iron oxide. Examples explaining the preparation of several fluoride impregnated catalysts were also provided. Test results were provided on only a limited number of these preparations.

All of the Fe-Tl catalysts that were prepared in the examples were run under FT conditions that gave CO conversions up to 97%. The product contained large concentrations of liquid hydrocarbons in the C_5 - C_{11} range that was rich in olefins and contained a lesser amount of aromatics. Data for a 10 Fe/1 Tl catalyst prepared by precipitating ferric nitrate and impregnating the resulting solid with thallium nitrate and reducing at 270°C/18 hrs are shown in Table X.17. Over a range of temperatures from 270 to 350°C, the maximum C_6 + yield at CO conversions >90% was ~20% with methane yields ranging between 6 and 15%. CO conversion is very dependent on space velocity, however, methane, C_5 - C_{11} liquid, C_1 - C_4 gas, alpha-olefin and aromatic selectivities are only weakly dependent on space velocity. It was suggested that the aromatics yield is probably related to conversion of olefins. None of the examples provided any data on CO_2 yields.

The performance of two Fe-Tl catalysts in the FT reaction was compared with an Fe/K and a commercial ammonia synthesis catalyst. Two Fe-Tl catalysts, having Fe/Tl ratios of 10/1 and 5/1, were prepared by precipitating ferric nitrate and impregnating the resulting solid with thallium nitrate. The method for preparing the Fe/K catalyst that contained 4% K is not clear and no further description of the commercial ammonia synthesis catalyst was given. Selected results from runs presented in Example 9 in the patent are shown in Table X.18. In the patent, in several instances, differing sets of results are given for the same run condition without any explanation. For example, included in Table X.18 are two sets of data that were both taken at 350°C and 300 GHSV for the 10 Fe/1 Tl catalyst. Due to the lack of clarity in the presentation of the data, it is difficult to draw any conclusions regarding the CO conversion activities of these various catalysts. However, the product selectivities in these runs are quite

similar. The discussion in Example 9 of the patent states that CO conversions were initially in the 80-98% range. Whereas the Fe/0.4K catalyst appeared to lose activity after about 18 hours on stream, conversion for the Fe/Tl catalyst decreased to only 40-60% after several days on stream. The selectivity for the 10 Fe/1 Tl catalyst appears to be maximum at 270°C at a CO conversion of 46.8%.

Iron - Cobalt Impregnated Slurry Catalysts

A patent issued to Fiato et al. (X.123) claims a process for preparing a slurry FT catalyst system in which an Fe-Co catalyst is formed (in situ) in the absence of air. A corresponding identical patent, except for references and claims, issued to Fiato et al. (X.124), claims a FT process utilizing this catalyst system. The catalyst is prepared by adding Fe and Co carbonyl compounds, or Fe and Co compounds which are capable of forming carbonyl complexes, in a CO atmosphere, along with a powdered support, to a hydrocarbon liquid. The iron and cobalt compounds are present in a ratio of from 35:1 to 1:10. This combination is decomposed in the presence of CO such that the cobalt complex is decomposed to the metal at a lower temperature followed by decomposition of the Fe complex at a higher temperature. The slurry is heated in H₂ to reduce the metals and their decomposition products. Representative complexes are Fe₃(CO)₁₂, bis(dicarbonylcyclopentadienyliron), [CpFe(CO)₂]₂, and Co₂(CO)₈. Potassium carbonate, that promotes olefin formation in the reaction and decreases the formation of methane, may be added to the mixture in the first step.

In the examples in the patent, [CpFe(CO)₂]₂ and Co₂(CO)₈ were added to the reactor either alone or in the presence of a support. In each case shown in Table X.19, the absolute amount of Fe and Co in the reactor was the same except for the run in which Fe₂O₃/1% K was added as the support. In runs with a 1:1 H₂/CO synthesis gas

mixture, CO conversions were 20-30% with the C₂-C₄ fraction being predominantly olefinic. After 96 hours on stream, conversion had increased from ~21 to 27%. In a comparative run, an *ex situ* catalyst, Fe_{2.85}Co_{0.15}O₄/1%K, gave <5% CO conversion. For this run, the preparation of the catalyst nor its concentration in the reactor were not given.

TITANIA AND TRANSITION METAL OXIDE SUPPORTS

An extensive number of patents were obtained related to the use of titania containing catalysts in various applications, including the FT reaction. Early patents in this area disclosed the unique features of titania containing supports but did not refer to any FT type of application. However, these cases were fundamental to many of the subsequent patents that were issued for FT application. A patent issued to Tauster et al. (X.125) disclosed compositions comprising Group VIII metals supported on bulk oxides of titanium, vanadium, niobium, tantalum, zirconium titanate and barium titanate which were reduced in H₂ before use. A corresponding approach of coating a support with titania and adding a Group VIII metal is disclosed in a related patent issued shortly thereafter to Wheelock (X.126). Numerous patents have subsequently been issued using these approaches.

Tauster et al. (X.27) claimed that H₂ reduced Group VIII metals supported on Group IVb and Group Vb oxides are distinctly different from the same metals deposited on common carriers such as alumina, silica, carbon, magnesia, and silica alumina. These metals deposited on common carriers are found to retain their capacity for H₂ chemisorption, whereas the same metals when supported on various Group IVb and Group Vb oxides exhibit a marked suppression of this capacity. This change is attributed to the chemical nature of a strong metal-support interaction (SMSI) that

consists essentially of covalent bond formation between metal atoms of the supported phase and metal cations of the oxide support at the surface.

Such an interaction between the supported metal and the support is highly unusual. Typically, the role of the support is simply a geometrical one which exerts the major influence in the preparation of a well dispersed supported-metal catalyst. Thus chemically dissimilar materials, such as alumina and carbon, are able to efficiently disperse supported metals, provided that they are employed in their high surface area form, e.g. $>100 \text{ m}^2/\text{g}$. In these situations no strong chemical interaction between the support and the metallic phase is required to bring about good dispersion. If surface interaction occurred, the results observed for temperature-programmed-desorption of H_2 from Pt/alumina and Pt/silica catalysts, which are very similar, would be expected to be quite different.

The patent argues that although covalently-bonded species are observed in the hexagonal barium titanates and Lewis acid-base intermetallic compounds, which are representative of cation to cation and metal-atom to metal-atom types of bonding, respectively, the metal-atom to cation bonding in the SMSI are unique to the structures of this invention. In a Lewis acid-base intermetallic type of bonding structure, the titanium would be present as zero-valent. By photoelectron spectroscopy, or ESCA (electron spectroscopy for chemical analysis), zero valent titanium was not found in a composition of this invention, i.e. a 2% Rh/ TiO_2 catalyst that had been reduced in H_2 at 550°C .

In the broadest sense, the catalyst composition consists of a catalytic metal component selected from the group consisting of Group VIII metals, and mixtures thereof, supported on a transition metal oxide selected from the group Ti, V, Nb, Ta,

alkaline earth titanates, and mixtures thereof. These SMSI oxides can be used either in the pure state or, alternatively, in combination with additional oxides such as alumina, silica, magnesia, zirconia, hafnia, thoria, ceria, etc. They may be prepared by coprecipitation from solutions containing precursor salts of the respective oxides or by deposition of the precursor salt of the SMSI oxide on a carrier. The latter compositions, comprising titania deposited on the surface of an inorganic oxide support to which Group VIII metals are added, were disclosed by Wheelock (X.28) who anticipated a stabilizing interaction between Group VIII metals and Group IVb metal oxides.

The key characteristic of the SMSI oxides is that after the critical temperature for reduction is reached, the supported metal is no longer able to absorb H_2 and CO at room temperature. However, the supported metal particles are still in a high state of dispersion and retain their ability to chemisorb oxygen resulting in high ratios of adsorbed oxygen to metal atoms. Since the SMSI effect is a chemical interaction between the supported metal and the carrier, it is necessary for the metal to be well dispersed in order to provide sufficient interfacial contact between metal and support. Thus large metal crystallites are incapable of significantly affecting the properties of the surface metal atoms in contact with the gas phase. Therefore, the particle size of the supported metal should be preferably 50 Å or less. There also is a difference in the temperature of H_2 -activation needed to confer SMSI properties on the Group VIII metal, which varies primarily with the particular SMSI support. A SMSI state is achieved when a composition, e.g. Group VIII metal supported on the oxide of Ti, V, Nb, Ta, a mixture thereof, or a Zr or Ba titanate, is subjected, as a final preparative step, to reduction in a reducing atmosphere at a temperature sufficient to cause the composition to exhibit the suppression of H_2 and CO chemisorption.

Properties of Titania Supports. Tauster et al. (X.27) did not address the question of surface area and how it relates to the development of the SMSI state, although they used the argument that chemically dissimilar materials, such as alumina and carbon, are able to efficiently disperse supported metals, provided they are employed in their high surface area form, e.g. $>100 \text{ m}^2/\text{g}$. Based upon data contained in a subsequent patent issued to Arcuri et al. (X.127) the titania supported catalysts prepared by Tauster et al. (X.27) probably had only moderate surface areas. Arcuri et al. (X.29) showed that the rutile to anatase ratio increased with higher air calcination temperatures which caused a corresponding decrease in surface area (see Table X.20). They also found reduction of a calcined sample with H_2 at 450°C did not prevent further decrease in surface area upon further calcination in air at 500°C . These data suggest that the surface areas of the titania used by Tauster et al. (X.27) was initially about $60 \text{ m}^2/\text{g}$ and because of the thermal transformation of anatase to the rutile form, the final surface areas were probably somewhat less than the starting material and somewhat enriched in the rutile form. In a still later patent issued to Mauldin and Riley (X.128), additional data were reported showing increases in rutile concentration with calcination temperature (see Table X.21).

Vannice and Garten (X.129) described the titania that was probably used in many of these patents as being prepared by flame hydrolysis of TiCl_4 and having a surface area of $\sim 60 \text{ m}^2/\text{g}$ after thermal treatment at temperatures $\leq 500^\circ\text{C}$. A number of the cases referred to a material of this type that was designated as Degussa P-25 and was described as having a BET surface area of $50 \text{ m}^2/\text{g}$ and contained 65% anatase and 35% rutile titania in Wachs and Yang (X.130). Although a number of these patents contained claims that specified limits on the concentrations of the crystalline forms in

the titania phase, several actually contained these limits in either the main claim or another independent claim. This, of course, provides an unalterable requirement for the catalyst of the invention and was peculiar to a series of five patents, four of which claim titanias having high rutile contents while the fifth claims a stabilized titania having a high anatase content. Interestingly, the four high rutile cases, that originated from work presumably done at the Baton Rouge laboratories, were filed on the same day, June 29, 1984, and no subsequent patents had such a restriction in their main claim, although several continued to claim such materials in dependent claims. The level of rutile specified in the claims is >40%.

An alternative to using bulk titania is supports in which titania would be coated onto common, inorganic oxides. Such compositions were covered in a patent issued to Wheelock (X.28) which disclosed compositions comprising Group VIII noble metals and titania deposited onto inorganic oxides. Interestingly, that patent actually specified in its main claim that the titania existed on the surface as clusters. Whether such speculation regarding the morphological form of the catalyst, which was based upon ion scattering experiments, limits the compositions claimed by the invention is not clear. Assuming that it does not, Exxon then has rights to all compositions comprising Group VIII noble metals on titania coated inorganic oxides, of which platinum was specifically mentioned.

Ruthenium on Titania and Transition Metal Oxide Supports

The earliest Ru on titania Exxon patent that was found related to application in NO_x reduction. A composition of matter patent issued to DeLuca et al. (X.131) claimed a composition comprising ruthenium in combination with zirconium titanate or zirconium titanate in admixture with titanium dioxide, but not with TiO₂ alone. Ruthenium on titania compositions had been disclosed in previous patents, one of which was issued to

Kobylinski and Taylor (X.132), and assigned to Gulf, which claimed a process for reducing the content of nitrogen oxides in the exhaust gases from internal combustion engines. Such patents probably precluded claiming such compositions.

A problem with Ru/TiO₂ catalysts is the loss of Ru oxide upon treatment at temperatures around 840°C. DeLuca et al. (X.33) claimed decreased volatility of Ru oxide from compositions comprising Ru on zirconium titanate, either with or without additional titania being present. Tauster et al. (X.27) claimed the use of these materials in hydrocarbon conversion reactions but not in a FT type application. Various combinations of these supports, either alone or in combination with supported metals, are claimed in subsequent composition of matter patents or as catalysts in various FT process application patents. Several patents were issued regarding ruthenium on titania type supports. The claims in all these cases included not only titania but numerous combinations with silica, alumina, carbon, Group Vb metal oxides, and various alkali, alkaline earth and rare earth oxides. Exxon came close to claiming the composition Ru on TiO₂ in a patent issued to Arcuri et al. (X.29) which claimed catalyst compositions comprising ruthenium with rhenium on titania. A companion process patent that utilized this catalyst, which was essentially identical except for the claims, was issued to Arcuri (X.133). The titania support in these compositions were specified as having rutile concentrations >40%. The examples in these patents showed in extended runs with synthesis gas that Ru/TiO₂ that contained rhenium had a longer half-life at a level of 97% CO conversion than rhenium-free catalyst (see Table X.22). The interactive effects of these two metals on catalysts containing 0.5-1.0% Re with ruthenium concentrations from 0.1-1.0% indicate that the highest CO conversions were obtained for catalysts containing 0.5% Re and 1.0% Ru (Table X.23). The effect of the

ratio of rutile to anatase in the catalyst is shown in Table X.24 in which the catalyst containing 67% rutile in the titania had the slowest deactivation rate when operating at the 90% CO conversion level. Also, methane selectivities were much lower for the catalysts containing higher levels of rutile.

Several of the ruthenium-titania patents that were issued relate to processes that use Ru on titania. Vannice and Garten (X.31) claimed the use of a reduced Ru on titania, which they prepared by impregnating RuCl_3 onto titania and reducing in H_2 for 1 hr at 450°C . The Ru/TiO_2 catalyst gave higher olefin yields than a related Ru on $\eta\text{-Al}_2\text{O}_3$ (see Table X.25), albeit at a CO conversion level of 10% or less in both cases. Mauldin (X.134) claims a process for converting methanol in the presence of H_2 using a catalyst comprising ruthenium composited with titania. At a 4/1 methanol to H_2 ratio, conversion to hydrocarbon product was 76% after 35 hrs on stream (see Table X.26). Either in the absence of H_2 or the presence of added CO, conversions dropped significantly. CO was presumed to adsorb preferentially on the catalyst preventing reaction of the methanol.

Vannice and Tauster (X.135) claimed a FT process using a catalyst comprising Ru deposited on V, Nb and Ta oxides either alone or in combination with silica, alumina, or carbon type supports. Titania was not included in the claims. Preparation of the catalysts was by methods as presented in Tauster et al. (X.27) which was incorporated by reference. Higher olefin yields were obtained with the catalysts of the invention under conditions that the CO conversions were less than 18% (see Table X.27).

Madon (X.136) also claimed a FT process using a catalyst comprising Ru deposited on the same supports claimed by Tauster et al. (X.27), i.e., Ti, V, Nb and Ta oxides. In an improvement over Vannice and Tauster (X.37), this case claimed a

process which employed a reduced catalyst which was contacted with a mixture of H_2 and CO for at least 10 hours, after which continued contact with H_2/CO gave a C_5-C_{40} hydrocarbon product having a paraffin to olefin ratio in the C_5-C_{20} fraction of ≥ 1.5 . With a 0.76% Ru on TiO_2 catalyst, in excess of 80% CO from a 1.39 H_2/CO synthesis gas mixture was converted to liquid products under conditions shown in Table X.28. All of these catalysts were shown to be more active than Ru supported on conventional SiO_2 or Al_2O_3 (see Table X.29).

A patent issued to Wachs and Yang (X.137) claims a catalyst comprising Ru supported on a surface modified titania support wherein the support comprises an oxide of a metal selected from the group Nb, V, and Ta supported on the titania. In a corresponding patent, Wachs and Yang (X.32) claim a method for preparing this catalyst composition by depositing noncrystalline metal oxides of V, Nb, and/or Ta on a titania support having a $50\text{ m}^2/\text{g}$ surface area. In a related patent, Wachs and Chersich (X.138) claim a simple Ta_2O_3/TiO_2 composition prepared in this manner. No related patents claiming V and Nb oxide modified titania surface compositions were found. In Wachs and Yang (X.39) the modified support was impregnated with a solution of the Ru precursor which was reduced to the metal form. In the examples, all of the catalysts contained 1% Ru loadings. The activity of the catalysts containing various concentrations of the oxide promoters were compared with an impregnated physical mixture of TiO_2 and Ta_2O_5 in a fixed bed reactor (see Table X.30). Although the patent states that the data clearly show the difference between the catalysts of this invention and prior art Ru/TiO_2 catalysts, it is a challenge to recognize any differences.

A patent issued to Fiato and Miseo (X.139) claims slurry catalyst compositions consisting of titania, the decomposition product of $Ru_3(CO)_{12}$ formed in the presence of

H₂, and an inert alkane hydrocarbon. Fiato and Miseo (X.140) claim a process for preparing the *in situ* Ru/TiO₂ slurry catalyst. Preparation includes adding TiO₂, a Ru carbonyl complex, and an inert alkane hydrocarbon to a slurry reactor and increasing the temperature of the reactor to 230-270°C and pressure from 4 to 20 atm for 2-6 hr while adding a gas mixture of N₂:H₂ to cause the decomposition of the Ru carbonyl complex to form a slurry catalyst composition. In the example, a TiO₂ that had been pretreated with H₂ for several hours was added to the reactor with the Ru carbonyl complex and then subjected to the carbonyl decomposition step. The catalyst was highly active and selective for production of liquid hydrocarbons giving 40 to 60% CO conversion at 240°C with an alpha of 0.80. When TiO₂ was not present in the reactor, the Ru carbonyl complex was incompletely reduced and gave only 15% CO conversion (see Table X.31). The performance of the slurry catalyst was compared with a particulate Ru/TiO₂ and a Ru supported on ceria and alumina. The Ru - TiO₂ slurry catalyst had the highest CO conversion (55%) with a selectivity very similar to the particulate Ru/TiO₂ catalyst.

A patent issued to Mauldin (X.141) claims a process wherein the Ru on titania catalyst is pretreated with steam or steam and H₂ at 200 to 550°C to mildly agglomerate the ruthenium. By this procedure, Ru particles are generated having the same size as obtained after start-up with synthesis gas. The same effect occurs upon treating in air at 500°C where the crystallite size of the Ru grows from 12 to 30 Å. In the examples, a Ru/TiO₂ was prepared by impregnating a titania having a rutile content of 73% with ruthenium nitrate in acetone solution. One portion of this material was calcined in air at 500°C for 4 hours. Another was contacted with mixtures of steam with H₂ or N₂ at elevated temperature, as shown in Table X.32. The oxygen chemisorption decreased

while the Ru crystallite size increased. The performance of the Ru/TiO₂ that had been treated in air at 500°C for 3 hrs was compared with an untreated sample. Results after several times on stream, as shown in Table X.33, indicate that the selectivity to methane was higher and to C₂+ hydrocarbons was generally lower than for the untreated catalyst. The catalyst treatments that were presented in the patent, including air or steam with H₂ or a carrier gas, provide an advantage over a non-treated catalyst, as determined by Ru crystallite size, oxygen chemisorption or synthesis gas conversion and selectivity.

A patent issued to Pruett and Bradley (X.142) claims compositions comprising bimetallic cluster compounds containing Ru with Tl, In or Ga. A cluster having the formula [(C₂H₅)₄N][(Ru₆C(CO)_{16/2}Tl)] deposited onto an alumina surface was reduced in H₂ at 200°C and used for conversion of 1.5/1 H₂/CO mixture at 7 MPa and 275°C. The product contained a mixture of linear hydrocarbons and alcohols.

Rhodium on Titania

A patent issued to Vannice and Garten (X.143) claims a process in which synthesis gas is passed over a catalyst comprising Rh on a titanium-containing oxide support. The activity of this catalyst, reduced at 450°C and 100 kPa, though quite low, was higher than for a Rh on alumina catalyst (Table X.34). The product was largely methane.

Cobalt on Titania and Transition Metal Oxide Supports

There has been a considerable amount of activity by Exxon regarding cobalt on titania catalysts with a number of patents being issued that parallel the ruthenium cases discussed above. Included in the series were three filed on June 29, 1984 from the Baton Rouge laboratory that relate to titanias having rutile concentrations ≥40%. Very

broad coverage was obtained in a patent issued to Payne and Mauldin (X.144) which claims catalyst compositions comprising cobalt on high-rutile titania which are useful for both synthesis gas and methanol conversion. A subsequent patent issued to Behrmann et al. (X.145) claims catalyst compositions comprising cobalt dispersed and impregnated upon the surface of titania to an average depth of 0.02 to 0.20 mm with a cobalt loading, on a total bulk basis, from 0.04 to 0.15 g/cc, which is ~4-17 wt.%, depending on the packing density of the titania. A related patent issued to Iglesia et al. (X.146) claims a method for preparing supported cobalt catalyst on which the Co is deposited to a depth of less than about 200 μm on the rim of the catalyst particles. Other patents issued to Payne and Mauldin (X.147) and Behrmann et al. (X.148) claim processes that utilize these catalysts for conversion of synthesis gas. The addition of rhenium as a promoter to this family of catalysts, i.e. rhenium with cobalt on titania, was also covered. Catalysts in which the Co and Re were concentrated at the surface of the spherical particle was claimed by Behrmann et al. (X.47). Rhenium is claimed to improve activity for CO conversion for cobalt as it does for ruthenium. Bulk Co/TiO₂ catalysts, either with or without thoria, were claimed in a patent issued to Mauldin (X.149) with addition of thoria being claimed to be especially beneficial for conversion of methanol. Since the main claim in this case specified an inorganic oxide support, with titania being mentioned in a dependent claim, compositions that were covered were actually broader than titania itself, although titania supports were the only ones used in the examples.

Of the nine examples on Co/TiO₂ in the Payne and Mauldin (X.46) case, the first six relate to conversion of methanol and the last three to conversion of synthesis gas. The latter examples with synthesis gas are repeated in Payne and Mauldin (X.49) while

the first six, which are related to methanol conversion, were probably included in Application Number 626,026, which was filed on the same day, as noted in Payne and Mauldin (X.49), but apparently never resulted in an issued patent. A process patent issued to Mauldin (X.150) used the Mauldin (X.51) catalyst comprising rhenium and cobalt on titania.

The examples of bulk titania catalysts in Payne and Mauldin (X.46) were prepared from calcined Degussa TiO_2 , which was impregnated with Co nitrate and/or perrhenic acid. The addition of perrhenic acid to the substrate is a puzzle, since none of the catalysts contain Re, nor do any of the claims refer to catalysts containing Re. At any rate, the impregnated materials were then calcined in air at 250 or 500°C and reduced in H_2 at 450°C. Thoria containing catalysts were prepared by impregnating the support with a thorium compound or salt in a similar manner to give thorium concentration up to 10%. Actually, the specific thorium compounds or salts that were used to impregnate the substrate were not mentioned anywhere in the specification. Another set of cobalt-titania catalysts were also prepared having both high and low rutile concentrations. The low rutile concentration catalyst was prepared by impregnating cobalt carbonyl onto uncalcined Degussa P-25 titania that had a rutile concentration of 28% while the high-rutile catalyst was prepared from Degussa P-25 that had been calcined at 600°C. The impregnated cobalt carbonyl was decomposed either by heating at 257°C in vacuo for 1 hr, or by calcining at elevated temperatures. Catalysts were tested in a fixed bed reactor either with synthesis gas or with methanol after reducing in H_2 .

A subsequent patent issued to Behrmann et al. (X.47) claims catalyst compositions comprising cobalt dispersed and impregnated upon the surface of

spherical titania with an average thickness of 0.02 to 0.20 mm. A corresponding patent issued to Behrmann et al. (X.50) claims use of these compositions in a FT process. The cobalt loading in these catalysts, on a total bulk basis, was from 0.04 to 0.15 g/cc, which is ~4-17 wt.%, depending on the packing density of the titania. Special techniques for depositing the cobalt along with Re as a promoter were used wherein the metals were concentrated at the surface of the spherical titania particles having diameters of approximately 1 mm. The activity of rhenium promoted Co/TiO₂ catalysts, in which the metals are deposited on the surface of spherical titania substrate, is related to the thickness of the metal layer. With these catalysts that were prepared from spherical titania, the methane concentrations in the hydrocarbon product, relative to the converted CO, was lower than for Co-Re/TiO₂ in which the metals were uniformly distributed onto powdered substrate (see Figure X.1). The metals were deposited onto the surface of the spheres by either spraying a metal-containing solution onto the titania spheres and quickly removing the solvent or treating spheres that had been saturated with one solvent with a metal-containing immiscible solvent which would not penetrate into the particle.

Another method to prepare rim-type supported cobalt catalysts is covered in a patent issued to Iglesia et al. (X.48) who claim that contacting a support particle with a molten cobalt salt results in deposit of the cobalt to a depth of less than about 200 µm on the rim of the support. After reduction in H₂, these catalysts are more active than incipient wetness impregnated catalysts where the Co is evenly distributed throughout the particle, as shown in Table X.35, where a lower GHSV is necessary to achieve the same level of CO conversion. Each of the rim-impregnated silica based catalysts have a higher volume of CO conversion per volume of catalyst per hour. Crushing the 2.2

mm spheres provided a slight increase in CO conversion which denotes some additional diffusional effect in the rim catalysts even though the Co is located primarily at the surface of the particle. There is also an advantage of having higher Co concentrations on higher surface area supports, as shown in Table X.35.

The advantage of incorporating a binder into titania was covered in patents issued to Mauldin and Riley (X.30) which claim support compositions comprising titania in which up to 20% alumina or zirconia is incorporated. A corresponding essentially identical patent issued to Mauldin and Riley (X.151) claims a FT process utilizing these catalysts. Their data show that incorporating a small amount of alumina increases the volume of CO converted per gram of cobalt/hr, as shown in Figure X.2. This increased activity is attributed to an increase in cobalt dispersion due to the increase in pore volume of the binder. Hydrocarbon synthesis activity suffers at higher alumina concentrations, however, because the Co oxide is only partially reduced on the alumina, as compared to titania where complete reduction occurs. This is reflected in the higher turnover numbers for the titania and the steady decline as incorporation of alumina increases (see Figure X.3). Thus, incorporation of small amounts of alumina results in an increase in activity. Higher dilutions, however, result in a decline in activity. An example is also presented that shows that catalysts prepared by spraying Co salts onto titania substrate containing 3.5% alumina binder using the method of Behrmann et al. (X.47) were more active than spherical titania without the binder.

A method for impregnating cobalt onto supports was covered in a patent issued to Mauldin and Riley (X.152) which claims a process for preparing a FT catalyst in which a catalytically effective amount of Co is impregnated and dispersed as a film or layer on the peripheral outer surface of a particulate porous inorganic oxide support,

wherein the catalysts are prepared by spraying a bed of the fluidized particulate support particles with a liquid containing a dispersed or dissolved Co metal compound. The operation is performed at specified operating conditions of 0.6 g liquid/ft³ fluidizing gas. Titania was one of the supports specified in a dependent claim. In the examples, solutions of cobalt nitrate and perrhenic acid were sprayed onto particulate material and reduced at 450°C for 1 hr. Conversion of a 2/1 H₂/CO feed at 200°C, 280 psig and 1000 GHSV after 20 hrs on stream was 79% with product selectivities for CH₄ of 6.0%, CO₂ of 6.0% and C₂+ of 93.6%.

Synthesis Gas Reactions. Co/TiO₂ catalyst has a higher activity toward synthesis gas conversion, as shown in Table X.36, than conventional cobalt on silica or alumina or Co-Mg-thoria on kieselguhr, which was prepared following a published procedure (X.153). The 0.91 Schulz-Flory alpha value for the titania catalyst was higher than for conventional catalysts and was reflected in a C₁₀+ hydrocarbon yield that was >75%. Higher CO conversions in these Co/TiO₂ catalyst appear related to higher rutile concentrations and higher O₂ chemisorption values of the starting catalysts as shown in Table X.37. The pseudo first-order CO conversion rate constants calculated by Equation 1 correlate directly with the oxygen chemisorption values for these four catalysts, as shown in Figure X.4.

$$k = \frac{GHSV}{P} \ln \frac{1}{(1-x)} \quad (52)$$

where:

x = fraction CO conversion,

P = reactor pressure in atm, and

GHSV = space velocity at ambient temperature and pressure in hr⁻¹.

Similar results were obtained with catalysts prepared by impregnating cobalt carbonyl onto 28% and 100% rutile titanias where the carbonyl was decomposed by heating in vacuum. Synthesis gas conversion over these catalysts shows that the high rutile catalyst gave much higher CO conversion (see Table X.38). Cobalt catalysts prepared either from the nitrate or the carbonyl gave essentially the same results.

Incorporation of 0.5 to 3% Re in the Co/TiO₂ catalyst further improved both oxygen chemisorption and CO conversion, as shown in Table X.37. The improvement resulting from addition of Re is probably through improving the reduction of the Co in the pretreatment step (X.154). Results from a 200 hr extended run, presented in (Figure X. show that CO conversion dropped from about ~98% to ~80%. Comparison with a Ru/TiO₂ catalyst with the Co-Re catalyst under the same conditions (Figure X.6) indicate the Co-Re catalyst was significantly more active than the Ru catalyst while both had similar selectivities for methane and CO₂ (Figure X.7).

Methanol Reaction. Examples of methanol conversions were given for a number of cobalt catalysts including Co/TiO₂, Co-Re/TiO₂, Co/ThO₂/TiO₂, and Co-Re/ThO₂/TiO₂. The effect of rutile concentration on methanol conversion was observed for catalysts containing 12% cobalt on titania. The 100% rutile catalyst completely converted the methanol while the 55% rutile titania support gave only 66% conversion (see Table X.39). The selectivities were also quite different with the catalyst having the lower rutile content being more selective for producing C₂+ hydrocarbon product and less CO₂.

Experimental data showing the effect of adding thorium on the conversion of methanol is provided in Payne and Mauldin (X.46). In these cases the rutile contents of the catalysts were not specified (see Table X.40). Assuming that the titania components in these catalysts had the same rutile concentration, the data show that

addition of thoria to the catalyst increases methanol conversion, decreases methane yield, and gives nearly the same Schulz-Flory alpha values. Comparisons with other state-of-the-art catalysts showed that conventional FT 100 Co/5 ThO₂/8 MgO/200 Kieselguhr catalyst gave higher methanol conversion but poorer C₂+ hydrocarbon selectivity under the run conditions. Compared to Co on silica or alumina, both Co-titania catalysts, with or without thoria, gave better C₂+ selectivity at comparable or higher methanol conversion levels. The liquid product was highly paraffinic as reflected in the 78.2% straight chain paraffinic content of the C₈ fraction from the thoria containing catalyst. Even over the Co/alumina catalyst, where methanol conversion was 64%, the yield of dimethyl ether was only 2.4%, indicating the non-acidic nature of the alumina support. At the low methanol conversion levels, dimethyl ether formation was quite small.

The presence of rhenium with cobalt in 56% rutile titania catalysts, either with and without added thoria, increased MeOH conversion (see Table X.41). Addition of 0.5 wt.% Re to Co/ThO₂/TiO₂ increased methanol conversion quite sharply from 49% to 100%. Conversion to CO₂ increased sharply while C₂+ yields decreased from 74% to 56%. The effect of Re/TiO₂ on methanol conversion was not provided.

Hydrogen partial pressure has a strong effect on methanol conversion and product selectivity. Payne and Mauldin (X.46) showed that increasing the H₂ partial pressure at constant methanol space velocity increased conversion from 38% to 83% (see Table X.42), decreased the yields of CO+CO₂, and sharply increased methane selectivity. The C₂+ yield appears to go through a maximum at a H₂ partial pressure of 17 psi. At low methanol pressures over a 12% Co/2% ThO₂/TiO₂ catalyst, the products are almost exclusively CO and H₂, except for a very small amount of methane.

A patent issued to Mauldin et al. (X.155) claims cobalt-titania catalyst to which is added small amounts of hafnium, zirconium, cerium or uranium to maintain the cobalt in a high state of dispersion and stabilize the catalyst during high temperature air treatment. The concentration of promoter to cobalt was specified as a weight ratio greater than 0.01 to 1 and typically between 0.04-0.25 to 1. Although there were no limits placed on the catalyst composition, the catalysts presented in the examples were prepared by impregnating high rutile titania either sequentially with Zr, Hf, Ce or U compounds followed by Co nitrate or simultaneously with the promoter metals and cobalt nitrate. In the preparation of these catalysts when the metals were added sequentially, the catalysts were calcined between metal additions. The final catalysts were then calcined at 400, 500 or 600°C to simulate catalyst regeneration and tested for synthesis gas reactions. CO conversions for the promoted catalysts were higher than for the non-promoted catalysts at all air treat temperatures >150°C, as shown in Figure X.8. The 500°C catalyst regeneration data plotted in Figure X.9 show that addition of approximately 0.5 wt.% promoter provides optimal thermal stabilization giving CO conversions of 70-80%. The examples also showed that addition of 0.06 wt.% Hf and 0.3 wt.% Zr, both of which fell within the limits of the claimed compositions, was not adequate to stabilize the Co/titania, although higher concentrations did stabilize the catalysts.

Synthesis gas conversion data were provided for a 2/1 H₂/CO mixture that was passed over a Co-Hf-TiO₂ catalyst at 1000 GHSV and 204°C at 280 psig to give 89% CO conversion with a 91% C₅+ hydrocarbon product selectivity. No other synthesis gas data were provided. Comparative runs with methanol, however, are reported for each of the metal promoters (see Table X.43). All of the promoted catalysts gave

higher MeOH conversion than the unpromoted catalysts with about the same selectivities for higher hydrocarbon product.

Silica Promoted Co/TiO₂

A patent issued to Iglesia et al. (X.156) claims compositions of cobalt on an inorganic refractory support comprised of a major portion of titania to which up to 15 wt.% silica has been added. This catalyst is utilized in another process related patent issued to Iglesia et al. (X.157). These two cases are identical except for the claims. The patent specifies that the Co may be incorporated onto the inorganic refractory titania support either before or after adding the silica or silica precursor. Incorporation of rhenium in the catalyst is covered in a subordinate claim. Although the main claim does not specify Re in the catalyst, the examples include only Re-containing catalysts.

In the examples, a series of catalysts, as described in Table X.44 were prepared starting with a CoRe/TiO₂ (Catalyst A) that was prepared by depositing Co and Re components from an acetone solution onto a 97% rutile titania and calcining at 250°C for 3 hrs. Two silica containing catalysts (Catalysts B and C) were prepared by impregnating Catalyst A with tetraethoxysilane (TEOS), treating with a stream of H₂O (40 Torr) in He while heating at 400°C for 13 hrs after which it was reduced at 250-400°C for 2-14 hrs. A catalyst that was free of silica but exposed to the same H₂O treatment (Catalyst D) was prepared by treating Catalyst A with H₂O (40 Torr)/He while heating at 400°C/13 hrs, after which it was reduced at 250-400°C for 2 to 14 hrs. The activities of the catalysts were determined at run times up to almost 200 hrs under conditions to give ~60% CO conversion. There was little difference in hydrocarbon selectivity observed by incorporating silica into the samples. Although the CO₂ yield was in every case quite small, it dropped to an almost imperceptible level with silica.

The increased stability of the silica containing catalysts was observed in reduced carbon buildup at low temperatures on the surface of the catalyst in the presence of CO. The "effect of SiO₂ during carburization suggests that it may prevent short term deactivation during the first few hours in H₂/CO environments; the effect is to increase the apparent site activity by maintaining surface cobalt atoms available during hydrocarbon synthesis."

Anatase Titania Supported Cobalt Catalysts

A patent issued to Soled et al. (X.158) claims both a composition of matter and a method for preparing a catalyst containing anatase titania. What appears to be the omnibus claim is claim 13 which claims a catalyst composition comprising Co composited with a ternary metal oxide support of titania having the general formula Co/Ti_{1-x}M_xO₂ where x is 0.01-0.14 and M is selected from the group consisting of silicon, zirconium, and tantalum and wherein the titania is an anatase polymorph stable under oxidative regeneration at temperatures of 400-750 °C. Claim 1, on the other hand, claims a method for preparing this catalyst which comprises contacting a titanium alkoxide or titanium chloride, such as TiCl₄, with a metal alkoxide or metal chloride, respectively, to form a solution; adding water to the mixture of alkoxides or an aqueous base to the mixture of chlorides to form a co-precipitate; separating the co-precipitate; calcining the dried co-precipitate to form a ternary metal oxide; depositing a cobalt metal compound solution onto the surface of the ternary metal oxide to form a composite; and activating the composite to form a catalyst. Activating the composite includes drying and calcining followed by reduction of the Co. Depending on the precedence of claims 1 and 13, the coverage may be broad as defined in claim 13 or it may be very narrow being confined to the composition prepared by the method disclosed in claim #1.

Neither the claims nor the specification in this case discuss the coexistence of mixtures of rutile and anatase forms in the titania. Likewise, the concentration of the anatase phase in the titania prepared by the method of this invention was also not revealed. If the composition of the claimed catalyst is limited to the material prepared according to the method in claim 1, then the question of anatase concentration is mute. However, if the patent covers all $\text{Co/Ti}_{1-x}\text{M}_x\text{O}_2$ compositions per claim 13 where M is silicon, zirconium, and tantalum and where titania is in an anatase form, the limits on anatase concentration covers only titania compositions that contain, at most, very small amounts of rutile. Regardless, this case is likely an improvement over Iglesia et al. (X.58) which claims cobalt on silica-modified titania wherein no limitation on the form of the titania is made. It also must be an improvement over Mauldin et al. (X.57) which claims catalysts comprising zirconium added to titania to maintain the cobalt in a high state of dispersion and stabilize the catalyst during high temperature air treatments. In the main claim, there are no limitations on the form of the titania. These three cases, however, provide Exxon with coverage for cobalt impregnated anatase to complement their many cases on rutile-rich titanias.

Apparently the reason why the anatase phase is stabilized at high temperatures is related to substitution of Si, Ta, and Zr cations into the anatase structure of the catalyst which apparently retards the formation of CoTiO_3 preventing the entrapment of the cobalt and preserving its specific surface area. Once cobalt titanates form, a higher temperature is required to reduce them to the metal. Through addition of Si, Ta, and Zr, the amount of the CoTiO_3 is decreased. For a Si incorporated polymorph, the concentration of the CoTiO_3 is decreased, as determined by XRD, and its concentration is a function of calcination temperature, as shown in Figure X.10. Silica incorporation

has no effect on the thermal properties of the catalyst but increases by approximately 100 centigrade degrees the temperature for onset of carburization in a synthesis gas stream, as shown in Figure X.11.

Catalysts incorporating each of the promoters were prepared and their stability to calcination was reported in the examples. Anatase titania was prepared by first hydrolyzing $\text{Ti}(\text{t-buO})_4$ and calcining at 430°C . Co as Co nitrate was then impregnated onto the substrate and calcined at $430\text{-}700^\circ\text{C}$. Calcining at 430°C gives anatase having a surface area of $120\text{ m}^2/\text{g}$ while calcining at 700°C transforms the anatase to rutile having a surface area of $2\text{ m}^2/\text{g}$. Silicon promoted titanate was prepared by adding the silicon alkoxide, tetramethylorthosilicate (TMOS), to $\text{Ti}(\text{t-BuO})_4$ following the above procedure. Surface areas containing various levels of silicon substitution were obtained upon calcination at 700°C :

<u>Si, %</u>	<u>m^2/g</u>
1%	52
3%	76
5%	119
14%	133

Zirconium promoted titanate was prepared by adding zirconium n-propoxide to $\text{Ti}(\text{t-BuO})_4$ following the above procedure. A catalyst containing 3% Zr had a surface area of $36\text{ m}^2/\text{g}$ while a 14% Zr catalyst had a surface area of $56\text{ m}^2/\text{g}$, both of which stabilized the anatase. A tantalum promoted titanate was prepared by adding tantalum ethoxide to $\text{Ti}(\text{t-BuO})_4$ following the above procedure. A catalyst containing 14% tantalum had a surface area of $71\text{ m}^2/\text{g}$. No FT data were provided in the patent.

Cobalt-Ruthenium on Titania

A patent issued to Iglesia et al. (X.159) claims a catalyst prepared by a process comprising impregnating titania with solutions of cobalt and ruthenium salts, drying, reducing the cobalt and ruthenium, treating the metals with an oxygen containing stream to form the oxides and reducing the oxides. A corresponding patent issued to Iglesia et al. (X.160) claims a process that utilizes this catalyst. The intimate contact of the Co and Ru in the catalyst lowers the temperature at which the cobalt is reduced to the metallic form. This results in a decrease in the amount of carbon deposited upon heating in synthesis gas at temperatures up to 500°C. Intimate contact is obtained by reducing the metals on the surface, calcining in air to reform the oxides and then reducing to the metal form. Unlike many of the other composition of matter patents, a corresponding process patent was not found.

TGA and DTA data provided in the patent showed that the carbon deposited more slowly on calcined Co-Ru/TiO₂ when subjected to a 1:1 H₂/CO synthesis gas mixture than on either Co/TiO₂ or uncalcined Co-Ru/TiO₂. The patent states that the advantage of the Co-Ru combination relative to other catalysts is that "a combination of increased cobalt oxide reducibility and inhibited catalyst poisoning by carbon are believed to account for the increased number of active sites observed on calcined CoRu/TiO₂ catalysts."

Energy dispersive X-ray (EDX) analysis of uncalcined versus calcined CoRu/TiO₂ catalysts that had been aged in process runs for 700 hrs showed that both aged catalysts were identical. Apparently Ru in fresh uncalcined CoRu/TiO₂ catalyst cannot be detected since its concentration over the surface is below detection limits. However, in calcined CoRu/TiO₂ catalyst that has been reduced, Ru can be detected in the cobalt

particles where it concentrates sufficiently to be detected by EDX. Apparently, Ru also concentrates in aged uncalcined CoRu/TiO₂ catalysts since the EDX analysis was the same as the calcined sample.

In the examples, three titania catalysts were prepared starting with a sample containing 70% rutile. The first catalyst, Co/TiO₂, was impregnated with cobalt, calcined at 400°C for 4 hrs in air and reduced in H₂ at 400°C for 16 hrs (Catalyst A). Ruthenium was then impregnated onto this catalyst and reduced to give reduced-Co-Ru/TiO₂ (Catalyst B). A portion of this material was calcined in air at 300°C/4 hrs and reduced in H₂ to give the calcined-reduced Co-Ru/TiO₂ composition of this invention (Catalyst C). A Co/SiO₂ catalyst was prepared for comparison by impregnating silica with a cobalt salt (Catalyst D). In synthesis gas runs in which the space velocity was adjusted to attain comparable conversion levels (see Table X.45), the cobalt time yields of the calcined-reduced Co/Ru/TiO₂ catalyst was higher than for the other three catalysts. This appears to be similar to Gulf patents where reduced-oxidized-reduced catalysts had a higher activity than the reduced catalyst (X.161). The methane and C₅+ selectivities of reduced-Co/Ru/TiO₂ and the oxidized-reduced Co/Ru/TiO₂ were very nearly the same, but slightly better than Co/TiO₂ or Co/SiO₂ catalysts.

Data were provided that showed that hydrogen regeneration of oxidized-reduced Co/Ru/TiO₂ catalysts that had been aged from 10-30 days, was more complete than for the untreated Co/Ru/TiO₂ catalyst (see Table X.46). CO conversions and methane and C₅+ selectivities were higher for both the fresh and regenerated oxidized-reduced Co/Ru/TiO₂ catalyst than for the untreated reduced Co/Ru/TiO₂ catalyst and the ruthenium free Co/TiO₂ catalyst.

Iron on Titania

A series of three patents were issued to Fiato and Kugler which are identical except for the claims. Fiato and Kugler (X.162) claim a composition consisting of a mixture of iron carbide and ilmenite, either with or without an alkali metal promoter, having an Fe_2O_3 concentration of 2-25 mg/cm², wherein the catalyst is formed by depositing an iron salt onto titania, calcining, treating with H_2 free of CO at 300-500°C until the composite is reduced and then contacting with CO at a temperature that is 100-200°C lower than the H_2 reduction temperature. In this preparation, the iron precursor deposited on the titania is calcined to form the iron oxide which is reduced in H_2 to form Fe metal which then reacts with CO to form carbide. X-ray diffraction showed that the calcined material contained anatase and rutile forms of TiO_2 , FeTiO_3 (ilmenite), and metallic Fe. X-ray diffraction of the sample after CO treatment showed that the TiO_2 and ilmenite were unchanged, metallic Fe disappeared, and Fe_5C_2 was formed.

In one of the other cases, Fiato and Kugler (X.163) claim a process for producing hydrocarbons from synthesis gas using this catalyst composition. In the other, Fiato and Kugler (X.164) claim a process for improving the activity of this catalyst in a FT reaction by cycling the temperature in the reaction zone, by increasing the temperature by 50-150°C above the FT reaction temperature in the absence of H_2 for from 1-6 hours and then returning to reaction temperature and reestablishing the H_2 content of the feed stream. None of the examples actually illustrated the effectiveness of this procedure.

The activity of a series of catalysts indicated that the Fe concentration in these catalysts must be ≥ 2 mg $\text{Fe}_2\text{O}_3/\text{m}^2$ of titania (see Figure X.12). The activity of an Fe supported titania catalyst of this invention that had been both reduced and subsequently carbided, with an Fe concentration of 0.002 g Fe/m² TiO_2 , was higher than a

corresponding material that had not been carbided, i.e. 27 versus 60% CO conversion, respectively. The hydrocarbon selectivities for the carbided catalyst was lower for methane and higher for C₅+

A patent issued to Wachs et al. (X.165) claims catalysts comprising an iron carbide on a modified titania support comprising at least 25% of an oxide of Nb, V, and Ta in a noncrystalline form and containing at least 2 mg Fe, as Fe₂O₃, per m² support surface. A corresponding process patent, which was essentially identical, issued to Wachs et al. (X.166) claims a process for producing hydrocarbons using this catalyst. These cases relate to an application by Wachs and Chersich (X.40), that was filed on the same day, that claims compositions of tantalum oxide on titania support that were used as catalyst supports. The background on this case was that the Fe/Group Vb oxide/TiO₂ combination was anticipated in the specification by Tauster et al. (X.27) but not actually claimed as compositions of that invention. The Wachs et al. patent (X.67) differs in that the titania surface was modified by addition of limited amounts of Nb, V, and Ta to modify the TiO₂.

The catalysts used in the example were prepared by slurring Degussa P-25 titania with an ethanol solution containing either Nb(C₂H₅O)₅ or VO(C₂H₅O)₃. The solvent was removed, the V or Nb ethoxides were oxidized, and the resulting powders calcined in pure O₂ at 575°C for 2 hours. The resulting supports contained 10% Nb₂O₅ or V₂O₅ on TiO₂. The Fe precursor was impregnated onto the support, reduced in H₂ at 500°C for 5 hrs, and carbided by exposure to synthesis gas. Results from runs with synthesis gas (see Table X.47) show that at similar CO conversions levels, i.e. 47-49% or 60-70%, the vanadia and niobia catalysts gave lower methane and higher olefin

selectivities than a Fe/TiO₂ catalyst. At the same run temperature, i.e. 270°C, the methane yields were lower for the catalysts of the invention.

Nickel on Titania

Two patents related to nickel-titania catalysts were issued; in one, Ni as a promoter of titania based catalysts was claimed while in the second, titania promoted bulk Ni catalysts were claimed. The first patent issued to Vannice and Garten (X.167) claims a FT process that uses a catalyst comprising nickel on a titanium-containing oxide support with a Ni concentration up to 75% by weight. The second patent issued to Kugler and Garten (X.168) claims a FT process using a catalyst comprising bulk nickel promoted with up to 10% titania. These two patents pretty well cover the use of all possible combinations of Ni and titania catalysts in the FT reaction.

In the first patent, Vannice and Garten (X.69) claim that nickel on titania exhibits higher activity, improved selectivity to higher hydrocarbons, improved life and tolerance to sulfur, and resistance to Ni carbonyl formation. The catalysts were prepared by impregnating nickel salts onto the titania support and reducing in H₂ at temperatures >400°C. Synthesis gas conversion at 1 atm over these Ni/TiO₂ catalysts was higher than with bulk nickel or Ni on silica, alumina, and graphite. C₂+ paraffin selectivity versus CO conversion is shown in Figure X.13. In these runs, the Ni/TiO₂ catalysts had higher CO conversions per gram Ni, and lower methane and higher C₂+ hydrocarbon selectivities. Still, the methanation reaction was quite high for the Ni/TiO₂ catalyst. An experiment was described in which the volatility of the Ni was shown to be lower over the TiO₂ catalyst than a Ni/SiO₂ catalyst (see Figure X.14).

In the second patent, Kugler and Garten (X.70) claim the addition of titania to bulk nickel shifts hydrocarbon selectivity from methane to C₂-C₆ hydrocarbons, along

with trace quantities of C₇ product. The influence of increasing titania concentration up to 8.4%, as shown in Table X.48, was to increase the CO conversion while the selectivity to higher hydrocarbons increased. Since the relative rates for CO conversion and CH₄ formation both increased, the changed product distribution reflected the much higher increase in the rate of CO conversion versus the smaller increase in methanation rate. The selectivity of the 8.4% TiO₂ on Ni catalyst is very similar to the selectivity of 10% Ni on TiO₂.

A physical mixture of 1/1 Ni powder and TiO₂ behaved very similarly to Ni powder indicating that for such a physical mixture a synergistic interaction did not occur upon activation in H₂. The effect that was observed with the catalysts prepared by addition of solutions of the Ti oxide precursor to bulk Ni indicates a chemical interaction between the titania and the Ni, since a change in activity and selectivity occurs. Evidence for a chemical interaction was observed in ESCA that showed that Ti exists on the catalyst surface before reduction as Ti⁺⁴. After reduction in H₂ at 250°C, some of the Ti is in a lower oxidation state but not reduced to the metallic form. The titanium promoter changes the surface area and chemisorption properties of the bulk nickel. Small quantities of Ti additive increases the surface area while creating an oxide layer, as observed by ESCA. Concomitantly, H₂ chemisorption was reduced due to physical blockage of the sites. The highest CO conversion level was observed at the lowest H₂ chemisorption level for the Ti promoted samples.

MANGANESE OXIDE SUPPORTS

Exxon has been assigned 2 patents which claim compositions, or use thereof, comprising the five Group VIII metal oxides of iron, cobalt, nickel, iridium and ruthenium on manganese oxide supports which are reduced at a temperature sufficient to

suppress hydrogen chemisorption. These cases parallel Tauster et al. (X.27) who claim catalyst compositions comprising Group VIII metals on Group IVb and Group Vb metal oxides that are reduced at a temperature to suppress hydrogen chemisorption. Since manganese falls in Group VIIb, it falls outside of Tauster et al. (X.27). There are other manganese patents assigned to Exxon which involve the use of manganese in spinels which are discussed elsewhere in this review.

Ruthenium

A patent issued to Kugler et al. (X.169) claims a FT process that provides improved yields of C_2 - C_4 olefins that uses a catalyst comprising ruthenium on a manganese containing support which has been reduced at a temperature sufficient to suppress hydrogen chemisorption. Manganese can be used in its pure form or combined with alumina, carbon, silica, or oxides of Groups IVb and Vb. A 1% Ru/MnO catalyst was prepared by impregnating MnO with $RuCl_3$ and reducing with H_2 at 450°C. Synthesis gas mixtures, having H_2/CO ratios from 1.6 to 3, were passed over the catalyst at 300°C and at 1 atm pressure to give CO conversions less than 10%. Under those conditions Ru/MnO catalyst gave higher yields of C_2 - C_3 olefins and lower yields of CH_4 relative to a Ru/ Al_2O_3 catalyst.

Iron, Cobalt, Nickel, Iridium

A composition of matter patent issued to Tauster and Fung (X.170) claims compositions comprising iron, nickel, cobalt and iridium supported on a manganese containing oxide support, the improvement comprising contacting said composition with a reducing atmosphere at temperatures $\geq 300^\circ C$, except for iridium which requires a temperature $\geq 250^\circ C$, to produce a catalyst composition which exhibits suppressed hydrogen chemisorption. Under these conditions, the reduced materials would,

therefore, be in the SMSI state as defined by Tauster et al. (X.27). Two different 2% Ir/MnO catalysts were prepared by impregnating the metal onto two different MnO substrates. The two MnO substrates prepared by reducing battery grade MnO_2 in H_2 at 540 and 740°C had surface areas of 21.7 and 7.8 m^2/g , respectively. Less than 0.01 atoms of hydrogen were adsorbed per atom of Ir for each of these catalysts that had been reduced in H_2 at 500°C versus values of 0.46-1.08 for samples reduced at 200°C. A sample (prepared at 740°C) reduced at 350°C adsorbed less H_2 (0.041 atoms per atom Ir) indicating it was in the SMSI state.

Cobalt - Manganese Spinel

A patent issued to Soled et al. (X.171) claims compositions comprising a copper promoted Co-Mn spinel having a formula $\text{Co}_{3-x}\text{Mn}_x\text{O}_4$ where x is 0.5-1.2. Subordinate claims specify a Cu concentration from 0.1 to 5 g-atom percent based on the total amount of Co and Mn in the catalyst and a surface area $>5 \text{ m}^2/\text{g}$. A corresponding patent, having an identical specification, which was issued to Soled et al. (X.172), claims a Fischer-Tropsch process using this composition. The spinel was prepared using the alpha-hydroxy aliphatic carboxylic acid method that has been used for all these high surface area spinels. A Co_2MnO_4 spinel, having a surface area of 30-60 m^2/g that is isostructural with Fe_3O_4 , was prepared from a solution of $\text{Co}(\text{NO}_3)_2$ and $\text{Mn}(\text{NO}_3)_2$ in the presence of citric acid and ethylene glycol, which was evaporated and calcined in air at 350°C for 30 min. The resulting spinel was impregnated to give a 1 wt.% Cu concentration. The activity of the Cu-promoted spinel in a slurry reactor with synthesis gas was compared with the spinel without added Cu under conditions shown in Table X.49. The catalyst was first reduced in situ with synthesis gas. The Cu-

promoted Co_2MnO_4 spinel had higher activity and gave higher olefin selectivity than unpromoted Co_2MnO_4 spinel or a Co_3O_4 /1% Cu catalyst.

GROUP VIII METAL SUPPORTED CATALYSTS

Several patents were issued in which inorganic metal oxides were used as supports for Group VIII metals. A patent issued McVicker and Vannice (X.173) claims catalysts prepared by depositing K or Rb Group VIII metal carbonyl cluster complexes on a high surface area support material, drying in the absence of oxygen and reducing at elevated temperatures. A companion case, issued to McVicker and Vannice (X.174), which is identical both in title and text, excluding claims, covers a process application for these catalysts. The catalysts were prepared by depositing bimetallic carbonyl compounds onto high surface area supports from solutions in organic solvents. At least some, if not all, of the materials were highly sensitive to air. A whole laundry list of potential bimetallic carbonyls were presented, of which 6 were actually used in catalyst preparations. Of the Group VIII carbonyls, only Pd and Os were not specifically included in dependent claims. Re, Ru and Ir, which were actually used in preparing catalysts, were specifically covered in dependent claims. Supports that were specifically claimed were alumina, silica, silica-alumina, titania, zirconia, hafnia, tantalum, niobia, vanadia, and magnesia.

Several catalysts were tested by passing a 3/1 H_2 /CO synthesis gas mixture over the catalysts at 250 to 284°C and 1 atmosphere. Under these conditions, very low CO conversions were observed. More long chain olefins were formed over the cluster catalysts of this invention than with conventional catalysts prepared by impregnating alumina (eta) with aqueous solutions of Fe nitrate and KNO_3 .

Palladium on Alumina

A patent assigned to Vannice and Garten (X.175) claims a process for producing methane by passing synthesis gas over palladium supported on an acidic metal oxide selected from alumina and HY zeolite with the palladium metal particle being maintained at $<100\text{\AA}$. CO conversions of 3.5% were obtained when a 3/1 H_2/CO mixture at 1 atm was passed over these catalysts. Methane was essentially the only hydrocarbon product. The methane yield per Pd surface was higher for the catalysts of this invention than for Ni on a 5% $\text{Ni}/\text{Al}_2\text{O}_3$ catalyst, although the CO conversion over the nickel catalyst was 55% under these conditions.

Platinum on Alumina

A patent issued to Vannice and Garten (X.176) claims a process for producing dimethyl ether by passing CO and H_2 over platinum supported on alumina. Over a 1.16% $\text{Pt}/\text{Al}_2\text{O}_3$ catalyst at 274°C for a 1/1 H_2/CO gas mixture at 10 atm pressure, 2.5% CO was converted to hydrocarbons with a hydrocarbon selectivity of 70% methane, 8% ethane, and 23% dimethyl ether.

Nickel on Silica or Alumina

A patent issued to Yates and Murrell (X.177) claim Ni catalysts having Ni surface areas of $200\text{--}400\text{ m}^2/\text{g}$ prepared by slurring a Ni metal precursor in a nonaqueous solvent with a high surface area refractory oxide, removing the solvent and reducing with H_2 to form Ni metal. A use for these catalysts is in hydrocarbon synthesis as in the FT reaction. Ethane hydrogenolysis and benzene hydrogenation are included in the examples. However, no examples are provided that cover conversion of synthesis gas. The specification states that several co-metals, of which potassium is one, should be avoided since they act as catalyst poisons.

MOLYBDENUM CATALYSTS

A patent issued to McCandlish and Kugler (X.178) claims a FT process using a catalyst comprised of molybdenum oxycarbonitride. The catalyst, in which the oxygen, carbon and nitrogen are distributed throughout the bulk structure, is prepared by thermally decomposing an ethylenediammonium molybdate at 650°C in an inert atmosphere. The catalyst was pyrophoric and could be passivated with oxygen for handling in air. The active form was easily regenerated in H₂ at 450°C. CO conversions up to 20% were obtained over this catalyst at 254 to 315°C with a 1/1 H₂/CO synthesis gas mixture at 1 atm and 2400 GHSV. Methane was the dominant product under these conditions.

ALCOHOL SYNTHESIS

A patent issued to Apesteguia et al. (X.179) claims catalyst compositions consisting of a solid solution or coprecipitated mixture of a first oxide and a second oxide, wherein the first oxide is selected from yttria and rare earth oxides and a second oxide is a Group Ia oxide and Group Ib metal. These catalysts are useful for conversion of synthesis gas to alcohols, especially isobutanol and methanol. Several representative catalysts were prepared: Cu impregnated onto cerium oxide; coprecipitated Cu, MgO and ceria; K impregnated onto coprecipitated Cu, MgO and ceria; Cu supported on MgO and yttria. These catalysts provided very large yields of alcohols, primarily methanol along with lesser amounts of isobutanol (see Table X.50). Methane and CO₂ yields were also quite sizable.

PROCESS IMPROVEMENTS

Although the overwhelming number of FT related patents that have been assigned to Exxon are related to catalyst compositions or their use, several patents

related to improvements in the design or operation of the FT process have been issued. Many of the more recently issued patents have concentrated on process improvements.

The FT-type process improvements that are covered are:

- ! use of 2-stage process configuration to improve hydrocarbon selectivity,
- ! improved product selectivity through olefin addition to the feed,
- ! improved CO conversion and C₅+ selectivity through water addition to the feed,
- ! modified gas inlet system to improve axial distribution of particulate catalyst in a slurry reactor,
- ! use of downcomers to redistribute catalyst in a slurry reactor,
- ! use of pentane as heat transfer fluid,
- ! bundled tubular reactor with shell-side cooling,
- ! fixed-bed start-up protocol to prevent temperature runaway,
- ! method for defining operating conditions for a slurry reactor,
- ! method for activating ex situ reduced cobalt slurry catalyst,
- ! method for rejuvenating and redistributing catalyst in a slurry reactor,
- ! method for removing fines from particulate catalysts.

2-Stage Processes

Two different 2-stage process configurations are covered. In one, a patent issued to Kim and Fiato (X.180) claims a process in which synthesis gas contacts in a reaction zone in a first bed a first catalyst having a high olefin selectivity and contacting the resulting olefins in a second bed with a catalyst having a high selectivity for converting olefins to heavier paraffinic hydrocarbons. The claim specifies that the first bed catalyst is selected from a group consisting of Fe/Zn/Ce/K, Fe/Mn/K and Fe/Co/K

and the second bed catalyst is selected from the group consisting of Ru/TiO₂, Ru/SiO₂, and Ru/Al₂O₃. The process operates at 150-220 psig with the temperature of the first catalyst being about 260-280°C and the second catalyst being about 190-210°C. The range of the preferred H₂/CO ratio, as stated in the specification, was 1.5 to 2.5. An example is provided that shows that over a Fe/Zn/Ce/K catalyst at a CO conversion of 59%, the selectivity to CO₂ was 26% with the remaining product being hydrocarbons (see Table X.51). Hydrocarbon formation is split between the 1st and 2nd catalyst beds in a ratio of 45/55. Based upon approximately equal yields from the two beds and equal yields from each of the two catalysts operating alone, a linear combination predicts a decrease in methane selectivity and an increase in C₁₀+ selectivity when operating in this fashion. Experimentally, the observed methane and C₁₀+ selectivities were even better than predicted (see Table X.52).

A second configuration involves an interstage product separation step. A patent issued to Fiato (X.181) claims a two stage hydrocarbon synthesis process comprising reacting synthesis gas at reaction conditions in a first stage in the presence of a supported cobalt or ruthenium catalyst at a pressure ≥ 10 atmospheres, separating liquid from H₂ and CO, and reacting the remaining H₂ and CO at a pressure less than 10-12 atmospheres, but no greater than the first stage, in the presence of cobalt supported on alumina at reaction conditions. This process configuration takes advantage of the apparently higher activity of Co/Al₂O₃ catalysts at lower partial pressures of CO and H₂ relative to catalysts comprising Co or Re on other oxides supports, such as titania. 2-Stage processes having interstage separation of hydrocarbon product, in which the remaining H₂ and CO are recompressed, have the additional advantage of lower energy requirement.

Product Improvement through Feed Modification

Olefin Addition to Feed. Two patents were issued for processes that reduce methane formation in the FT process through injection of olefins. The first patent issued to Kim (X.182) claims a process with a catalyst comprising Group VIII (Fe, Co, Ru) metals supported on an inorganic oxide support wherein olefins are added to the feed to reduce methane formation. The second patent issued to Iglesia (X.183) claims further methane reduction by injecting the olefins at a point below the inlet of the reactor.

Kim (X.84) showed that injection of ethylene in the feed stream increased CO conversion and decreased methane selectivity. A 2/1 H₂/CO synthesis gas mixture gave a CO conversion of 8.4% and a methane selectivity of 6.4% when passed over a Ru/TiO₂ catalyst at 200°C at 70 psig at a flow rate of 55 standard cm³/3 g catalyst/min. When 8.2 mol % ethylene was injected into the feed stream, CO conversion increased slightly to 9.0% and methane selectivity dropped to 3.5%. When 20% ethylene was added, the methane selectivity dropped even further to 2.7%. In another case, when 4% 1-decene was substituted for ethylene, an approximate 20% decrease in methane selectivity occurred. Over a precipitated bulk Fe catalyst the introduction of 9.6% ethylene into the same synthesis gas mixture at the same temperature and pressure at a flow rate of 100 standard cm³/10 g catalyst/min caused a 30% decrease in methane selectivity.

In the 2nd case, methane was further reduced through adding the ethylene downstream of the inlet of the reactor. A patent issued to Iglesia (X.58) claims that for a FT process using an Fe, Co or Ru catalyst, the methane yields are further reduced when the olefins are added to the reactor bed below a point equivalent to 10% of the distance from the top to the bottom of the reactor bed and above a point in the reactor

bed equivalent to 10% of the distance from bottom to the top of the reactor bed. The addition level is stated as the amount sufficient to suppress methane formation. In the examples, for ruthenium and cobalt-ruthenium on titania catalysts, adding ethylene below the top 1/3rd of the catalyst bed decreased the amount of ethane produced relative to the amount of ethylene added to the feed. Likewise, the amount of C₃+ increased accompanied by a small decrease in methane yield, as shown in Table X.53.

Water Addition to Feed. A patent issued to Kim (X.184) claims enhanced CO conversion and C₅+ selectivity for a once-through, fixed or slurry bed FT process comprising contacting the synthesis gas containing 1-70 vol % water in a reaction zone with a catalyst consisting of cobalt, ruthenium and mixtures thereof on titania converting 90% of the CO to liquid hydrocarbons in the substantial absence of CO₂. This case involved numerous filings and abandonments over an eight year period from the time of the first filing on July 13, 1985. The long background discussion of numerous prior patents outlines the extensive number of related cases. Numerous examples were shown for a range of catalysts exhibiting increased CO conversion, decreased methane selectivity and increased C₁₀+ liquid yield in the presence of added water.

Reactor Design

Modified Gas Inlet System. Two patents were issued related to the design of FT reactors. One patent issued to Chang and Coulaloglou (X.185) claims a method for improving axial distribution and mixing of particulate catalyst in a slurry bubble column by introducing a secondary gas into the column at a location within the lower 20% of the vertical height of the column but above the gas distributor plate. This gas stream can be part of the synthesis gas feed, recycle gas, inert gas, condensed light hydrocarbons or light synthesis hydrocarbons which vaporize under conditions present in the column.

A figure is presented of experimental data taken in a 5 ft diameter by 30 foot high slurry bubble column that shows that the solids distribution in the reactor is more uniform when using this gas inlet configuration.

The basis of this design is that since solids distribution along the axis of a column is a function of gas velocity in the column, by increasing gas velocity, solids distribution will decrease in the lower part of the column and increase in the upper part. The key to the method disclosed in this patent is that introducing a disproportionate share of the gases at an inlet point source close to but above the distributor inlet will reduce the concentration of solids in that particular portion of the reactor and result in an increase in solids concentration in other portions of the reactor. The overall result is a more even distribution of solids in an axial direction.

Downcomers. A patent issued to Behrmann et al. (X.186) claims a method for redistributing catalyst in a slurry reactor by use of a downcomer. The downcomer is specified as a vertical conduit which is open at both ends, fully submerged in the slurry with the bottom near the bottom of the reactor and the top near the top surface of the slurry. The bottom is shielded by a baffle plate to divert gases from rising from the bottom and gas free slurry enters at the top and passes down the conduit and out at the bottom. The preferred cross sectional area of the downcomer should be no more than 2% of the total cross sectional area of the entire reactor. An example is provided using the same equipment described under Pedrick et al. (X.187) in which the bubble column was run both with and without a downcomer in operation. In both cases rejuvenation tubes were operated in an equivalent manner. The results showed that axial distribution of the catalyst was more uniform when the downcomer was in operation, as shown in Figure X.15.

A patent issued to Chang (X.188) claims a slurry bubble column reactor design incorporating a peripheral downcomer. The reactor comprises a double walled vessel wherein the inner vessel serves as the main reactor zone and the peripheral circumferential top rim of the inner vessel wall, having attached to it an inverted channel having an apex and two edges, being attached to the inner wall along the outer edge of the inverted channel. The second edge of the inverted channel extending over the main reaction zone creating a gas space within its inverted contour with a gas vent extending upward from the inverted channel. A liquid by-pass pipe extends from below the top of the liquid level interface through the inverted channel between the attachment of the inverted channel to the inner reactor wall and the apex of the channel providing a means through which slurry flows into the peripheral downcomer section. This design is shown in Figure X.16 wherein the outer edge 8A of the inverted channel is attached to the top of the inner vessel wall. The innermost edge is in contact with the slurry in the main reaction zone. Gas disengaging from the slurry trapped in the inverted channel exits into the gas disengagement space 5 through line 12 and slurry exits through line 13 onto the top of inverted channel outside the apex 10 through line 13 into the downcomer section 4. The higher density in the downcomer section promotes flow from the top of the vessel to the bottom. A more complete description of this invention can be obtained by referring to the patent specification.

Heat Transfer System. A patent issued to Stark (X.189) claims a method for removing heat from a FT reactor which comprises passing pentane through the tube-side of cooling tubes, vaporizing the pentane to a pressure greater than the pressure in the reaction zone and recovering the vaporized cooling medium. In a preferred embodiment of this invention the vaporized pentane is sent to an expander where the

high pressure energy is recovered. The low pressure vapor leaving the expander is fed to a condenser where it is liquified and then pumped up to pressure and fed back to the reactor. The recovered energy can be used to drive compressors for an air separation plant or turbogenerators to generate electricity.

Tube-in-Shell Reactor. A patent issued to Koros (X.190) claims a slurry FT reactor wherein the slurry catalyst is disposed in a plurality of vertically arranged tubes having a length/diameter ratio of at least 10 with each tube surrounded by a common heat transfer medium disposed within the shell of a shell and tube reactor, the heat transfer medium not in fluid communication with the slurry liquid. The description of the operation of a reactor comprising a 5.76 in ID x 50 ft long pipe mounted in a 12 inch pipe cooling jacket was provided. Liquid heights varied between 12 and 32 feet with linear gas velocities up to 7.9 cm/sec. For a 2.1/1 H₂/CO synthesis gas mixture at a superficial velocity of 5 cm/sec, 2200 GHSV, reactor pressure of 285 psig, and steam jacket pressure of 140 psig, CO conversions in excess of 50% were obtained. The temperature of this run was not given.

Reactor Operation

Reactor Start-up. A patent issued to Arcuri (X.35) claims a procedure for the start-up of a fixed-bed FT reactor that allows a flexible and more effective response to a potential temperature runaway. While elevating the temperature, pressure and feed flow rate to line-out levels, the composition of the H₂ and CO in the feed is maintained at a H₂/CO mole ratio not exceeding 90% of the mole ratio at lineout. After the temperature, pressure and feed flow rate reach normal operating levels, the H₂/CO ratio is gradually increased to the operating lineout mole ratio.

The patent illustrates the advantage of using this operating protocol relative to using temperature as the main control parameter. Comparative exotherms are provided for two different startup procedures used on a 1/2 inch ID, 6 foot long tubular pilot scale FT reactor that was submerged in a sand bath, as shown in Figure X.17. Following a conventional start-up procedure in which temperature is slowly increased to bring the reactor online, a very significant temperature runaway occurred. In this example, the final target operating conditions were 359°F with a 2.08/1 H₂/CO synthesis gas mixture at 1000 GHSV at 280 psig. The steps that were followed and the corresponding exotherms that resulted in each step were as follows:

1. Synthesis gas mixture and flow rate were established at lineout conditions at a pressure of 60 psig and a sand bath temperature of 337°F. The maximum exotherm in the bed during this period was 5°F.
2. Pressure was then increased to lineout pressure of 280 psig and held 3 days. A maximum exotherm of 12°F resulted.
3. Then temperature was increased slowly from 337 to 353°F and held 24 hours. During this period the maximum exotherm was 21°F.
4. Afterwards, the temperature was increased 2°F over a 40 min period to 355°F. The magnitude of the maximum exotherm remained the same at 22°F.
5. However, when the temperature was increased over a 2 hour period to 359°F, which was a 4°F change in temperature, the maximum exotherm increased to 242 F°, indicating a severe temperature runaway.

By contrast, the exotherms were much less when the procedure taught in the patent was followed, namely using a decreased H₂ content in the feed gas. In this

example, the target lineout reactor conditions were 380°F with a 2.1/1 H₂/CO synthesis gas mixture flowing at 1000 GHSV at 280 psig. The steps that were followed and the corresponding exotherms that resulted in each step, as shown in Figure X.18, were as follows:

1. The H₂ feed gas (1.8/1 H₂/CO) rate was brought to 910 GHSV at 60 psig and 337°F. The maximum exotherm was 7°F.
2. The pressure was increased to the lineout pressure of 280 psig over 0.5 hours. The maximum exotherm was 9°F.
3. The temperature was increased almost to the lineout temperature of 374°F in 1 hour during which the maximum exotherm was 17°F.
4. H₂ in feed gas was increased to a 2.0/1 H₂/CO ratio in 1 minute as flow rate increased to 970 GHSV. Maximum exotherm was 23°F.
5. The H₂ in feed gas was increased to a 2.1/1 H₂/CO ratio as flow rate increased to the final 1000 GHSV. The maximum exotherm was 25°F.

During this sequence the exotherm remained under control and space time yield data was higher with a higher CO conversion. Another example was also given that illustrates how rapidly an exotherm can occur in a FT synthesis reactor.

Setting Operating Conditions. A patent issued to Herbolzheimer and Iglesia (X.191) claims a method for operating a solid-liquid-gas bubble column having a diameter >15 cm for FT synthesis over a supported cobalt catalyst in which the solids are fluidized by the gas. The invention comprises:

- (a) injecting gas at an average gas velocity >2 cm/sec;

- (b) fluidizing the particulate catalyst having an average diameter $>5 \mu\text{m}$ in an expanded liquid column >3 meters in height and a particle settling velocity U_s and a dispersion coefficient D , such that

$$0.5 (U_s - U_L) \leq \frac{D}{H}, \text{ where } H > 3\text{m}$$

where

$$U_s = \frac{1}{18} d_p^2 \frac{\rho_s - \rho_l}{\mu} g f(C_p), \text{ where } d_p > 5 \mu\text{m}$$

- (c) operating at plug flow at a gas velocity U_g , expanded liquid height H , and dispersion coefficient D such that

$$U_g \geq 0.2 \frac{D}{H} \text{ where } H > 3 \text{ m}, U_g > 2 \text{ cm/sec.}$$

In one example using a Co-Re/TiO₂ catalyst having a density of 2.7 g/cm³, a liquid density of 0.7 g/cm³, and a wax viscosity of 0.01 g°cm/sec, the particle settling velocity is:

$$U_s (\text{cm/sec}) = 1.1 \times 10^{-4} [d_p (\mu\text{m})^2]$$

For a 60 μm average particle, $U_s = 0.39 \text{ cm/sec}$. For a liquid velocity of $0.5 U_s$, and a column height of 3 m, a gas velocity of 2 cm/sec provides a Peclet number of 10, which

is the minimum gas velocity allowed that would maintain suspension of the solids in the column and maintain a plugflow operation in the column.

Catalyst Pretreatment

Catalyst Activation and Rejuvenation. A patent issued to Mitchell (X.192) claims a method for activating a fresh, reduced cobalt containing FT catalyst by treating the catalyst with H_2 in hydrocarbon liquids for a period sufficient to increase catalyst productivity. A patent having an identical specification issued to Mitchell (X.193) claims a process using the method of catalyst activation that is run under FT conditions. The method applies specifically to treating catalysts that had been previously reduced ex situ and exposed to the atmosphere before introduction into a slurry system. Such catalysts are suspended in a slurry and treated with H_2 at hydrocarbon synthesis temperature and pressure with temperatures no lower than $40^\circ C$ below hydrocarbon synthesis temperature. Another patent issued to Mitchell (X.194) claims a method for rejuvenating partially deactivated catalysts which is essentially the same procedure described above. An example for activating a 12% Co-1% Re on a 94% TiO_2 -5% Al_2O_3 catalyst by reducing the catalyst with H_2 was given. Following reduction, catalyst was passivated with a CO/H_2 stream. This passivated catalyst was combined with wax in a slurry reactor and treated with H_2 . Synthesis gas productivity over the treated catalyst increased to 100% relative to 25-60% productivity for the non- H_2 treated catalyst. The effect of several periods of catalyst rejuvenation during a 50 day run on catalyst productivity following this method is shown in Figure X.19.

A patent issued to Pedrick et al. (X.89) claims a method by which reversibly deactivated particulate hydrocarbon synthesis catalyst in a gas-slurry reactor is rejuvenated and more uniformly distributed in the reactor. A hydrogen rich gas, injected

into the bottom of a vertical draft tube which is fully immersed in the slurry, forces the catalyst up the draft tube while concomitantly reactivating the catalyst, which is discharged from the top into the upper portion of the slurry phase. The examples contained results from a series of balances made during a run in a 4 ft diameter by 35 ft high reactor that show both activation and axial redistribution of the catalyst. During the run, various combinations of draft tubes fed with H_2 , which were commonly referred to as rejuvenation tubes, and draft tubes fed with tail gas, were employed. The maximum flue-gas fed draft tube plus rejuvenation tube cross-sectional area for any of the run conditions was 2.6% of the cross sectional area of the reactor. A feed gas mixture comprising 56% H_2 /26% CO/13% CO_2 /5% CH_4 , by volume, was fed to the reactor containing a 12% Co-1% Re on a 94% TiO_2 -5% Al_2O_3 slurry catalyst at 210-230°C and 20 atm. When operating the reactor with two-2 inch diameter and two-4 inch diameter flue-gas fed draft tubes and one-3 inch diameter rejuvenation tube, the superficial velocities in the respective locations were:

inlet,	12-14 cm/sec;
outlet,	10.5-12.1 cm/sec;
draft tubes,	58-60 cm/sec;
rejuvenation tubes,	40-70 cm/sec.

Under these conditions the axial dispersion of the catalyst in the reactor improved significantly (Figure X.20) and productivity increased from 41 to 69 (vol CO/hr/vol slurry). The overall reactor temperature differentials from the bottom to the top of the reactor for the individual balances using both lift and rejuvenation tubes was only a couple of degrees.

The effect of rejuvenation tubes on catalyst activity is shown in runs where both flue gas fed draft tubes as well as rejuvenation tubes were used. In a run sequence described in Figure X.21, the decline in activity of catalyst was followed for a period of 3 days after which one 3 inch rejuvenation tube was brought on line. Immediately upon addition of H₂ an exotherm was observed followed by an immediate increase in catalyst activity recovering its initial activity in 1-2 days, after which it remained constant. After lineout, adding another rejuvenation tube provided no additional benefit. The exotherm in the rejuvenation tube was also used as a method to determine the degree of aging of the catalyst.

The beneficial effect of heating the rejuvenation tube to a temperature higher than the surrounding slurry was also demonstrated. Although the temperature in the rejuvenation tube is typically a few degrees higher than the surrounding slurry, through insulation of the tube and heating with steam, even higher temperatures can be attained. During one period in which the rejuvenation tube was heated sufficiently to raise the temperature an additional 10°F, CO conversion in the reactor increased from 26 to 36% over a 24 hr period whereas in a prior balance period without external heating being applied to the rejuvenation tube, CO conversion had dropped from 32 to 26% over a 12 hr period, as shown in Table X.54.

A patent issued to Hsia (X.195) claims a FT process comprising a slurry reactor design coupled with a continuous rejuvenation reactor. Deactivated catalyst is reactivated and rejuvenated using an external rejuvenation reactor vessel to which catalyst from the synthesis reactor is continuously fed via a downcomer from the top of the slurry bed in the synthesis reactor to the bottom of a slurry bed in the external rejuvenation reactor vessel (see Figure X.22). Likewise, rejuvenated catalyst is fed to

the synthesis reactor via a downcomer from the top of the slurry bed in the rejuvenation reactor to the bottom of the slurry bed in the synthesis reactor. Slurry flow from synthesis reactor vessel to the rejuvenation vessel and the flow of rejuvenated catalyst back to the synthesis reactor vessel are driven by gravity since both vessels are under the same pressure. A drawing is included but no examples are given.

Removal of Catalyst Fines. A patent issued to Hsu and Robbins (X.196) claims a method for removing $<1\ \mu\text{m}$ particles adhering to catalyst particles containing a Group VIII metal supported on an inorganic refractory oxide. The method comprises dispersing the particles to which the $<1\ \mu\text{m}$ particles adhere in a liquid comprising a Fischer-Tropsch derived wax, agitating the dispersion and concentrating the $<1\ \mu\text{m}$ particles in the supernatant liquid and separating the $<1\ \mu\text{m}$ particles by decanting this layer from the larger particle containing phase. Although examples are given in which the liquid used in the particle classification step includes solvents other than Fischer-Tropsch derived wax, the claims only apply to the latter (see Table X.55). Catalysts stirred with FT wax at 130°C gave initially a filtration rate of $5.8\ \text{gal/ft}^2/\text{min}$ which decreased to $0.05\ \text{gal/ft}^2/\text{min}$ after stirring for 44 hours. Using the method of this invention of extended stirring and separating the decant after 3 cycles, the filtration rate improved to $14.5\ \text{gal/ft}^2/\text{min}$.

Apparatus for Substantially Plug-Flow, Slurry Phase Synthesis

Koros (X.92) has patented a slurry apparatus that permits a substantially plug-flow slurry-phase operation in an arrangement of multiple tube reactors in a shell. Thus, the concept of the mechanical part of the tube and shell reactor resembles a Sasol Arge reactor; however, numerous additional features are incorporated to permit slurry-phase operation.

In Figure X.23, the syngas is added through 12 and is dispersed through sparger 14 into the liquid slurry medium, held at a level so as to maintain a gas-liquid interface, with the gas held in the space between 15, the slurry-gas interface and 18, a distributor tray.

A series of reactor zones, 20, are arranged within the shell, such as the ones shown by the example in Figure X.24.

The reactor tubes are held in place by lower, 22, and upper, 28, tube sheets. The space between the distributor plate, 18, and the lower tube sheet, 22, may or may not contain catalyst in addition to the slurry liquid. A detail of the distribution zone is provided in Figure X.25. The bubbly liquid from area 9 enters the tube/bubble cap 19A/19B. The bubble cap is aligned vertically with the reaction zone tube 20. The bubble cap is sized to give a pressure drop and injection velocity sufficient to decrease the size of the bubbles and to suspend the catalyst in the reaction zone (injection velocity about 20 to 100 ft/sec.). The gas to liquid transfer rates are at least equal to the conversion rate of the syngas gas.

Preferred slurry materials are stated to be Fischer-Tropsch waxes and C_{16} - C_{18} hydrocarbons. The concentration of solids are usually about 10-50 wt.%, preferably 30-40 wt.% solids.

Catalyst/slurry addition/withdrawal may be effected through line 32. The region between tube sheets, 28 and 30, allows interconnection between the upper ends of the reaction zones for gas, liquid and catalyst. Tube sheet 30 holds filter cartridges, 31, which may be manufactured from sintered metal mesh, woven metal fibers, glass fibers, cloth or fibrous carbon, which can retain the catalyst particles while allowing the wax to pass. The filter cartridges are aligned vertically above each reaction zone. A gas-liquid

disengagement zone lies above the filter cartridge tube sheet, and liquid product, separated from catalyst, can be withdrawn through tube 40 and/or 33. A demister, 41, separates gas from liquid droplets; residual gases are withdrawn through tube 42.

During operation the catalyst, 21, is preferably located in the reaction zone although some catalyst may be found in the liquid zones above or below the upper and lower tube sheets.

The catalyst most preferred is cobalt on titania (primarily in the rutile form) with less than about 70 m²/g. Preferred promoters are stated to be rhenium and hafnium.

It is stated that "...catalyst particle size is not critical..." but is preferably in the 20-150 micron size range.

The example described the operation of a single reactor (6" o.d., 5.76 i.d.) about 50 ft. tall mounted inside a 12" pipe to serve as a cooling jacket. Feed gas to the reactor was preheated.

The catalyst was prepared by impregnation cobalt onto titania extrudates which were crushed and screened to give ca. 30 micron diameter particles (presumably the catalyst contained promoters). The catalyst was reduced in hydrogen in a fluidized bed, and then the slurry wax was introduced. Following a prescribed procedure of start-up, they attained a CO conversion in excess of 50% at GHSV = 2800. Following a brief reactor upset, the unit was restarted at a higher steam jacket pressure (140 psig) and higher reactor pressure (285 psig at the reactor gas outlet). The reactor maintained CO conversion of 60-70% (2800-3600 hr⁻¹) for nearly seven days of synthesis. This material was stated to be a "...very active HCS catalyst." Methane selectivities were in the range of 2.7 to 3.2%. Assuming the steam jacket pressure represents steam/water,

this corresponds to 354°F (178°C); presumably the reactor side would not be at a much higher temperature.

This summarizes the patents abstracted through October 19, 1994; Appendix will cover later period.

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Table X.1. Activity of laser generated iron carbide catalysts Reaction Conditions: 270°C, 2/1 H ₂ /CO, 200 sccm, 75 psig, in octacosane				
	Carbide from Fe ₃ O ₄	Laser derived carbide	Laser derived carbide + K	Laser derived carbide + Si
Preparation Method	Fe ₃ O ₄ reduced in H ₂ @ 450°C/5-7 hrs and treated with H ₂ /CO/350°C	Fe(CO) ₅ /C ₂ H ₄ laser feed	Fe(CO) ₅ /C ₂ H ₄ laser feed/ impregnated with 2% K as K ₂ CO ₃	Fe(CO) ₅ /C ₂ H ₄ / SiH ₂ (CH ₃) ₂ laser feed
V/V cat/hr	2000	4000	4000	500
% CO conversion	71.9	82.5	66.5	5.0
Selectivity, wt% CO ₂ free basis				
CH ₄	16.1	9.5	5.6	15.9
C ₂ -C ₄ Paraffins	17.3	7.8	0.8	27.0
C ₂ -C ₄ Olefins	18.9	27.0	11.5	19.0
% olefins in C ₂ -C ₄	50.7	77.6	93.5	41.0

Table X.2. Activity of high and low surface-area Fe-Co spinels for synthesis gas conversion. <i>In situ</i> catalyst reduced in slurry with H ₂ at 200°C and 1 atm for 1 hr. <i>Ex situ</i> catalyst reduced with H ₂ at 300°C+ and then H ₂ /CO at 350°C+. Run in slurry reactor at 250°C, 1200 v/v/hr, 2/1 H ₂ /CO, 70 psig, 600 rpm in octacosane; time on stream not specified.						
	Starting Spinel					
	Fe _{2.85} Co _{0.15} O ₄ /1 wt.% K high surface area		Fe ₃ O ₄ /1%K high surface area		Fe _{2.85} Co _{0.15} O ₄ /1 wt.% K low surface area	
	in situ	ex situ	in situ ^a	ex situ	in situ	ex situ
Spinel surface area, m ₂ /g	>100	>100	>100	>100	0.29	<0.3
CO Conv, mol %	60	64	8.0	65	<4.0	42
CO ₂	36	36	5.2	39	na	24
Hydrocarbons	24	28	2.8	26	na	18
HC Selectivity wt%						
CH ₄	4.5	8.2	11.4	12.8	na	9.3
C ₂ -C ₄ paraffins	2.5	3.6	8.6	8.0	na	5.5
C ₂ -C ₄ olefins	17.5	27.4	34.3	32.2	na	27.0
C ₅ +	75.5	60.8	31.4	47.0	na	58.2
Taken from Example 3, Table III and Example 5, Table IV U.S. Patent 4518707 (X.4). a. Taken from Table V of U.S. Patent 4518707 (X.4).						

Table X.3. Activity of *ex situ* reduced and carbided high and low surface-area Fe-Co spinels. High and low-surface-area spinels were reduced *ex situ* with H₂ at 300°C+ followed by carbiding with H₂/CO at 350°C+. Reactions run in slurry reactor at 250°C, 1200 v/v/hr, 1/1 H₂/CO, 70 psig, in octacosane.

	Starting Spinel x = 2.85	
	high >100 m ² /g	low < 5 m ² /g
CO conv, mol %	45	44
CO ₂ , mol %	26	29
HC yield, mol %	19	15
HC Selectivity wt%		
C ₁	4.4	5.9
C ₂ -C ₄	19.3	25
C ₂ -C ₄ olefins	90	90
C ₅ +	76.3	69.1
Data taken from Example 2, Table II in U.S. Patent 4544672 and Ex 4, Table III in U.S. Patent 4518707 (X.4).		

Table X.4. Activity of alloys in a slurry reactor prepared *ex situ* from high surface-area Fe-Co spinels. Spinels reduced *ex situ* with H₂ at 350°C /12 hrs followed by 400°C/24 hrs, but not carburized. Run in slurry reactor at 270°C, 70 psig, 1200 v/v/hr, 600 rpm in octacosane.

	Fe ₃ O ₄ /1%K high surface area		Fe _{2.85} Co _{0.15} O ₄ /1 wt.% K high surface area	
H ₂ /CO	1.0	2.0	1.0	2.0
CO Conv, mol %	44	28	55	54
CO to CO ₂ , mol %	26	15	34	34
CO to HC, mol %	18	13	21	20
HC Selectivity Wt. %				
CH ₄	4.4	2.1	5.8	6.5
C ₂ -C ₄ paraffins	1.9	0.6	3.4	2.7
C ₂ -C ₄ olefins	25.2	10	25.2	27.3
C ₅ +	68.7	87.2	65.0	63.4
Data taken from Example 7, Table VI, U.S. Patent 4518707 (X.4).				

Table X.5. Activity of low-surface area spinel derived catalysts in a fixed-bed reactor. Catalysts treated with flowing 90% H₂/N₂ at 500°C at 100 psig for 5-7 hrs. Run in fixed bed reactor with 1/1 H₂/CO at 300 psig.

	Fe ₃ O ₄ /1%K		Fe _{2.85} Co _{0.15} O ₄ /1 wt.% K	
Time on stream, hrs	1	12	1	12
V/V/hr	570	1000	570	1000
Furnace Temp°C	305	305	270	270
CO Conv, mol %	79	67	98	98
CO to CO ₂ , mol %	36	31	42	40
CO to HC, mol %	43	36	56	58
Wt% selectivity				
C ₁	8.5	5.8	9.1	7.4
C ₂ -C ₄ paraffins	5.2	4.7	6.2	6.2
C ₂ -C ₄ Olefins	26.6	30.6 ^b	39.4	50.3 ^b
C ₅ +	59.7	-	45.2	
C ₆ +	-	58.9	-	36.1

Data taken from Example 1 of U. S. Patent 4537867 (X.8). Catalysts prepared by sintering mixtures of metal oxides.

b. Applies to C₂-C₅ olefins.

c. Actual bed temperatures were not reported.

Table X.6. Effect of Co concentration on Fe-Co spinel catalyst performance after 12 hrs on stream. Catalysts treated with flowing 90% H₂/N₂ at 500°C at 100 psig for 5-7 hrs. Catalysts run in fixed bed reactor at furnace temperature of 295°C, 300 psig, 1000 v/v/hr, 1:1 H₂:CO.

x in Fe _x Co _{3-x} O ₄	2.97	2.85	2.625	2.20
Time on stream, hrs	12	12	12	12
CO Conv, mol %	97	98	97	98
CO ₂ , mol %	27	40	41	42
HC, mol %	70	58	56	56
Selectivity				
CH ₄	8.3	7.4	18.0	13.2
C ₂ -C ₆ olefins	46.5	53.1	41.4	53.0
C ₂ -C ₆ paraffins	6.9	7.2	13.3	10.6
C ₇ +	38.3	32.3	27.3	23.2

Data taken from Example 7, Table 7 of U. S. Patent 4537867 (X.8).

Table X.7. Effect of temperature on performance of Fe-Co spinels in fixed bed reactor
Samples for 1-12 hrs on stream at 300 psig, 1000 v/v/hr, 1/1 H₂/CO.

	Starting Spinel						
	Fe _{2.625} Co _{0.375} O ₄ /1 wt.% K					Fe _{2.85} Co _{0.15} O ₄ /1 wt.% K	
Furnace Temperature, °C	225	240	260	270	290	235	270
Bed Temperature, °C	230	248	304	325	340	na	na
CO Conv, mol %	30	31	97	98	98	29.4	98.0
CO ₂ , mol %	4	7	40	33	41	8.0	42.0
HC, mol %	26	24	57	55	57	21.4	56.0
Selectivity							
CH ₄	8.1	8.2	19.1	16.7	19.1	2.6	5.2
C ₂ -C ₅ olefins	42.3	55.3	37.1	31.9	24.8	18.1	33.6
C ₂ -C ₅ paraffins	14.4	22.0	17.7	10.6	14.8	2.7	4.4
C ₆ +	35.2	34.5	26.1	40.8	41.3	76.8	55.9
Taken from Examples 8 and 12 of U.S. Patent 4537867 (X.8). na = not available							

Table X.8. Cu promoted high-surface area Fe-Co spinels as slurry catalysts.
Slurry reactor runs at 270°C, 2000 v/v/hr, 2/1 H₂/CO, 75 psig, 600 rpm in octacosane.

	Fe ₃ O ₄ /2%K		Fe _{2.85} Co _{0.15} O ₄ /2 wt.% K	Fe _{2.85} Co _{0.15} O ₄ /2 wt.% K/1 wt% Cu	
	In-situ	Ex-situ	In-situ	In-situ	Ex-situ
CO Conv, mol %	67	49	77	86	54
Wt% Selectivity					
CH ₄	2.0	3.8	4.4	4.2	4.5
C ₂ -C ₄ Olefin %	47.5	77	91	87	85
C ₁₀ Distribution					
α-olefins		50	49	59	46
n-paraffins		8	14.9	15	18
n-alcohols		2	1.0	3	1
β-olefins		17	4.1	2	6.0
all else		23	31	21	29
Taken from Tables I and II, U.S. Patent 4607020 (X.6).					

Table X.9. Effect of promoters on both high and low surface area $\text{Fe}_{2.25}\text{Mn}_{0.75}\text{O}_4$ spinels. Runs made at 270°C, 75 psi, 120 H₂/60 CO/20 N₂ cc/min flows, 70-80 g octacosane solvent, 20+ hrs on feed, 2 gm cat.

atomic % K	-	2.0	2.0	2.0	2.0	2.0
atomic % Cu	1.0	-	1.0	1.0	-	1.0
Surface area, m ² /g	>50	>50	>50	>50	<5	<5
gm catalyst	2	2	1	2	2	2
% CO conv	34	36	69	83 ^a	nil	nil
wt Selectivity						
CH ₄	8.8	3.5	1.7	2.3		
olefins in C ₂ -C ₄	78	91	94	92		
olefins in C ₁₀ +	?	?	63	65		
Taken from Example 2, Table 2 of U.S. Patent 4618597 (X.11).						
a. 30+ hours on feed						

Table X.10. Effect of Fe-Mn ratio in $\text{Fe}_x\text{Mn}_{3-x}\text{O}_4$ /2% K/ 1% Cu (>50 m²/g) on synthesis gas conversion. Runs made at 270°C, 75 psi, 120 H₂/60 CO/20 N₂ cc/min flows, 72 g octacosane solvent, 30+ hrs on feed, 2 gm cat.

gm catalyst	2	2	2	8	8
x	0.25	1.5	2.25	2.25	2.85
CO Conv	nil	30	83	87	79
Selectivity					
CH ₄	na	2.6	2.3	4.1	4.2
olefins in C ₂ -C ₄	na	86	93	92	94
Taken from Tables 3-4 of U.S. Patent 4618597 (X.11).					

Table X.11. Activity of $\text{Fe}_{2.25}\text{Mn}_{0.75}\text{O}_4/2$ at % K/1 at % Cu as catalysts for FT fixed bed and slurry reactors with 2/1 H_2/CO synthesis gas.			
	Fixed-Bed		Slurry
Temperature, C	263	275	270
Pressure, psig	65	65	75
Cat mesh	40-100	40-100	>140
Fe-SV	2.0	9.0	11.2
CO Conv	50	43	69
Selectivity			
CH ₄	8.6	9.5	1.1
C ₂ -C ₄	26.4	25.0	1.8
C ₅ +	65	65.5	97
CO ₂	35	44.0	38
Olefin % Content			
C ₂ -C ₄ olefin fraction	82	84	93
C ₁₀ + olefin fraction	65	67	63
Taken from Tables 2 and 4 of U.S. Patent 5118715 (X.13).			

Table X.12. Activity of Fe-Zn Spinel. Catalysts pretreated to 500°C in a 9/1 H_2/N_2 mixture at 100 psi and 100 v/v/hr space velocity for 5-8 h. Runs made in 1.7/1 H_2/CO at 300 psi at 550 vol/vol/h, 270°C furnace temperature, 10.5 hrs on stream.		
	1.0 Fe/0.065 Zn/0.030 Ce/0.030 K	Fe/1% K
CO conversion	98	96
wt% selectivity		
CH ₄	3.0	9.4
C ₂ -C ₆	36.0	50.1
C ₇ +	21.4	14.5
CO ₂	39.6	26
Specific olefin/paraffin prodn. ratios were:		
C ₂	3.1	2.5
C ₃	7.5	8.0
C ₄	15.0	8.3
C ₅	7.5	3.7
C ₆	4.6	2.0
Taken from Example 3, Table V of U.S. Patent 4639431 (X.16).		

Table X.13. Activity of Fe-Zn spinels promoted with Cu and K prepared with glycolate. Runs made with 2 g catalysts in at 270°C in 2/1 H₂/CO, 75 psig at 180 cc/min in octacosane for 40-100+ hr periods.

	CO Conv	CH ₄ selectivity	% olefins in C ₄	% Olefins in C ₂ -C ₄	% α-Olefin in C ₁₀ +
Fe _{2.8} Zn _{0.2} O ₄ ·2 at% K	33	2	89		
Fe _{2.8} Zn _{0.2} O ₄ ·1 at%Cu	34	10.1	81		
Fe _{2.8} Zn _{0.2} O ₄ ·2 at%K+1 at%Cu	73	1.9	89		
Fe _{2.8} Zn _{0.2} O ₄ ·2 at% K, 1 at% Cu	80	1.7		93	63
Fe _{2.45} Zn _{0.55} O ₄ ·2 at% K, 1 at% Cu	84	1.7		92	61
Fe _{2.3} Zn _{0.7} O ₄ ·2 at% K, 1 at% Cu	32	2.3		85	nd
Taken from Example 2, 6 and 7 of U.S. Patent 5100856 (X.17). Spinels having Fe concentrations greater than Fe _{2.5} Zn _{0.5} O ₄ fall within claimed compositions.					

Table X.14

Conversion of Synthesis Gas with Fe_{3-x}Zn_xO₄ in 0.3 L CSTR at 270°C, C₂₈ Solvent, H₂/CO = 2, 75 psig (from U.S. Patent 5118715, (X.13))

Catalyst	Fe _{2.8} Zn _{0.2} O ₄ A	Fe _{2.55} Zn _{0.45} O ₄ B	Fe _{2.3} Zn _{0.7} O ₄ C	Fe _{2.79} Zn _{0.21} O ₄	Fe _{2.79} Zn _{0.21} O ₄	Fe _{2.79} Zn _{0.21} O ₄
% Fe	66.87	60.28	53.70	71.50	71.50	71.50
% g-atom K	---	---	---	2	2	0
% g-atom Cu	---	---	0	1	0	1
CO Conv., %	80	84	32	73	33	34
CH ₄ /% Carbon	1.7	1.7	2.3	1.9	2.0	10.1
Olefin, %						
C ₂ -C ₄	93	92	85			
% α- in C ₁₀	63	61	*			
% α- in C ₄	---	---	---	89	89	81
NL/gFe-hr**	8.97 (7.18)	9.95 (7.96)	11.17 (8.94)	8.89 (7.11)	8.89 (7.11)	8.89 (7.11)
NL/g cat-hr	6.00	6.00	6.00	6.36	6.36	6.36

* Insufficient yield of liquids.

** NL total flow; parentheses, flow based on CO + H₂.

Table X.15. Comparison of Ce,K and K/Ce promoters for 1.0 Fe/0.30 Ti/0.065 Zn/0.03 Ce and/or 0.03 K in fixed-bed reactor. Pretreated at 500°C with 9/1 H₂/N₂ at 800 v/v/hr for 5-6 hrs. Runs made at 270°C, 1/1 H₂/CO at 2.6 MPa at 870 v/v/hr space velocity for time on stream of 30-50 hrs

	K	Ce	K/Ce
CO Conv	2	17	24
wt HC selectivity			
CH ₄	42	24.5	14.8
C ₂ -C ₃ paraffins	6	14.6	12.2
C ₂ -C ₃ olefins	42	14.1	32.5
C ₄ +	10	46.8	40.5

Taken from Example 5, Table VII in U.S. Patent 4657885 (X.18).

Table X.16. Manganese Catalysts with Ce,K and K/Ce in fixed-bed reactor. Pretreated at 500°C with 9/1 H₂/N₂ at 800 v/v/hr for 5-6 hrs. Runs made with 1/1 H₂/CO, 870 v/v/hr, 305°C, 2.0 MPa

	K	Ce	K/Ce
CO Conv	18	62.5	54.9
HC selectivity, wt. %			
CH ₄	10.2	17.5	7.5
C ₂ -C ₃ paraffin	4.1	10.0	2.6
C ₂ -C ₃ olefin	29.2	20.6	24.4
C ₄ +	56.5	51.9	65.5

Taken from Example 6, Table VIII in U.S. Patent 4657885 (X.18).

Table 17. Activity of a 10/1 Fe/Ti catalyst in a fixed bed reactor for synthesis gas conversion. Pretreated with 49 H₂/50 CO/1 N₂ at 270°C at 1 atm and 500 v/v/hr for 18 hrs. Runs made at 270 to 350°C, 1/1 H₂/CO at 120 psia and 150-1200 v/v/hr.

Temp, °C	270	300	325	350
CO Conv, %	90-20	65-40	96-80	97-90
Selectivity				
CH ₄	6-4	6-3	6-10	9-15
C ₅ -C ₁₁	50-54	51-57	50-51	42-51
C ₄ - (Gas)	35-30	34-26	35-39	39-50
Olefins in C ₆ +	21-26	23-26	21-16	14-8
Aromatics	2-3	2-3	4-8	7-14

Taken from Example 5, Tables 1 to 6 in U.S. Patent 4513104 (X.24).

Table X.18. Performance of Fe/Ti Catalysts in a fixed-bed reactor.

Pretreated with 49 H₂/50 CO/1 N₂ at 270°C at 1 atm and 500 v/v/hr for 18 hrs. Runs made with 1/1 H₂/CO at 300 GHSV and 0.9 MPa (130 psi).

	Fe/0.1 Ti			Fe/0.2 Ti	Fe/.04 K		NH ₃ synthesis catalyst
Temp	350	350	270	350	350	270	350
GHSV	300	300	300	300	300	300	300
CO Conv	96.7	63.6	46.8	45.0	55.5	68.9	97.1
Selectivity to HC %	60.9	62.5	69.9	59.6	66.0	wax	69.5
C ₁	10.1	13.0	3.4	16.6	11.1	3.0	3.3
C ₁ -C ₅	38.4	44.7	30.4	46.6	31.8	-	42.2
C ₆ -C ₁₁	45.3	45.4	44.8	39.0	32.5	-	42.3
C ₁₂ -C ₂₃	16.0	9.7	23.8	13.6	24.9	-	14.8
C ₂₃ +	0.3	0.2	1.0	0.8	10.8	-	0.7
Aromatics	12.7	14.02	2.92	10.3	6.57	-	8.65
α-olefins	14.9	9.66	22.31	10.0	16.6 9	-	11.43

Taken from Example 9, Tables 10 and 11 in U.S. Patent 4513104 (X.24).

Table X.19. Activity of *in situ* prepared catalyst in a slurry reactor.

Runs made at 270°C, 1:1 H₂/CO at 70 psig at 1200 V/V/hr in C16 paraffin solvent, 600 rpm.

Support	wt% support ^a		CO Conv	CO ₂	CH ₄	C ₂ -C ₄ olefins	C ₂ -C ₄ paraffins	C ₅ +
	Fe	Co						
None (Complexes only)	-	-	25	35.4	15.4	17.8	5.3	26.1
Fe ₂ O ₃ /1% K	9.5	3.2	54	50	3.0	7.2	1.1	38.5
Al ₂ O ₃	4.8	1.6	21	25	20.0	18.3	9.0	27.7
Al ₂ O ₃ ^b	"	"	27	9.2	19.8	12.9	6.8	60.5
MgO	4.8	1.6	30	35	18.6	16.1	6.8	23.5
MgO/1% Cu	9.5	3.2	26	50	9.6	14.7	3.8	21.9

Taken from Example 1, Tables I and II, and Example 4, Table V, of U.S. Patent 4532229 (X.25).

a. Same weight of Fe and Co in reactor in all runs, except for Fe₂O₃/1% K run.

b. Product yield after 96 hours on stream.

Table X.20. Effect of air calcination on the crystalline form of titania		
	Rutile content, wt%	Surface Area, m ² /g
Degussa P-25	28 ^a -35 ^b	60 m ² /g
500°C in air/16 hrs	55	33-36
500°C in air/16 hrs and H ₂ at 450°C	67	22-26
560°C in air/ 4 hrs ^d	70	30
600°C in air/16 hrs	~100 (>30/1)	10-16
650°C in air/16 hrs ^c	97	14
a. From U.S. Patent 4711871 (X.32). b. From U.S. Patent 4595703 (X.49). c. From U.S. Patent 4663305 (X.57). d. From U.S. Patent 4738948 (X.61).		

Table X.21. Effect of calcination on rutile content of titanias							
Source	Description	Binder/%	Hg PV ^a , cc/g	Hg PD ^b , Å	BET SA, m ² /g	% Rutile in titania	Calcination, °C/hr
Company A	-	none	0.253	140	45	27	-
Company A	-	none	0.162	270	15	92	700/1
Company A	-	none	0.134	250	14	95	700/1
Company A	-	none	0.120	481	5	100	840/1
Company A	Extrudate	none	0.154	389	8	98	650/16
Ti(OC ₃ H ₇) ₄ hydrolysis	-	none	0.160	n.a.	10	94	650/50
Ti(OC ₃ H ₇) ₄ hydrolysis	Extrudate	none	0.299	n.a.	41	n.a.	500/16
Ti(OC ₃ H ₇) ₄ hydrolysis	Extrudate	none	0.180	n.a.	15	n.a.	600/16
Company A	Extrudate	M/3.5	0.387	454	27	82	750/3
Company A	Extrudate	M/3.5	0.326	590	22	96	800/1
Company A	Extrudate	M/3.5	0.354	678	15	98	800/3
Company A	Extrudate	M/3.5	0.301	697	15	100	800/16
Company A	Extrudate	M/3.5	0.276	590	12	100	850/3
Company A	Extrudate	M/3.5	0.254	1151	13	100	850/10
Company A	Extrudate	M/3.5	0.237	1706	10	100	850/72
Taken from Example 1, Table 1 of U.S. Patent 4992406 (X.30). M binder = 30 TiO ₂ /70 Al ₂ O ₃ a. PV = pore volume. b. PD = pore diameter.							

Table X.22. Effect of rhenium on stability of Re/TiO ₂ for synthesis gas conversion. Conditions of run: 230°C, 280 psig, 2/1 H ₂ /CO, 1000 GHSV		
	1% Ru and 0.5% Re/TiO ₂	1% Ru/TiO ₂
Half-life, days	231	26
CO Conv	97	97
HC Yield	90	94
Selectivities		
CH ₄	3.7	3.5
CO ₂	7.0	1.5
Taken from Example 1, Table I of U. S. Patent 4558030 (X.29).		

Table X.23. Effect of Re/Ru ratios on Re promoted Ru/TiO ₂ catalyst. Conditions: 280 psig, 2/1 H ₂ /CO, 1000 GHSV				
Wt.% Ru	Wt% Re	CO Conv	C ₁ select	CO ₂ select
0.1	1.0	11	4	20
0.5	0.5	33	7.5	5
0.75	0.5	43	9	6
1.0	0.5	82	5.6	6
Taken from Example 2, Table II of U. S. Patent 4558030 (X.29).				

Table X.24. Effect of rutile content on activity of 1% Ru-0.5% Re on TiO ₂ . Conditions: 230°C, 280 psig, 2/1 H ₂ /CO, 1000 GHSV at 90% CO conversion			
Rutile/Anatase ratio wt	1.2/1	2/1	>30/1
Rutile, wt% in TiO ₂	55	67	~100
C ₁ selectivity	7	4.5	2
Half-life days	4	231	87
Deactivation, Δ <i>ln</i> k/day	-0.18	-0.003	-0.008
Pore Vol ml/g	0.4	0.2	0.15
SA m ² /g	35	24	12
Taken from Example 3, Table III of U. S. Patent 4558030 (X.29).			

Table X.25. Selectivity of Ru Catalysts for synthesis gas conversion. Conditions: Catalysts reduced in H ₂ at 450°C for 1 hr before introducing 1/1 H ₂ /Co at 980 kPa (9.5 psig),						
	Temp	%CO Conv	Prod	Total wt%	Olefin, wt%	Paraffin wt%
2% Ru/TiO ₂	267	7	C1	14	-	-
			C ₂ -C ₄	47	32	15
			C ₅ -C ₇	39	23	16
			C8+	-	-	-
5% Ru/ η Al ₂ O ₃	274	10	C1	24	-	-
			C ₂ -C ₄	43	19	14
			C ₅ -C ₇	32	6	6
			C8+	12		
Taken from Example 1, Table II of U. S. Patent 4042614 (X.31).						

Table X.26. Methanol conversion over Ru/TiO ₂ . Conditions: 230°C, 500 v/v/hr, fixed bed reactor			
Methanol, psi	236	236	236 ^a
H ₂ , psi	0	59	59
CO, psi	0	0	31
Methanol conv at 35 hrs, %	13	76	<3
Reactor effluent composition			
CO	38	1	84
CO ₂	4	12	n.a.
CH ₄	1	24	n.a.
C ₂ +	55	63	n.a.
Taken Example 4, Table IV and Example 6, Table VI of U.S. Patent 4513161 (X.36). a. GHSV=560.			

Table X.27. Activity of Ru on V, Nb and Ta oxides versus prior art.
Conditions: 3/1 H₂/CO, 1 atm, no other data provided.

	Temp C	CO Conv %	Hydrocarbon selectivities		
			CH ₄	C ₂ -C ₅ Olefins	C ₂ +
1% Ru/Nb ₂ O ₅	234	7.8	48	22	52
1% Ru/Ta ₂ O ₅	228	17.7	46	17	54
1% Ru/V ₂ O ₅	243	4.1	45	28	55
1% Ru/SiO ₂	232	4.1	87	2	13
1% Ru/Al ₂ O ₃	244	14.1	71	10	29
Data taken from U. S. Patent 4171320 (X.37).					

Table X.28. Reaction of a 0.76% Ru on TiO₂ in a fixed bed reactor.
Conditions: reduced at 400-450°C for 2-4 hrs in H₂. Run in 1.39/1 H₂/CO

Run No	3	5	7	14
Pressure,atm	3.0	3.0	5.0	4.3
°C	206	224	218	213
GHSV	198	301	494	1240
H ₂ Conv	84	84	89	26
CO Conv	84	84	89	30
Selectivity on CO ₂ free basis				
CH ₄	4.8	6.1	5.4	6.9
C ₂ /C ₄	9.15	11.6	7.9	17.8
C ₅ -C ₂₀	76.5	74.4	72.7	64.1
C ₂₀ -C ₄₀	8.3	6.2	11.3	8.3
C ₄₁ +	0.15	0.13	1.5	0.2
Oxygenates	1.13	1.4	1.2	2.7
C ₂ = in C ₂				40
C ₃ = in C ₃				84
C ₄ = in C ₄				82
Total olefin in C ₇ -C ₁₂				39
Total olefin in C ₄ -C ₂₀				31
Taken from U. S. Patent 4477595 (X.38).				

Table X.29. Effect of support on activity of Ru catalysts
Fixed bed reactor with supported Ru, reduced at 400-450°C for 2-4 hrs in H₂

	0.76 Ru/ TiO ₂	0.56 Ru/ Nb ₂ O ₃	0.67 Ru/ Ta ₂ O ₃	1.57Ru/ SiO ₂	0.56Ru/ Nb ₂ O ₃	1.1 Ru/ TiO ₂	1.57Ru/ SiO ₂	1.1Ru/ TiO ₂	1.1Ru/ Al ₂ O ₃
H ₂ /CO	1.39	1.39	1.39	1.39	2	2	2	2	2
Pressure, atm	5.0	5.0	5.2	21	7	4.6	4.6	2.1	2.1
°C	203	196	200	251	229	209	209	214	214
GHSV	298	300	303	200	1225	300	300	303	303
H ₂ & CO Conv	86	88.3	79	88.7	81	82	5	87	32
Selectivity									
CH ₄	2.9	2.0	5.5	7.5		4.3	10.6	6.7	16.6
C ₂ /C ₄	6.2	2.5	18.5	17.4		12.5	34.0	12.8	19.5
C ₅ -C ₂₀	65.5	62.1	66.5	71.3		81.6	51.1	68.8	59.2
C ₂₁ +	25.4	33.4	9.5	3.8		-	-	9.2	2.1
Taken from U. S. Patent 4477595 (X.38).									

Table X.30. Activity of Ru on oxide modified titania surfaces.
Conditions: 230-250°C, 300 v/v/hr, H₂/CO=2, 60 psig, fixed bed reactor

	1% Ru/TiO ₂	1% Ru/TiO ₂ +10%Nb	1% Ru/TiO ₂ +10%Ta	1% Ru/TiO ₂ +1%Ta	1% Ru/TiO ₂ +2%V	Physical Mixture 1% Ru/TiO ₂ +10%Ta
Temp	238	230	235	232	252	240
H ₂ +CO conv	37	43	19.5	31.5	71.3	47.4
CO ₂	3.8	1.9	3.7	3.2	3.5	5
CH ₄	14.5	10.9	10.9	15.3	12.5	8.4
C ₂	8.3	6.6	14.8	4.2	3.3	4.2
C ₃ +C ₄	23.0	17.3	13.8	24.0	10.0	16.9
C ₅ +	50.4	63.3	56.8	53.3	70.7	65.5
HC products						
Alcohols	5.1	0	0	1.4	3.8	3.0
olefins	39.1	67.7	6.3	44.2	15.6	46.4
paraffins	34.	32.3	93.7	54.4	80.6	50.3
Taken from U. S. Patent 4711871 (X.32).						

Table X.31. Activity of Ru/TiO ₂ slurry catalyst. Conditions: 1 g catalyst, 50 g octacosane, 6/3/1 H ₂ /CO/N ₂ , 1200 v/v/hr, 6 atm, 1 std L/g catalyst/hr						
Catalyst 1% Ru	°C	% CO Conv	Selectivity			
			CO ₂	CH ₄	C ₂ -C ₄	C ₅ +
Ru/TiO ₂ Particulate, reduced 450°C	250	49	3.2	14.4	8.9	73.5
Ru/TiO ₂ Particulate, not prereduced	260	10	2.0	20.0	30.0	48.0
Carbonyl based						
Ru	260	15	tr	4.7	19.5	75.8
Ru/CeO ₂	240	<5	nil	na	na	na
Ru/Al ₂ O ₃	240	25	3.0	19.3	9.4	68.3
Ru/TiO ₂	240	55	6.7	12.3	17.5	63.5
Taken from U.S. Patent 4752600 (X.41).						

Table X.32. Effect of steam treatment of Ru/TiO ₂		
Treatment of Ru/TiO ₂	O/Ru ratio from O ₂ chemisorption	Ru crystallite size Å
None	1.46	12
Air at 1 atm, 500°C/3 hrs	not reported	30
9/1 H ₂ O/H ₂ at 280 psig, 300°C/4 hrs	1.08	15
9/1 H ₂ O/H ₂ at 280 psig, 230°C/16 hrs	0.88	18
3% H ₂ O in N ₂ at 1 atm, 500°C/3 hrs	0.98	16
Taken from Table 1, U.S. Patent 4647592 (X.43).		

Table X.33. Effect of air treat on activity of Ru/TiO ₂ Run in 2/1 H ₂ /CO, 210°C, 280 psig, and 1000 v/v/hr					
Hrs	CO Conv	Selectivity to HC, %	wt.% selectivity		
			CH ₄	CO ₂	C ₂ +
No air treat					
0.7	84.8	80.3	7.3	5.3	87.4
1.4	94.8	90.8	4.9	4.2	90.9
2.4	94.7	88.2	3.6	6.9	89.5
3.0	98.3	89.6	3.6	8.8	87.6
3.7	97.7	89.5	3.8	8.4	87.8
Air treated sample					
0.7	78.6	72.1	3.0	8.3	88.7
1.3	91.9	85.0	2.3	7.5	90.2
2.2	94.5	88.5	2.3	6.4	91.3
3.0	93.7	88.6	2.5	5.4	92.1
3.7	93.1	88.9	2.5	4.5	93.0
Taken from Table II, U.S. Patent 4647592 (X.43).					

Table X.34. Activity of Rh Catalysts for synthesis gas conversion. Conditions: 1.6/1 H ₂ /CO, 100 kPa (1 atm), Catalyst reduced 450°C 1 hr,				
	Temp	%CO Conv	CH ₄ mol %	C ₂ -C ₅ yield, mol %
2% Rh/TiO ₂	248	1.3	74	26
2% Rh/Al ₂ O ₃	265	3.5	15	85
Taken from U. S. Patent 4116994 (X.45).				

Table X.35. Activity of rim-impregnated Co/TiO ₂ catalysts Conditions: 200°C, 2/1 H ₂ /CO, 2.1 MPa				
Particle size, mm	2.2	2.2	0.1-0.2	2.2
Co Conc, wt%	13.0	13	13	20.9
Co Distribution	even	rim	rim	rim
Rim thickness, μm	-	80±30	80±30	120±30
Surface area, m ² /g	80	80	80	350
Hrs on stream	193	318	175	315
GHSV	420	650	940	1750
CO Conv, %	64.5	66.0	48.0	64.0
CO Conv, vol/vol/hr	90	150	210	342
Selectivity				
CH ₄	12.0	8.3	4.7	12.7
C ₂ -C ₄	5.1	4.4	4.7	5.3
C ₅ +	82.0	87.0	90.5	81.3
CO ₂	0.9	0.4	0.1	0.7
Taken from Tables 1, 2, and 3 or U.S. Patent 5036032 (X.48).				

Table X.36. Activity of Co/TiO ₂ catalyst in a fixed-bed reactor. Runs at 230°C, 150 psig, 400 GHSV, 2/1 H ₂ /CO						
Cat		CO Conv	Selectivities			Schulz-Flory
			CO ₂	CH ₄	C ₂ +	
A	12 Co/TiO ₂ ^b (this invention)	88	1.1	8.6	90.3	0.91
B	100 Co/5 ThO ₂ /8 MgO/200 Kieselguhr ^a (known)	43	4.3	10.3	86.4	-
C	12 Co/SiO ₂ (known)	72	1.6	8.7	89.7	0.85
D	25 Co/1.8 Ti/100 SiO ₂ (known)	21	1.9	13.8	84.3	0.74
Taken from Example 7 in U. S. Patent 4542122 (X.46).						
a. Conventional FT catalyst						
b. Rutile/anatase ratio of 3.2. Reduced in H ₂ at 450°C for 1 hr						

Table X.37. Activities of Co and Co-Re on TiO₂ in a fixed-bed reactor. (Data shown in Figure 1 in Patent 4542122) Catalyst impregnated with nitrate/perrhenic acid and calcined in air at 500°C/3 hrs. Catalysts reduced in H₂ at 450°C for 1 hr. Runs made at 200°C, 2.15/1 H₂/CO, 280 psig, GHSV=1000.

Metals, wt% on TiO ₂	Rutile in TiO ₂ , wt%	Air treat°C for 3 hrs	O ₂ chemisorp. μ mol O ₂ / g cat	%CO Conversion	Surface area m ² /g	CH ₄	CO ₂	C ₂ +
12 Co	53	250	213	67	36	9.7	0.2	90.1
12 Co	100	250	265	79	10	11.5	0.7	87.8
12 Co	56	500	178	54	33	9.9	-	90.1
12 Co	100	500	202	67	10	11.7	0.3	88.0
12 Co-0.1 Re	100	500	145	67				
12 Co-0.5 Re	56	500	343	85				
12 Co-0.5 Re	100	500	285	82				
12 Co-3 Re	56	500	399	81				

Table I in U.S Patent 4568663 (X.51).

Table X.38. Effect of Anatase-Rutile Ratio on Co/TiO₂ catalyst. Catalysts impregnated with cobalt carbonyl from pentane solution. Run conditions: 200°C, 280 psig, 1000 GHSV, H₂/CO=2.15/1

Co, wt%	10.1	9.2
Rutile in Titania, wt%	28	~100
Pretreatment Conditions:		
1st Stage	250°C/ air/3 hrs	250°C/ air/3 hrs
2nd Stage	450°C/ H ₂ /1 hr	450°C/ H ₂ /1 hr
CO Conv, mol %	5	97
CH ₄ Yield, mol %	15.1	5.4
O ₂ Chemisorption, μ mol/g cat	53	205
Example 9 in U.S. Patent 4542122 (X.46) and Example 3 in U.S. Patent 4595703 (X.49).		

Table X.39. Effect of rutile content on Co/TiO ₂ . Run at 230°C, 40 MeOH:2 H ₂ :1 CO ₂ :7 Ar, 400 psig, GHSV=500.		
Rutile content, %	55	100
MeOH Conv	66	100
Carbon Product Distribution		
CO	2.6	0.8
CO ₂	15.6	27.8
CH ₄	9.0	17.1
C ₂ +	72.8	54.3
Taken from Example 6 in U.S. Patent 4542122 (X.46).		

Table X.40. Activity and selectivity of Co on titania based catalysts for methanol conversion (rutile not specified). Run conditions: 230°C, 400 psig, GHSV=500, 40 MeOH:2 H ₂ :1 CO ₂ :7 Ar						
	12% Co/TiO ₂	12% Co/2% ThO ₂ /TiO ₂		100 Co/5 ThO ₂ /8 MgO/200 Kieselguhr ^a	12% Co/SiO ₂	12% Co/Al ₂ O ₃
MeOH Conv, 35 hr	52	70 ^b		97	38	64
Carbon Product Distribution						
CO	5.5	3.1	2.9	1.0	4.3	2.8
CO ₂	12.9	17.0	12.6	38.4	22.3	21.8
CH ₃ OCH ₃	0.2	0.3	0.5	-	0.1	2.4
CH ₄	11.2	8.6	7.4	19.5	7.0	9.9
C ₂ +	70.2	71.0	76.6	41.1	66.3	63.1
Schulz-Flory Alpha	0.86	0.88	n.p.	n.p.	n.p.	n.p.
Example 5 of U.S. Patent 4542122 (X.46). a. Conventional FT catalyst b. Two sets of data provided for the same conditions having the same MeOH conversion that was not otherwise specified. n.p. = not provided						

Table X.41. Effect of Re on MeOH conversion over Co/TiO ₂ with or without ThO ₂ . Run conditions: 230°C, 400 psig, GHSV=500, MeOH/Argon=4. Catalysts calcined 500°C			
	12 Co/ 2 ThO ₂ /TiO ₂	12 Co/2 ThO ₂ / 0.5 Re/TiO ₂	12 Co/ 0.5 Re/TiO ₂
Rutile Conc, %	56	56	56
MeOH Conv	49	100	87
Product Distribution			
CO	6	2	2
CO ₂	14	28	22
CH ₄	6	14	9
C ₂ +	74	56	67
Table III in U.S. Patent 4568663 (X.51).			

Table X.42. Effect of H ₂ partial pressure on MeOH conversion. Co/ThO ₂ /TiO ₂ (rutile and catalyst composition not specified) at 230°C, 500 GHSV, 400 psig			
Partial Pressures, psig			
MeOH	332	332	332
Ar	83	66	0
H ₂	0	17	83
MeOH Conv, wt%	38	52	83
Carbon Product Distribution			
CO	8.5	3.9	0.9
CO ₂	11.3	8.9	12.2
CH ₃ OCH ₃	1.0	0.4	0.1
CH ₄	4.6	5.7	15.9
C ₂ +	74.6	81.1	70.9
CH ₄ in hydrocarbon, wt%	5.8	6.6	18.3
Table IV in U. S. Patent 4542122 (X.46).			

Table X.43. Effect of promoter on MeOH Conversion on Co/TiO ₂ . Conditions: 230°C, 400 psig, LHSV=0.67, 20 MeOH/1 H ₂ /4 Argon					
Catalyst composition					
Wt% Co	5.0	4.34	4.65	4.55	4.73
Promoter @ 1 wt%	none	Zr ^a	Hf	Ce	U
MeOH Conv	31	37	34	49	46
Rate MeOH Conv, g/hr/g Co	1.6	2.3	1.9	2.8	2.6
Carbon Prod Distribution					
CO	16	13	16	10	9
CO ₂	8	9	7	9	13
CH ₄	8	8	8	7	9
C ₂ +	68	70	69	74	69
Table IV, Example 2 in U.S. Patent 4663305 (X.57). a. The Zr salt was ZrO(O ₂ CCH ₃) ₂ .					

Table X.44. Effect of silica promotion on CoRe/TiO ₂ in a fixed-bed reactor. Conditions: 200°C, 2.1 MPa, H ₂ /CO=2, run at space velocity to give ~60% CO conversion.								
	(A) CoRe/TiO ₂		(D) CoRe/TiO ₂		(B) CoRe/TiO ₂ +SiO ₂		(C) CoRe/TiO ₂ +SiO ₂	
% SiO ₂	0		0		4		5.2	
Steam treat H ₂ O (40 Torr)/He at 400°C/13 hrs	No		Yes		Yes		Yes	
reduction in H ₂	250°C for 13 hrs		250-400°C for 2-14 hrs		250-400°C for 2-14 hrs		250-400°C for 2-14 hrs	
Hrs on stream	50	139	49	190	47	120	49	119
CO Conv	61.5	64	67	58	69	61	60	55
mol CO conv/g atom Co-hr	5.7	5.5	5.1	4.4	7.5	6.8	8.3	7.5
CH ₄	5.3	5.1	4.6	5.0	5.2	5.6	5.4	5.8
C ₂ (O/P)	0.6 (0.12)	0.6 (0.14)	0.6 (0.17)	0.6 (0.19)	0.7 (0.11)	0.7 (0.13)	0.6 (0.13)	0.6 (0.14)
C ₃ (O/P)	2.1 (1.9)	1.9 (2.1)	2.2 (2.6)	2.1 (2.8)	2.4 (2.0)	2.5 (2.1)	2.3 (2.0)	2.3 (2.1)
C ₄ (O/P)	2.3 (0.70)	2.16 (0.63)	2.0 (1.6)	1.9 (1.6)	2.4 (1.1)	2.6 (1.3)	2.6 (1.2)	2.5 (1.3)
C ₅ +	89.5	89.9	90.3	90.1	89.3	88.5	89.1	89.1
CO ₂	0.2	0.2	0.3	0.3	0.07	0.06	0.05	0.04
Combined Table 1 and Table 2 of U.S. Patent 4794099 (X.58). (O/P) = olefin/paraffin ratio								

Table X.45. Effect of Precalcination on FT activity of Co-Ru/TiO ₂ catalyst in fixed-bed reactor. Runs made at 200°C, 60H ₂ /30CO/7N ₂ , 75 psia, space velocity adjusted; catalysts 70% rutile titania,				
	D	A	B	C
	20% Co/ SiO ₂	11.6% Co/ TiO ₂	Reduced 11.6% Co/ 0.14% Ru/TiO ₂	Calcined-reduced 11.6% Co/ 0.14% Ru/TiO ₂
1st Calcination	none	400°C/16 hrs	400°C/16 hrs ^a	400°C/16 hrs ^b
Reduction/oxidation /reduction step ^c	No	No	No	Yes
CO Conv	65	50	64	68
CH ₄ select	7.4	9.3	6.8	6.5
C ₅ + select	82	80.2	87.3	87.8
Co time yield ^d	1	0.6	2.0	2.9
Taken from Table III in U. S. Patent 4738948 (X.61). a. Ru impregnated to catalyst A after 1st calcination. b. Started with catalyst B. c. Calcined in air at 300°C/4 hrs and then reduced in H ₂ d. moles CO converted per hr g-atom Co in catalyst.				

Table X.46. H ₂ Regeneration of Air-calcined-reduced Co-Ru/TiO ₂ Catalysts Aged 10-30 days				
	CO Conv, %	Co time yield, hr ⁻¹	CH ₄	C ₅ +
Cat A. Co/TiO ₂	At 560 kPa, 200°C, H ₂ /CO=1			
Initial	20	0.6	8.9	80.1
Aged	20	0.5	9.5	81
H ₂ Treated	20	0.5	9.5	80.5
Cat. B CoRu/TiO ₂	At 2060 kPa, 200°C, H ₂ /CO=1			
Initial	50-60	2.6	7.0	86
Aged	50-60	2.0	8.2	84
H ₂ Treated	50-60	2.6	6.5	87
Cat. C. CoRu/TiO ₂ Calc	At 2060 kPa, 200°C, H ₂ /CO=1			
Initial	50-60	4.5	5.5	91.0
Aged	50-60	3.9	6.4	88.8
H ₂ Treated	50-60	4.8	4.9	91.5
Taken from Example 5, Table IV in U. S. Patent 4738948 (X.61).				

Table X.47. Synthesis gas conversion activity of Fe-coated, vanadia and niobia modified titanias in a fixed-bed reactor. Runs made with 1:1 H₂/CO, 500 v/v/hr, 300 psig

	4% Fe/TiO ₂			4% Fe/TiO ₂ +V			4%Fe/TiO ₂ +Nb
Temp	305	315	270	290	305	270	270
CO Conv	47	60	27.0	49	70	34.3	20.1
Selectivity (CO ₂ free)							
CH ₄	21.0	24.4	21.0	16.1	17.8	13.0	14.6
C ₂ -C ₄ olefins	14.6	13.3		42.7	23.4		
C ₂ -C ₄ paraffins	35.9	36.3	55.0	21.2	44.2	41.5	32.9
C ₅ +	27.5	26.0	24.0	20.0	14.6	45.5	52.5
Taken from Tables 1 and 2 in U. S. Patent 4559365 (X.68).							

Table X.48. Selectivity of TiO₂ Promoted Nickel Catalysts for Synthesis gas conversion in a fixed-bed reactor.
Run conditions: 250°C, 3/1 H₂/CO, 1 atm., catalyst reduced in H₂ at 250°C/1 hr.

	CO Conv %	HC Selectivity, wt%			umol/min/g of Ni ^a		H ₂ chemisorption umol/g	BET SA m ² /g	H/M
		CH ₄	C ₂ -C ₃	C ₄ -C ₆	CH ₄ formation rate	CO Conv rate			
Ni Powder	4.9	88	12	-	9.7(.0115)	11.0 (.0131)	7.0	0.41	0.0131
0.007% TiO ₂ on Ni	11.6	74	16	9	19.1(.0295)	26.3 (.0406)	5.4	0.48	0.0006 3
0.07% TiO ₂ on Ni	27.2	38	42	19	21.9(.0468)	60.2 (.129)	3.9	0.60	0.0004 6
0.20% TiO ₂ on Ni	25.4	39	44	17	21.2 (.0281)	56.6 (.0748)	6.4	1.15	0.0007 5
1.66% TiO ₂ on Ni	15.9	36	44	21	11.7 (.0244)	34.7 (.0723)	4.0	7.69	0.0004 7
8.40% TiO ₂ on Ni	18.8	33	42	24	14.3	46.0			
10% Ni on TiO ₂	49.0	37	34	28	14.6 (0.0194)	41.6 (0.0550)			
1/1 Ni powder + TiO ₂	2.1	92	8	-	7.6 (0.0101)	8.3 (0.0110)			

Taken from U.S. Patent 4273724 (X.70).

a. ( ) numbers in parenthesis are reactions/site/sec or turnover number.

Table X.49. Activity of Cu-promoted Co-Mo spinel catalysts in a slurry reactor. Conditions: CSTR: 2/1 H ₂ -CO feed, 270°C, 75 psig, and 2000 h ⁻¹ gas space velocity in octacosane. Catalyst first reduced <i>in situ</i> at 100-270°C with H ₂ /CO at 1000-2000 v/v/hr flow rate at 75 psig.			
	Co ₂ MnO ₄ /1% Cu	Co ₃ O ₄ /1% Cu	Co ₂ MnO ₄
CO Conv	45	23	nil
wt% Prod Select			
CO ₂	16	54	-
CH ₄	7	40	-
C ₂ -C ₄	26	6	-
C ₅ +	51	nil	-
%olefins in C ₂ -C ₄	83	52	-
Taken from U. S. Patent 5162284 (X.73).			

Table X.50. Synthesis gas conversion for making alcohols Conditions: 1/1 H ₂ /CO, 50 atm.. GHSV 1832			
	Cu _{0.5} Mg ₅ CeO _x	0.9%K on Cu _{0.5} Mg ₅ CeO _x	Cu _{0.45} NdCeMgO _x
Temp, °C	290	320	290
CO conv, %	25.5	15.5	20.6
CO ₂	22.5	31.0	17.1
Selectivity, % C exclusive of CO ₂			
Methanol	70.7	57.2	82.6
Isobutanol	8.2	10.4	8.2
Other alcohols	4.9	6.9	2.4
Methane	8.4	11.5	3.7
Higher Hydrocarbons	4.1	12.8	2.7
DME	3.3	1.2	1.6
Taken from U. S. Patent 5387570 (X.81).			

Process Tables

Table X.51. Synthesis gas reaction in dual fixed-bed reactors with different catalysts . First stage bed: 20g Fe/Zn/Ce/K Second stage bed: 1.5 g Ru/TiO ₂ + quartz	
Temp, °C	220
Pressure, atm	6.47
H ₂ /CO mole ratio	1.64
Flow rate, sccm/min	36.5
CO Conv	59.0
CO ₂ Selectivity in upper bed	26
CH ₄ Selectivity	2.5
HC Selectivity in upper bed	33
HC Selectivity in lower bed	41
Taken from U. S. Patent 4624968 (X.82).	

Table X.52. Hydrocarbon selectivity from one and two-stage beds				
	First stage Fe/Zn/Ce/K	Second stage Ru/TiO ₂	2-Stage Beds	
			Predicted	Observed
CH ₄	3.5	6.1	4.9	3.9
C ₂ -C ₄	18.5	11.0	15.4	13.8
C ₅ -C ₉	22.9	24.7	23.9	22.6
C ₁₀ +	55.1	58.2	56.8	60.3
Taken from U. S. Patent 4624968 (X.82).				

Table X.53. Effect of adding ethylene to the feed						
	Catalyst					
	Ru-Co/TiO ₂			Ru/TiO ₂		
C ₂ H ₄ in feed, %	0	2.5	2.5	0	6.2	6.2
Location of C ₂ H ₄ Addition ^a	-	inlet	below top one-third	-	inlet	below top one-third
CO Conv %	25-27	25-27	25-27	35-45	35-45	35-45
C ₂ H ₄ Conv		99.5	89.5		97	45.3
C ₂ H ₄ Selectivity	-			-		
to C ₂ H ₆	-	86.5	69.5	-	82	44
to C ₃ +	-	13.5	30.5	-	18	56
Added C ₂ H ₄ that appears as C ₃ + %		13.5	27.3	-	17	26
% Selectivity ^b						
CH ₄	9.4	8.3	7.2	5.5	4.3	3.9
C ₂	1.3	-	-	0.7	-	-
C ₃	2.7	3.3	3.7	2.1	2.6	3.4
C ₄	2.4	2.9	3.7	3.5	4.0	5.1
CO ₂	0.4	0.5	0.4	0.7	0.7	0.7
C ₅ +	83.8	92.9	99.3	87.5	105.6	117.0
Example 3 in U.S. Patent 4754092 (X.85).						
a. Downflow reactor.						
b. Selectivity defined as percent CO converted. When ethylene is added, the sum of selectivities is >100%.						

Table X.54. Effect of heating rejuvenation tubes on catalyst activation.		
Heat addition	no	Yes
Gas rate in tube, scfh	5100	4800
Avg reactor temp, °F	427	427
Avg rejuvenation temp, °F	430	440
CO conv, start to end of run, %	32 to 26 (over 12 hrs)	26 to 36 (over 24 hrs)
Conv, change/day	-12.4	+10.4
Example 4 in U.S. Patent 4754092 (X.85).		

Table X.55. Improvement in catalyst/wax separation in slurry FT processes by removal of catalyst fines.

Classification Solvent	Catalyst/solven t wt/wt	Other	Cycle s	Acetone cycles	Filter time	Filter rate	
						(gm/min)	gal/ft ² /min
0.45 μm Millipore filter paper							
Blank	-	-	-	-	95.0	0.5	
Water	15/85	-	6	2	0.9	55.0	
i-C ₃ H ₆ OH/n-C ₇ H ₁₆ (1/9)	10/150	1% Oleic acid added	7	2	1.0	50.0	
i-C ₃ H ₆ OH/n-C ₇ H ₁₆ (1/9)	10/150	1% Aerosol OT-100 added	7	2	1.0	50.0	
0.3 μm glass fiber filter							
FT wax @ 130°C	2/98	Stirred 5 min	none	none	-	-	5.8 @ 14 psig
		Stirred 44 hrs	none	none	-	-	0.05 @ 14 psig
FT wax @ 120°C	2/98	Stirring per cycle19/48/2 4	3	none	-	-	14.5 @ 14 psig
Taken from U.S. Patent 5070064 (X.98).							

LEGEND :
 ● UNIFORMLY IMPREGNATED SPHERES, INSCRIPTION INDICATES CATALYST NUMBERS
 ○ RIM IMPREGNATED SPHERES, INSCRIPTION INDICATES CATALYST N° & RIM THICKNESS (MICRONS)

Figure X.1. Plot of methane production for various catalysts (from ref. X.50).

Figure X.2. Plot of cobalt productivity versus binder content in the titania support (from ref. X.30).

Figure X.3. Plot of wt.% of binder versus turnover number (TON) (from ref. X.30).

Figure X.4. Effect of dispersion on cobalt catalyst activity (from ref. X.51).

Figure X.5. Dependence of CH_4 and CO_2 production on presence of ruthenium or rhenium in the cobalt catalyst (from ref. X.51).

Figure X.6. Dependence of CO conversion on presence of ruthenium or rhenium in the cobalt catalyst (from ref. X.51).

Figure X.7. The CO conversion and the methane and CO₂ production at increasing conversion time using a Co-Ru-TiO₂ catalyst (from ref. X.51).

Figure X.8. Comparison of activity for Zr, Hf, Ce and U promoted Co-TiO₂ catalysts and unpromoted catalysts after simulated catalyst regeneration (from ref. X.57).

Figure X.9. Effect of promoter loading on Co-TiO₂ catalyst after simulated regeneration at 500°C (from ref. X.57).

Figure X.10. Relationship between wt.% Co-TiO₃ and total TiO₂ versus temperature (from ref. X.60).

Figure X.11. Effect on catalysts A and B (see text) of carburization showing that silica suppresses carbon growth (from ref. X.58).

Figure X.12. Plot of CO conversion rate as a function of the iron loading on titania (from ref. X.64).

Figure X.13. C₂₊ selectivity for increasing conversion with nickel catalysts (from ref. X.69).

Figure X.14. Impact of support on the rate of nickel carbonyl fraction (from ref. X.69).

Figure X.15. Catalyst concentration versus reactor height for (!) no downcomer and for one 3" downcomer (Q).

Figure X.16. Schematic of reactor for enhanced gas separation for bubble column draft tubes (from ref. X.90).

Figure X.17. Temperature exotherm within bed position for different start-up procedure (see text) (from ref. X.35).

Figure X.18. Temperature exotherm within bed position for low $H_2:CO$ ratio start-up (from ref. X.35).

Figure X.19. Relative volumetric productivity represented by activity with days on stream with intervals of hydrogen rejuvenation (12 wt.% Co on titania with 6 wt.% Al_2O_3 as binder (from ref. X.96).

Figure X.20. Catalyst concentration versus elevation in the reactor with (Q) and without (F) use of draft tubes (from ref. X.89).

Figure X.21. Conversion using hydrogenation rejuvenation (to day 3 no rejuvenation; rejuvenation after day 3) (from ref. X.89).

Figure X.22. Schematic of multiple vessels for catalyst rejuvenation (from ref. X.97).

Figure X.23. Elevation of a shell and tube reactor arrangement showing the gas, liquid, catalyst interconnection both above and below the upper and lower tube sheets.

Figure X.24. Horizontal Section A - A through the elevation of Figure 23 showing a possible arrangement of tubes, that is, reaction zones.

Figure X.25. Detail of a possible distribution zone for one reaction tube/zone.

APPENDIX - EXXON PATENTS

The following provides a listing of the primary claim from the patents reviewed during the preparation of this document. It is intended to provide a scope of the coverage of the initial report and the first addendum.

1. Gates, William, R. Fiato; Catalysts in FT process for producing olefins; Patent 4,639,431 (1987). **Claim 1:** A hydrocarbon synthesis catalyst comprising a sintered combination of metal oxides having the following components: (a) an oxide of a Group VIII metal; (b) an oxide of a Group IIB metal; (c) an oxide of a Group IA alkali metal; and (d) an oxide of a lanthanide metal, such that said sintered combination comprises a series of the Group VIII metal and the Group IIB metal spinels and the alkali metal oxide dispersed in a lanthanide metal oxide matrix.
2. Kim, Chang; R. Fiato; Multi-state FT process, patent 4,624,968, (1986). **Claim 1:** A process for producing paraffinic hydrocarbons from carbon monoxide and hydrogen comprising: (a) introducing carbon monoxide and hydrogen into a reaction zone wherein the carbon monoxide and hydrogen contact in a first bed a first catalyst having a high olefin selectivity selected from the group consisting of Fe/Ce/Zn/K, Fe/Mn/K and Fe/Co/K; and (b) contacting the resulting olefin in a second bed with a second catalyst having a high selectivity for converting olefins to heavier paraffinic hydrocarbons selected from the group consisting of Ru/TiO₂, Ru/SiO₂ and Ru/Al₂O₃.
3. Fiato, Rocco; S. Soled; FT hydrocarbon synthesis with high surface area Cu and K-promoted reduced-carbided iron/manganese spinels; Patent 4,621,102, (1986). **Claim 1:** A process for synthesizing a hydrocarbon mixture containing C₂-C₂₀ olefins comprising contacting a catalyst composition, comprising at least one unsupported, single phase, iron-manganese spinal dual promoted with both copper and a Group IA and IIA metal, said spinel exhibiting a single phase being isostructural with Fe₃O₄ as determined by powder X-ray diffractometry, and possessing a BET surface area greater than 30 m²/G and an Fe:Mn atomic ratio of at least 2/1, with a mixture of CO and hydrogen under conditions of pressure, space velocity, and elevated temperature for a time sufficient to produce said C₂-C₂₀ olefins.
4. Soled, Stuart, R. Fiato; Copper promoted iron/cobalt spinels and their preparation; patent 4,607,020 (1986). **Claim 1:** A composition of matter comprising a reduced and carbided, copper promoted iron-cobalt alloy, said composition being substantially isostructural with chi-Fe₅C₂, as determined by X-ray diffractometry and possessing a BET surface area of greater than 5 m²/g, said composition produced by contacting, with a carbiding atmosphere for a time sufficient to produce said composition, said copper-promoted iron cobalt alloy, being isostructural with metallic alpha iron as determined by powder X-ray diffractometry, possessing a BET surface area of greater than 5 m²/g, wherein said alloy was produced by contacting, with a reducing atmosphere, an

unsupported Group IA or IIA metal salt promoted iron-cobalt spinel, or mixture thereof, said spinel exhibiting a single phase powder X-ray diffraction pattern substantially isostructural with Fe_3O_4 , and possessing a BET surface area greater than $5 \text{ m}^2/\text{g}$ and an iron-cobalt atomic ratio of 4 to 1 or above.

5. Iglesia, Enrique, S. Soled, R. Fiato, J. Baumgartner; Selective fixed-bed FT synthesis with high surface area Cu and K promoted, iron/manganese spinels; Patent 5,118,715 (June 1992). **Claim 1:** A hydrocarbon synthesis process for preparing a product containing C_5+ hydrocarbons and less than about 30% CO_2 comprising contacting in a fixed-bed a pelletized catalyst composition wherein the particle size is greater than about 200 microns average diameter, at a temperature of $200\text{-}400^\circ\text{C}$, the catalyst comprising at least one unsupported, single phase, iron-manganese spinel dual promoted with both copper and a Group IA or IIA metal, said spinel exhibiting a single phase being isostructural with Fe_3O_4 as determined by powder X-ray diffractometry, and possessing a BET surface area greater than $30 \text{ m}^2/\text{g}$ and an Fe:Mn atomic ratio of at least 2/1, with a mixture of CO and hydrogen under conditions of pressure, space velocity, and elevated temperature for a time sufficient to produce said C_5+ hydrocarbons.
6. Soled, Stuart, S. Miseo, E. Iglesia, R. Fiato; Iron-zinc based catalysts for the conversions of synthesis gas to alpha-olefins; patent 5,100,856 (Mar. 1992). **Claim 1:** A composition comprising of iron, zinc, copper, an alkali metal selected from the group consisting of potassium, rubidium, cesium, or mixtures thereof, wherein the iron:zinc atomic ratio is at least about 5:1, and the alkali metal:copper atomic ratio is at least about 2:1.
7. Fiato, Rocco; G.McVicker, A. Montagna; Process for preparing a Fe-CO catalyst slurry system for alpha olefin production; Patent 4,532,229 (Jul 1985). **Claim 1:** A process for preparing a slurry Fischer-Tropsch catalyst system comprising the steps of: (a) heating a slurry mixture comprised of a Fischer-Tropsch slurry liquid, an iron carbonyl compound, a cobalt carbonyl compound, or iron and cobalt compounds capable of forming carbonyl complexes in an atmosphere of CO, and mixtures thereof, and a powdered support, wherein said iron and cobalt compounds are present in a total iron:cobalt atomic ratio of about 35:1 to 1:10, taken as free metals, and wherein the cobalt carbonyl compound has a lower melting point/decomposition temperature than the iron carbonyl compound; in a carbon monoxide atmosphere under pressure, at a temperature above the melting point/decomposition temperature of the cobalt compound for a time sufficient to substantially decompose the cobalt compound; and (b) heating said slurry mixture from step (a) at a temperature above the melting point/decomposition of the iron compound in said CO atmosphere under pressure, to substantially decompose the iron compound; and (c) heating and slurry mixture from step (b) in an atmosphere of hydrogen gas to substantially reduce said iron and cobalt carbonyl compounds and their decomposition products.

8. Cody, Ian; D. Brown; Wax isomerization using small particle low fluoride content catalysts; patent 4,923,588 (May 1990). **Claim 1:** A method for the isomerization of waxes into liquid hydrocarbons comprising passing the wax to be isomerized in the presence of hydrogen and under isomerization conditions over an isomerization catalyst comprising a noble Group VIII metal on small particle size, fluorided, refractory metal oxide wherein the catalyst possesses a fluoride content in the range of 0.1 to up to but less than 2.0 wt.% and the small particle size refractory metal oxide has a particle diameter of less than 1/16 inch.

9. Pedrick, Larry; C. Mauldin, W. Behrmann; Draft tube for catalyst rejuvenation and distribution; Patent 5,268,344 (Dec. 1993); **Claim 1:** A method for rejuvenating reversibly deactivated particulate hydrocarbon synthesis catalyst in a slurry phase reactor, said method comprising the use of substantially vertical draft tube means, open at both ends, fully immersed in the slurry containing the catalyst and injecting a hydrogen containing gas at or substantially near the bottom of said draft tube means thereby lifting catalyst in slurry from the bottom of the slurry phase reactor into and through the open bottom end of the draft tube means, rejuvenating catalyst in the presence of said hydrogen containing gas in the vertical draft tube means and ejecting the rejuvenated catalyst into the top of the slurry phase in the slurry phase reactor through the open top of the draft tube means.

10. Kugler, Edwin, S. Tauster, S. Fung; Ruthenium supported on manganese oxide as hydrocarbon synthesis catalysts in Co/H₂ reactions; patent 4,206,134 (June 1980). **Claim 1:** A process for the enhanced synthesis of C₂-C₄ olefins with reduced production of methane comprising the steps of passing H₂ and CO in an H₂/CO ratio of from about 10 to about 0.1 over a catalyst reduced at a temperature greater than about 300°C comprising ruthenium on a manganese-containing oxide support, wherein said manganese-containing oxide support is selected from the group consisting of MnO, Al₂O₃-MnO, SiO₂-MnO, MnO-carbon, Group IVB-manganese oxide, Group VB-manganese oxides, Group IA-manganese oxides, Group IIA-manganese oxides, rare earth-manganese oxides and mixtures thereof, at a space velocity of from about 100 hr⁻¹ to about 50,000 hr⁻¹, at a temperature of from about 100°C to about 500°C at a pressure of from about 103 to about 1.03 x 10⁵ kPa for a time sufficient to effect the generation of the desired olefinic product, wherein the concentration of said ruthenium in said catalyst is from about 0.01 to about 15% by weight.

- II. Madon, Rostam; Liquid hydrocarbon synthesis using supported ruthenium catalysts; patent 4,477,595 (Oct. 1984). **Claim 1:** A process for selectively producing paraffins comprising (a) first contacting a mixture of H₂ and CO for at least 10 hours with a reduced and supported ruthenium catalyst, said ruthenium catalyst comprising ruthenium on a support selected from the group consisting of TiO₂, ZrTiO₄, TiO₂-carbon, TiO₂-Al₂O₃, TiO₂-SiO₂, alkaline earth titanates, alkali titanates, rare earth titanates, V₂O₃, Nb₂O₅, Ta₂O₅, Al₂O₃-V₂O₃, Al₂O₃-Nb₂O₅, Al₂O₃-Ta₂O₅, SiO₂-V₂O₃, SiO₂-NbO₅, SiO₂-Ta₂O₅, V₂O₃-carbon,

Nb₂O₅-carbon, Ta₂O₅-carbon, alkaline earth Group VB oxides, alkali-group VB oxides, rare earth-Group VB oxides, Group IVB-Group VB oxides, and mixtures thereof, at Fischer-Tropsch conditions such that the temperature ranges from about 100 to 400°C, the pressure ranges from about 0.2 to 10 MPaA, the gas hourly space velocity, GHSV, ranges from about 100 to 50,000 v/v/hr, and wherein the ratio of GHSV/pressure is below about 24,000 v/v/hr/MPaA, and at least about a 20% CO conversion is effected; and (b) continuing said contacting as in step (a) at a H₂/CO molar ratio from about 0.1 to 4 and thereafter recovering a hydrocarbon mixture comprising C₅-C₄₀ hydrocarbons, containing C₅-C₂₀ paraffins and olefins in a paraffins to olefins weight ratio of at least about 1.5.

12. Wachs, Israel, C. Chersich; Catalysts comprising tantalum supported on titania; patent 4,544,649 (Oct. 1985). **Claim 1:** A catalyst composition comprising an oxide of tantalum supported on titania wherein at least a portion of the supported tantalum metal oxide is in a non-crystalline form.
13. Kim, Chang; Reducing methane productions in FT reactions; patent 4,547,525 (Oct. 1985). **Claim 1:** A process for reducing methane formation in a Fischer-Tropsch process for synthesizing hydrocarbons which comprises contacting, at an elevated temperature of 100-500°C and a pressure of from about 100-10,000 kPa, a H₂/CO feed mixture with a heterogeneous catalyst comprising one or more Group VIII metals supported on an inorganic refractory oxide support for a time sufficient to produce hydrocarbons, including methane, wherein one or more olefins is added to the H₂/CO feed mixture in an amount sufficient to reduce said methane formation to a level lower than it would be without adding said olefin to said feed.
14. Mauldin, Charles; Cobalt catalysts for the conversion of methanol to hydrocarbons and for FT synthesis; patent 4,568,663 (Feb. 1986). **Claim 1:** A catalyst useful for the conversion at reaction conditions of methanol or synthesis gas to hydrocarbons by contact with a catalyst which comprises cobalt and thorium in catalytically active amounts and ruthenium, composited with an inorganic oxide support in weight ratio of ruthenium:cobalt ranging from about 0.025:1 to about 0.10:1.
15. Arcuri, Kym; C. Mauldin, D. Shaw; Ruthenium rhenium catalyst on titania support for FT synthesis; patent 4,558,030 (Dec. 1985). **Claim 1:** A catalyst composition useful for the synthesis of hydrocarbons from admixtures of carbon monoxide and hydrogen at reaction conditions which comprises: ruthenium in catalytically active amount composited with titania, or titania-containing support, having a rutile:anatase ratio of at least about 2:3 and rhenium in amount sufficient to provide a weight ratio of rhenium:ruthenium which ranges from about 2:1 to about 1:4, sufficient at corresponding reaction conditions to obtain improved activity maintenance vis-a-vis a ruthenium catalyst otherwise similar except that it does not contain rhenium.

16. Payne, Virgil; C. Mauldin; Preparation of hydrocarbons from synthesis gas; patent 4,959,703 (June 1986). **Claim 1:** A process useful for the conversion of synthesis gas to hydrocarbons which comprises contacting at reaction conditions a feed comprised of an admixture of carbon monoxide and hydrogen, in $H_2:CO$ molar ratio equal to or greater than about 0.5:1 at total pressure equal to or greater than about 80 psig, over a catalyst which comprises cobalt, or cobalt and thoria in catalytically active amount composited with titania or titania-containing support, wherein the titania support is one having a rutile:anatase ratio of at least about 2:3.
17. McVicker, Gary; M. Albert Vannice; Preparation and use of supported potassium (or rubidium)-group VIII metal cluster catalyst in CO/H_2 FT synthesis reactions; Patent 4,154,751 (May 1979). **Claim 1:** In a Fischer-Tropsch process reaction for the production of hydrocarbons from CO and H_2 wherein CO and H_2 are passed over a catalyst the improvement comprising using as the catalyst a supported potassium or rubidium-Group VIII metal cluster catalyst which catalyst is prepared by depositing a known, well-characterized potassium or rubidium-Group VIII metal carbonyl cluster complex on a high surface area support, drying the carbonyl cluster complex impregnated support in the absence of oxygen and reducing the supported complex at elevated temperatures, wherein using this catalyst in Fischer-Tropsch processes results in the selective formation of higher molecular weight paraffinic and olefinic hydrocarbons.
18. Fiato, Rocco; S. Soled; Cobalt promoted catalyst for use in FT slurry process; patent 4,544,672 (Oct. 1985). **Claim 1:** A slurry process for synthesizing a hydrocarbon mixture containing C_2 - C_4 olefins comprising the step of contacting a liquid slurry catalyst system, comprised of a slurry liquid and a carbided and reduced, unsupported iron-cobalt single phase spinel catalyst containing a Group IA or IIA metal salt promoter agent, and said spinel having the initial empirical formula: $Fe_xCo_yO_4$, wherein x and y are integer or decimal values, other than zero, with the provisos that the sum of $x+y$ is 3 and the ratio of x/y is 7:1 or above, said spinel exhibiting a single phase X-ray diffraction pattern substantially isostructural with that of Fe_3O_4 and said spinel having a measured BET surface area of up to $5\text{ m}^2/\text{g}$, said process being conducted with a mixture of CO and hydrogen under conditions of pressure, space velocity, and elevated temperature, for a time sufficient to produce said product C_2 - C_4 olefins.
19. Fiato, Rocco, S. Soled, A. Montagna; Cobalt promoted FT catalysts patent 4,544,674 (Oct. 1985). **Claim 1:** A fixed bed process for synthesizing a hydrocarbon mixture containing C_2 - C_6 olefins comprising the step of contacting a fixed bed of a catalyst composition comprised of an unsupported Group IA or IIA metal salt promoted iron-cobalt spinel: said spinel exhibiting a single spinel phase, being isostructural with Fe_3O_4 as determined by X-ray diffractometry and possessing a BET nitrogen surface area of up to $5\text{ m}^2/\text{g}$, and an iron-cobalt atomic ratio of 7:1 or above; with a mixture of CO /hydrogen under process

conditions of pressure, space velocity (SHSV) and elevated temperature for a time sufficient to produce said C₂-C₆ olefins.

20. Vaughan, David; K. Strobmaier; Synthesis of ECR-26(C-2646); patent 5,283,047 (Feb. 1994). **Claim 1:** A synthetic transition metal aluminosilicate crystalline zeolite having the gmelinite structure and a chemical composition in the dehydrated form: 0.8 to 1.3 M_{2/n}O:(Al,Fe,Cr)₂O₃:4 to 8 SiO₂, where n is the valence of metal M; the atoms of Al $\geq$ atoms of

$$(Cr + Fe), \frac{Cr}{Cr + Al + Fe} \geq 0.05$$

and characterized by an X-ray diffraction pattern having the following essential lines:

dD	I/I ₀
11.9	VS
6.8	S
5.0	VS
5.59	M
4.11	MS
3.44	MS
2.97	MS
2.85	M
2.59	M

21. Iglesia, Enrique, S. Soled, R. Fiato; SiO₂ promoted cobalt catalyst on a support of TiO₂ for converting synthesis gas to heavy hydrocarbons; patent 4,794,099 (Dec. 1988). **Claim 1:** A hydrocarbon synthesis catalyst comprising cobalt in a catalytically active amount composited with an inorganic refractory support comprised of a major portion of titania to which a lesser portion up to about 15 wt.% of silica in the form of silica or a silica precursor has been added.
22. Iglesia, Enrique, R. Madon; Reducing methane production and increasing liquid yields in FT reactions; patent 4,754,092 June (1988); **Claim 1:** A process for reducing methane formation and increasing liquid (C₅+) yields in a Fischer-Tropsch hydrocarbon synthesis process comprising adding an olefin to a gas feed and contacting said gas feed comprising a mixture of H₂ and CO with a catalyst at an elevated temperature of at least about 100°C, said addition of said olefin and said contacting with said gas feed occurring within the reactor bed in the area of the reactor bed below 10% of the distance from the top to the bottom

of the reactor bed and above 10% of the distance from the bottom to the top of the reactor bed in an amount sufficient to reduce said methane formation, wherein said catalyst comprises a catalytic metal selected from the group consisting of iron, cobalt and ruthenium supported on an inorganic refractory oxide support.

23. Fiato, Rocco, S. Miseo; Process for the preparation of slurried CO hydrogenation catalysts; patent 4,749,677 (June 1988) **Claim 1:** A process for forming a slurry catalyst composition produced by the steps of: (a) adding to a stirred slurry reactor TiO_2 , ruthenium carbonyl complex and an inert alkane hydrocarbon; (b) sealing said stirred slurry reactor and adding a gas mixture of $\text{N}_2:\text{CO}$ at room temperature and one atmospheric pressure to said stirred slurry reactor to purge said stirred slurry reactor; (c) heating said stirred slurry reactor to about 100°C and raising the pressure of said stirred slurry reactor to about 4 to about 10 atmospheres and adding a gas mixture of $\text{N}_2:\text{H}_2$ to said stirred slurry reactor; and (d) increasing the temperature of said stirred slurry reactor to about 230°F to about 270° and the pressure of said stirred slurry reactor from about 4 to about 20 atmospheres for about 2 to about 6 hours to cause the decomposition of said ruthenium carbonyl complex to form said slurry catalyst composition.
24. Iglesia, Enrique, S. Soled, R. Fiato; Cobalt-ruthenium catalysts for FT synthesis and process for their preparation; patent 4,738,948 (Apr. 1988). **Claim 1:** A hydrocarbon synthesis catalyst prepared by a process comprising impregnating a refractory support comprising titania with solutions of catalytically active amounts of cobalt and ruthenium salts, drying the impregnated support, reducing the cobalt and ruthenium, treating the reduced metals with an oxygen containing stream at conditions sufficient to form oxides of cobalt and oxides of ruthenium and reducing the cobalt and ruthenium oxides.
25. Wachs, Israel, D. Yang; Catalysts comprising ruthenium on titania surface modified with group VA oxide of vanadium, niobium or tantalum; patent 4,711,871 (Dec. 1987). **Claim 1:** A process for preparing a catalyst comprising ruthenium supported on a surface-modified titania support wherein said support comprises an oxide of a metal selected from the group consisting of niobium, vanadium, tantalum or mixture thereof, in a non-crystalline form, supported on said titania wherein said process comprises the sequential steps of: (a) forming said support comprising titania whose surface has been modified with and supports an oxide of a metal selected from the group consisting of niobium, tantalum, vanadium or mixture thereof wherein said supported, modifying oxide is a non-crystalline form; (b) impregnating said so-formed surface modified titania support with a solution of a ruthenium precursor compound; and (c) converting said ruthenium precursor compound to ruthenium to form said catalyst.
26. Mauldin, Charles, S. Davis, K. Arcuri; Cobalt catalysts for the conversion of methanol and for FT synthesis to produce hydrocarbons; patent 4,663,305 (May 1987). **Claim 1:** A regeneration stable catalyst for the conversion at reaction conditions of methanol or synthesis gas to liquid hydrocarbons which consists

essentially of from about 2% to about 25% cobalt, based on the weight of the catalyst composition, composited with titania, or a titania-containing support, to which is added sufficient of a zirconium, hafnium, cerium, or uranium promoter to provide a weight ratio of the zirconium, hafnium, cerium, or uranium metal:cobalt greater than about 0.101:1.

27. Fiato, Rocco, R. Bar-Gadda, S. Miseo; Cerium promoted FT catalysts; patent 4,657,885 (Apr. 1987). **Claim 1:** A hydrocarbon synthesis catalyst composition comprising sintered combination metal oxides having the following components in the stated weight percentage of the catalyst composition: (a) about 5 to about 80 wt.% of a Group VIII metal oxide; (b) about 4 to about 40 wt.% of a Group IIB metal oxide; (c) about 10 to about 40 wt.% of a Group IVB and/or VIIB metal oxide; (d) about 1 to about 5 wt.% of a Group IA metal oxide; and (e) about 1 to about 10 wt.% of a Lanthanum Group metal oxide, such that where the catalyst contains a Group VIII metal, said sintered combination comprises a series of spinels of a Group VIII metal, a Group IIB metal, and/or a Group IVB metal, and/or a Group VIIB metal, and a Group IA metal oxide in a lanthanum Group metal oxide matrix.
28. Mauldin, Charles; Start-up with ruthenium catalysts; patent 4,647,592 (MAR. 1987). **Claim 1:** In a process for the conversion of synthesis gas to hydrocarbons by contacting at reaction conditions a feed characterized as an admixture of carbon monoxide and hydrogen with a bed of particulate ruthenium catalyst constituted of a catalytically active amount of ruthenium composited with titania, or a titania-containing support, the improvement comprising contacting and pretreating the catalyst, prior to initiating the conversion reaction, with an admixture of steam and hydrogen at temperatures ranging from about 200°C to about 550°C sufficient to mildly agglomerate and ruthenium and form on the particles of catalyst larger agglomerates of ruthenium of average crystallize size from about 15 D to about 25 D approximating that obtained on completion of the startup portion of a synthesis gas operating run.
29. Arcuri, Kym; Process for the start-up of a FT reactor; patent 4,626,552 (Dec. 1986). **Claim 1:** In a process for the startup of a reactor wherein a feed comprised of hydrogen and carbon monoxide is contacted with a bed of hydrocarbon synthesis catalyst in which perturbations of the temperature profile across the bed can develop, and which, at line-out conditions defined by feed flow rate, pressure, temperature, and the molar ratio of hydrogen:carbon monoxide of the feed is sufficient to synthesize hydrocarbons from the hydrogen and carbon monoxide, the improvement which comprises: elevating, while maintaining the molar feed ratio of hydrogen:carbon monoxide at below about 90% of its line-out value, the feed flow rate, pressure and temperature to values approaching line-out feed flow rate, line-out pressure and line-out temperature and then gradually increasing the molar feed ratio of hydrogen:carbon monoxide to essentially that employed at line-out.

30. Davis, Stephen M.; Silica modified hydroisomerization catalyst; U.S. patent 5,187,138 (Feb. 1993). **Claim 1:** A catalyst composition comprising: a Group VIII metal; a support therefore of alumina or silica-alumina wherein the silica content is less than about 35 wt.%; at least about 0.5 wt.% silica other than the support silica; and a surface area of about 180-400 m²/gm.
31. Hamner, Glen P.; Process for the isomerization and hydrocracking of FT waxes to protect a syncrude and upgraded hydrocarbon products; patent 4,832,819 (May 1989). **Claim 1:** A process for producing a pumpable syncrude from a Fischer-Tropsch wax containing oxygenate compounds, which comprises: (1) separating the FT wax into (a) a low-boiling fraction which contains most of the oxygenate compounds and (b) a high-boiling fraction which is substantially free of water and oxygenate compounds, (2) reacting the high-boiling fraction from step (1) with hydrogen at hydroisomerization and mild hydrocracking conditions in the presence of a fluorided Group VIII metal-on-alumina catalyst to produce a C₅+ hydrocarbon product, and (3) combining the C₅+ hydrocarbon product from step (2) with the low-boiling fraction from step (1) to produce a pumpable, refinery processable syncrude that can be transported at atmospheric conditions.
32. Hsia, Stephen J.; External catalyst rejuvenation system for the hydrocarbon synthesis process; patent 5,260,239 (Nov. 1993). **Claim 1:** A process for practicing catalytic hydrocarbon synthesis and reactivation rejuvenation of deactivated hydrocarbon synthesis catalyst on a continuous basis, said process comprising combining catalyst and synthesis feed and hydrocarbon liquid in a hydrocarbon synthesis first vessel means to produce a reactor slurry comprising catalyst, synthesis feed and synthesis product, collecting deactivated catalyst from the top of the reactor slurry by means of a first downcomer C conduit means the top of which is fitted with gas disentrainment means and which is located just below the top surface of the reactor slurry, passing the deactivated catalyst down this first downcomer C conduit means from the top of the first vessel means to the bottom of a reactivation C rejuvenation second vessel means, said second vessel means having rejuvenating gas introduction means located at its bottom, forming a reactivating slurry of catalyst in reaction product and rejuvenating gas, wherein the deactivated catalyst is reactivated C rejuvenated in said second vessel means, collecting reactivated C rejuvenated catalyst from the top of the reactivating slurry by means of a second downcomer C conduit means the top of which is fitted with gas disentrainment means and which is located just below the top surface of the reactivation slurry and passing the reactivated C rejuvenated catalyst down the second downcomer C conduit means from the top of the second vessel means to the bottom of the first vessel means, all catalyst downward flows on both the first and second downcomer means occurring solely under the influence of gravity.
33. Mitchell, Willard N.; Activation of hydrocarbon synthesis catalyst; patent 5,292,705 (Mar. 1994). **Claim 1:** A method for activating an essentially fresh, reduced cobalt containing FT catalyst which comprises treating the catalyst with

hydrogen or a hydrogen containing gas in the presence of hydrocarbon liquids for a period sufficient to increase substantially the initial catalyst productivity.

Examples. In a hydrocarbon synthesis process demonstration unit, hydrogen treatment of the catalyst to enhance initial activity for slurry phase operations was demonstrated. In the unit, fresh catalyst 12 st% Co, 1 wt% Re on a titania support with 6 wt% Al_2O_3 as a binder material, was activated by first reducing the catalyst in hydrogen to reduce the cobalt oxide to the cobalt metal. This was accomplished in a **fluid bed reactor** at temperatures up to about 375°C. The H_2 treat gas rate was 8-18 SCFH H_2 /lb catalyst with a H_2 concentration of 18-25% in N_2 . Following the reduction the catalyst was passivated with 0.25-1.3 SCFH of CO in N_2+H_2 for 1-2 hours.

The dry reduced catalyst [presumably they mean the dry reduced and passivated catalyst] was combined with a wax to form a slurry in a slurry mix vessel. The slurry was transferred to the hydrocarbon synthesis reactor and synthesis was initiated. Following a short test to measure initial catalyst productivity, a hydrogen treat was conducted in the slurry reactor ("super" activation). The following table shows two samples of this "super" activation:

	Relative Productivity	
	Before	After
Example 1	60	100
Example 2	25	100

In the first example the relative productivity increased from 40% to 100% and the second case from 25% to 100%. The conditions for the H_2 treat of the slurry were typical of conditions described earlier.

In order to determine the real increase in initial activity, the catalyst had to be run at synthesis conditions for a period sufficient to obtain an initial activity or productivity. However, this minimal operation at synthesis conditions is not believed to change or effect the catalyst in any substantive way and the catalyst may be considered as essentially fresh catalyst.

34. Chang, Min; C. Coulaloglou; Enhanced catalyst mixing in slurry bubble columns (OP-3723); patent 5,252,613 (Oct. 1993). **Claim 1:** A method for improving the axial distribution of catalyst in a hydrocarbon synthesis slurry bubble column which uses rising synthesis gas introduced by means of synthesis gas distribution means located at the bottom of said column to provide the majority of the energy used in distributing catalyst in said column, the improvement in axial distribution of catalyst being achieved by using a secondary fluid introduction means in said slurry bubble column at a location above the synthesis gas

distribution means located at the bottom of said column to introduce a secondary fluid stream into said column.

35. Kim, Chang J.; Water addition for increased Co/N₂ hydro-carbon synthesis activity over catalysts comprising cobalt, ruthenium and mixtures thereof which may include a promoter metal; patent 5,227,407 (Jul 1993). **Claim 1:** A once-through, fixed or slurry bed FT process with CO conversion activity and C₅+ liquid hydrocarbon selectivity comprising contacting a feed mixture of carbon monoxide and hydrogen in a reaction zone with about 1 vol.% to about 70 vol.% water based on the total volume of feed mixture, at a pressure above one atmosphere and a temperature ranging from about 150°C to about 300°C, with a catalyst selected from the group consisting of cobalt, ruthenium, and mixtures thereof on a titania support, wherein said titania support is less than 40 m²/g, converting at least 90 vol.% of the carbon monoxide to liquid hydrocarbons, and in the substantial absence of CO₂ formation.
36. Soled, Stuart, E. Iglesia, R. Fiato, G. Ansell; Method for stabilizing titania supported cobalt catalyst and the catalyst for use in FT process; patent 5,169,821 (Dec. 1992). **Claim 1:** A method of preparing a 400-750°C regeneration stable catalyst composition comprising: (a) coprecipitating a titanium metal complex from a solution of a titanium alkoxide and a metal alkoxide or a solution of titanium chloride and a metal chloride wherein said metal is selected from the group consisting of silicon, zirconium and tantalum; (b) recovering the coprecipitate and calcining at temperatures of 400-750°C, to form a ternary metal oxide support; (c) depositing a cobalt compound onto said calcined ternary metal oxide support; (d) activating said cobalt calcined support to form a catalyst comprised of cobalt on a substituted ternary metal oxide support of titania having the general formula Co/Ti_xM_{1-x}O₂ wherein x is from 0.01 to 0.14 and M is selected from the group consisting of silicon, zirconium, and tantalum, wherein the titania is an anatase polymorph.
37. Soled, Stuart, E. Iglesia, R. Fiato; Copper promoted cobalt-manganese spinel catalyst and method for making the catalyst for FT synthesis; patent 5,162,284 (Nov. 1992). **Claim 1:** A composition of matter comprising a copper promoted cobalt-manganese spinel, the spinel having the formula: Co_{3-x}Mn_xO₄, where x is from about 0.5 to about 1.2.
38. Mauldin, Charles, K. Riley; Process for the preparation of surface impregnated dispersed cobalt metal catalysts; patent 4,977,126 (Dec. 1990). **Claim 1:** In a process for the production of catalysts wherein a catalytically effective amount of cobalt is impregnated and dispersed on the outer surface of a particulate porous inorganic oxide support to form a catalyst useful for the conversion of synthesis gas to hydrocarbons, and the support particles are contacted with a spray containing a decomposable compound of cobalt, the improvement comprising: maintaining a bed of the support particles in a fluidized state at temperature ranging from about 50°C to about 100°C by contact with a gas at temperature ranging from about 50°C to about 100°C; spraying the bed of the heated support

particles with a liquid in which a cobalt compound is dispersed at flow rate sufficient to provide a ratio between the flow rate of the liquid: flow rate of the fluidizing gas below about 0.6 grams liquid/ft³ of fluidizing gas to form on the particles a surface layer of cobalt compound in average thickness ranging from about 20 microns to about 250 microns, with the loading of cobalt compound ranging from about 0.01 g/cc to about 0.15 g/cc, calculated as metallic cobalt per packed bulk volume of catalyst.

39. Iglesia, Enrique; S. Soled, R. Fiato; Synthesis gas to heavy hydrocarbons on SiO₂ promoted Co/TiO₂; patent 4,960,801 (Oct. 1992). **Claim 1:** A process for preparing C₅+ hydrocarbons which comprises reacting hydrogen and carbon monoxide at hydrocarbon synthesis reaction conditions in the presence of a catalyst comprising cobalt in a catalytically active amount composited with an inorganic refractory support comprising a major portion of titania to which a lesser portion up to about 15 wt.% silica in the form of silica or a silica precursor has been added.

40. Pedrick, Larry E.; C. Mauldin, W. Behrmann; Draft tube for catalyst rejuvenation and distribution; patent 5,268,344, (Dec. 1993). **Claim 1:** A method for rejuvenating reversibly deactivated particulate hydrocarbon synthesis catalyst in a slurry phase reactor, said method comprising the use of substantially vertical draft tube means, open at both ends, fully immersed in the slurry containing the catalyst and injecting a hydrogen containing gas at or substantially near the bottom of said draft tube means thereby lifting catalyst in slurry from the bottom of the slurry phase reactor into and through the open bottom end of the draft tube means, rejuvenating catalyst in the presence of said hydrogen containing gas in the vertical draft tube means and ejecting the rejuvenated catalyst into the top of the slurry phase in the slurry phase reactor through the open top of the draft tube means.

45. McVicker, Gary; M. Albert Vannice; Preparation and use of supported potassium (or rubidium)-group VIII metal cluster catalysts in CO/H₂ FT synthesis reactions; patent 4,192,777 (Mar. 1980). **Claim 1:** Supported, highly dispersed, high activity potassium or rubidium-Group VIII metal cluster catalysts demonstrating improved selectivity olefinic and paraffinic hydrocarbons in CO/H₂ reactions prepared by the process which comprises depositing known, well-characterized potassium or rubidium-Group VIII metal carbonyl cluster complexes and mixtures thereof on a high surface area support material, drying the carbonyl cluster complex impregnated support in the absence of oxygen, and reducing the supported complex at elevated temperatures to effect the essentially complete reduction of the supported potassium or rubidium-Group VIII metal carbonyl cluster complexes to discrete potassium or rubidium-Group VIII clusters of metals on the support surface.

46. Wright, Franklin; M. Richard, J. Pirkle; Process using iron-thallium catalysts in CO hydrogenation; patent 4,513,104 (Apr. 1985). **Claim 1:** A process for producing liquid hydrocarbons, including those in the C₆-C₁₁ hydrocarbon range,

comprising the steps of: (a) first depositing thallium on the surface of a supported or unsupported iron catalyst wherein the weight ratio of iron-thallium, taken as the free metals, is from about 100:1 to 1:100, and wherein said iron compounds contain iron value substantially in the trivalent state; (b) contacting said iron-thallium catalyst with a mixture of CO and H₂ in a volume ratio of about 1:4 to 4:1, respectively, at a temperature ranging from 270 to 550°C, a pressure ranging from 0.1 to 10 MPa and a space velocity ranging from 10 to 10,000 v/v/hr, or equivalent conditions, for a sufficient time to substantially convert said thallium compounds to metallic thallium and said iron compounds to reduced and carbided iron; and (c) continuing said contacting as described in step (b) at a pressure above 0.1 MPa, a temperature ranging from 230 to 550°C, to produce liquid hydrocarbons comprising about 40 wt.% and greater C₆-C₁₁ liquid hydrocarbons and below about 5 wt.% C₂₃+ hydrocarbons.

47. Wright, Franklin; Iron-thallium catalysts for use in CO hydrogenation and process of preparing the catalysts, Patent 4,436,834 (Mar. 1984). **Claim 1:** A catalyst composition consisting essentially of a mixture of an iron compound and a thallium compound, being supported or unsupported, said compound of iron and thallium being selected from the group consisting of an oxide, hydroxide, carbonate, sulfate, carbide, halide, nitrate, or mixtures thereof, wherein the weight ratio of iron-thallium, taken as the free metals, is from about 100:1 to 1:100, and wherein said iron compound contains iron value substantially in the trivalent state, and wherein said thallium compound is substantially deposited on the surface of said iron compound.
48. Soled, Stuart, R. Fiato; Process for preparing high surface area iron/cobalt FT slurry catalysts; patent 4,518,707 (May 1985). **Claim 1:** A composition of matter comprising an unsupported, Group IA or IIA metal salt promoted iron-cobalt spinel, or mixture thereof, said spinel exhibiting a single phase powder X-ray diffraction pattern substantially isostructural with Fe₃O₄, and possessing a BET surface area greater than 5 m²/g and an iron-cobalt atomic ratio of 4 to 1 or above.
49. Soled, S. L. and R. A. Fiato; Process for preparing high surface area iron/cobalt Fischer-Tropsch slurry catalysts; U.S. Patent 4,544,671, Oct. 1, 1985. **Claim 1:** A slurry process for synthesizing a hydrocarbon mixture containing C₂-C₂₀ olefins comprising the step of contacting a catalyst composition, comprised of an unsupported iron-cobalt spinel, said spinel exhibiting a single phase being isostructural with Fe₃O₄ as determined by powder X-ray diffractometry, and possessing an initial BET surface area greater than 5 m²/g and an Fe:Co atomic ratio of 7:1 and above, with a mixture of CO and hydrogen under conditions of pressure, space velocity, and elevated temperature, for a time sufficient to produce said C₂-C₂₀ olefins.
50. Fiato, Rocco; S. Soled, A. Montagna; Promoted iron-cobalt spinel catalyst for FT process; patent 4,537,867 (Aug. 1985). **Claim 1:** A hydrocarbon synthesis catalyst composition comprising an unsupported, Group IA or IIA metal salt

promoted iron-cobalt single phase spinel, said spinel having the initial empirical formula: $\text{Fe}_x\text{Co}_y\text{O}_4$, wherein x and y are integer or decimal values, other than zero, with the proviso that the sum of x+y is 3 and the ratio of x/y is 7:1 or above, said spinel exhibiting a powder X-ray diffraction pattern substantially isostructural with Fe_3O_4 and said spinel having an initial BET surface area of up to about 5 m^2/g .

51. Vannice, M. A. and R. L. Garten; Hydrocarbon synthesis from CO and H_2 using Ni supported on a titanium oxide; U. S. Patent 4,042,615, Aug. 16, 1977. **Claim 1:** A process for the synthesis of higher molecular weight paraffins comprising the steps of passing CO and H_2 in a CO/ H_2 ratio of 10 to 0.1 over a catalyst comprising nickel on a titanium-containing oxide support, wherein said titanium-containing oxide support is selected from the group consisting of TiO_2 , ZrTiO_4 , TiO_2 -carbon, TiO_2 - Al_2O_3 , TiO_2 - SiO_2 , alkaline earth titanates, alkali titanates, rare earth titanates and mixtures thereof, at a space velocity of from 100 to 50,000 v/v/hr and a temperature of from 100 to 500 $^\circ\text{C}$ at pressure of from 103 to 1.03×10^5 kPa for a time sufficient to effect the generation of the desired paraffinic products in the desired ratio, wherein the concentration of said nickel in said catalyst is from 0.01 to 75% by weight.
52. Tauster, S. J. and S. C. Fung; Group VIII metals on manganese-containing oxide supports which exhibit strong metal support interactions; U.S. Patent 4,402,869, Sept. 6., 1983. **Claim 1:** Improved catalytic compositions comprising catalytic metal selected from the group consisting of iron, nickel, cobalt and mixtures thereof supported on a manganese-containing oxide support, the improvement comprising as a final step before use, contacting said catalyst composition with a reducing atmosphere at a temperature of at least about 300 $^\circ\text{C}$ to produce a catalyst composition which exhibits suppressed hydrogen chemisorption.
53. Wachs, Israel; R. Fiato, C. Chersich; Iron carbide on titania surface modified with group VA oxides as FT catalysts; patent 4,559,365 (Dec. 1985). **Claim 1:** A process for producing hydrocarbons, including alkane hydrocarbons, from gaseous feed mixtures of CO and H_2 comprising contacting said feed, at a temperature ranging from about 200 to 350 $^\circ\text{C}$ and for a time sufficient to convert at least a portion of said feed to alkane hydrocarbons, with a catalyst comprising iron carbide supported on a surface modified titania support wherein said support comprises an oxide of a metal selected from the group consisting of niobium, vanadium, tantalum and mixture thereof supported on titania wherein at least a portion of said supported oxide is in a non-crystalline form.
54. Soled, Stuart, R. Fiato; FT hydrocarbon synthesis with copper promoted iron/cobalt spinel catalyst; patent 4,584,323 (Apr. 1986). **Claim 1:** A process for synthesizing a hydrocarbon mixture containing C_2 - C_{20} olefins comprising contacting a catalyst composition, comprising an unsupported, copper promoted iron-cobalt spinel, said spinel exhibiting a single phase being isostructural with Fe_3O_4 as determined by powder X-ray diffractometry, and possessing an initial

BET surface area greater than 5 m²/g and an Fe:Co atomic ratio of 4:1 and above, with a mixture of CO and hydrogen in a slurry liquid under conditions of pressure, space velocity and elevated temperature, for a time sufficient to produce said C₂-C₂₀ olefins.

56. Kugler, E. L. and R. L. Garten; Hydrocarbon synthesis from CO and H₂ using titanium promoted bulk nickel catalysts; U.S. Patent 4,273,724, June 16, 1981. **Claim 1:** A process for the synthesis of higher molecular weight paraffinic hydrocarbons of from C₂ to C₇ carbon number comprising the steps of passing CO and H₂ at a CO/H₂ ratio of from 10 to 0.1 at a space velocity of from 100 hr⁻¹ to 50,000 hr⁻¹, at a temperature of from 100 to 500°C and at pressures of from 103 to 1.03 x 10⁵ kPa over a catalyst comprising bulk nickel promoted with from 0.07 to 10 wt.% titanium containing oxide (calculated as TiO₂) for a time sufficient to effect the generation of the desired paraffinic products.
57. Vannice, M. A. and S. J. Tauster; Hydrocarbon synthesis from CO and H₂ using Ru supported on group VB metal oxides; U.S. Patent 4,171,320, Oct. 16, 1979. **Claim 1:** A process for the synthesis of olefins of from C₂ to C₅ chain length inclusive, said process comprising the steps of passing H₂ and CO at a H₂/CO ratio of 0.1 to about 10 over a catalyst comprising ruthenium on a support selected from the group consisting of V₂O₃, Nb₂O₅, Ta₂O₅, Al₂O₃-V₂O₃, Al₂O₃-Nb₂O₅, Al₂O₃-Ta₂O₅, SiO₂-V₂O₃, SiO₂-Nb₂O₅, SiO₂-Ta₂O₅, V₂O₃-carbon, Nb₂O₅-carbon, Ta₂O₅-carbon, alkaline earth group VB oxides, alkali Group VB oxides, rare earth Group VB oxides, Group IVB-Group VB oxides and mixtures thereof, at a space velocity of from 100 to 50,000 hr⁻¹, at a temperature of from 100 to 500°C, at a pressure of from 100 to 10⁵ kPa for a time sufficient to effect the generation of the desired olefinic products wherein the concentration of said ruthenium in said catalyst is from 0.01 to 15 wt.% based on total catalyst weight.
58. Fiato, Rocco; S. Soled; High surface area dual promoted iron/manganese spinel compositions; patent 4,618,597 (Oct. 1986). **Claim 1:** A composition of matter comprising an unsupported, Group IA or IIA metal and copper promoted, single phase, iron-manganese spinel, said spinel exhibiting a powder X-ray diffraction pattern substantially isostructural with Fe₃O₄ and possessing a BET surface area greater than 30 m²/g and an iron-manganese atomic ratio greater than about 2:1.
59. DeLuca, J. P., L. L. Murrell, R. P. Rhodes and S. J. Tauster; Stabilized ruthenium catalysts for selective reduction of oxides of nitrogen; U.S. Patent 3,922,235, Nov. 25, 1975. **Claim 1:** A stabilized supported ruthenium catalyst, said catalyst comprising ruthenium metal in combination with an oxide support, said support being one selected from the group consisting of zirconium titanate, and zirconium titanate mixed with titania, the ruthenium being present in an amount which does not exceed 0.003 grams of ruthenium per gram of oxide support.
71. Kugler, E. L. and S. J. Tauster; Catalyst comparison nickel supported on tantalum oxide or niobium oxide and their use as hydrocarbon synthesis catalysts in CO/H₂ reactions; U.S. Patent 4,206,135, June 3, 1980. **Claim 1:** A process

for the enhanced synthesis of paraffinic hydrocarbons of from 2 to 6 carbon atoms inclusive with reduced production of methane comprising the steps of passing H_2 and CO in an H_2/CO mole ratio of from about 0.1 to about 10 over a catalyst reduced at a temperature of at least $375^\circ C$ comprising nickel on a tantalum or niobium-containing oxide support wherein said tantalum or niobium-containing oxide support is selected from the group consisting of tantalum oxides, niobium oxides, $Al_2O_3-Ta_2O_5$, $Al_2O_3-Nb_2O_5$, $SiO_2-Ta_2O_5$, $SiO_2-Nb_2O_5$, Ta_2O_5 -carbon, Nb_2O_5 -carbon, alkaline earth-tantalum oxides, alkaline earth-niobium oxides, alkali-tantalum oxides, alkali-niobium oxides, rare earth-tantalum oxides, rare earth-niobium oxides, Group IVb-tantalum oxides, Group IVb-niobium oxides, and mixtures thereof, at a space velocity of from 100 hr^{-1} to about $50,000\text{ hr}^{-1}$, at a temperature of from about $100^\circ C$ to about $500^\circ C$, at a pressure of from about 100 to about $1 \times 10^5\text{ kPa}$, for a time sufficient to effect the generation of the desired paraffinic product, wherein the concentration of said nickel in said catalyst is from about 0.01 to about 75 wt.%.

72. Murrell, L. I. and S. J. Tauster; Catalytic process for NO_x reduction under lean conditions; U.S. Patent 4,039,622, Aug. 2, 1977. **Claim 1:** A process for effecting the selective reduction of NO_x in lean effluent waste streams containing NO_x , CO, O_2 , H_2 , CO_2 and water, wherein the concentration of CO is at least equivalent to the concentration of NO_x present in the waste stream, a lean effluent waste stream being defined as one in which the concentration of oxygen is in excess over the concentration of reductants to a level as high as 8%, i.e., about 800% excess oxygen, over the total of reductants present, said reductants being selected from the group comprising CO and H_2 so that when such a waste stream is reacted to completion, the residuum is oxidizing in character, said process comprising the steps of contacting said lean exhaust stream in a reaction zone with an iridium catalyst, said contacting occurring at a temperature between $300^\circ C$ to $750^\circ C$ thereby effecting the selective reduction by CO of the oxides of nitrogen to molecular nitrogen.
73. Vannice, M. A. and R. L. Garten; Hydrocarbon synthesis from CO and H_2 using Rh supported on titanium oxides; U.S. Patent 4,116,994, Sept. 26, 1978. **Claim 1:** A process for the enhanced synthesis of olefins and paraffins, wherein said paraffins are other than methane, comprising the steps of passing H_2 and CO in a H_2/CO ratio of 0.1 to 10 over a catalyst comprising rhodium on a titanium-containing oxide support, wherein said titanium-containing oxide support is selected from the group consisting of TiO_2 , $ZrTiO_4$, TiO_2 -carbon, $TiO_2-Al_2O_3$, TiO_2-SiO_2 , alkaline earth titanates, alkali titanates, rare earth titanates and mixtures thereof, at a space velocity of from 100 to $50,000\text{ v/v/hr}$ and at a temperature of from 100 to $500^\circ C$, at a pressure of from 100 to 10^5 kPa for a time sufficient to effect the generation of the desired olefinic and paraffinic products in the desired ratio, wherein the concentration of said rhodium in said catalyst is from 0.01 to 10% by weight.
74. Vannice, M. A. and R. L. Garten; Catalytic formation of hydrocarbons from CO, H_2 mixtures and process for maintaining catalytic activity; U.S. Patent 4,093,643,

- June 6, 1978. **Claim 1:** A process to produce low molecular weight organic compounds comprising substantially methane, said process consisting of the steps of passing a mixture of CO and H₂ over palladium supported on an acidic metal oxide selected from the group consisting of alumina and hydrogen-y-zeolite wherein the palladium metal particle size is maintained at less than 100 Å by running at a reactor bed temperature of less than 350°C, at a pressure ranging from 1 to 500 atm. and a GHSV of from 1200-4600 hr⁻¹.
75. Voorhies, Alexis, Jr., Hydrocarbon synthesis process, U.S. Patent 2,479,439, Aug. 16, 1949. **Claim 1:** An improved hydrocarbon synthesis process which comprises reacting together, under synthesis conditions, hydrogen and carbon monoxide initially in the presence of an unpromoted powdered iron catalyst in the form of a fluidized bed contained in a reaction zone, adding an alkali metal compound to the reaction zone at a slow rate during such a period of time as to cause a slow and homogeneous impregnation of said alkali metal compound within said catalyst, and to the extent that the desired yields or normally liquid hydrocarbons are obtained from the reaction zone, whereupon the feeding of the alkali metal compound is discontinued, the amount of said promoter with respect to the catalyst and contained thereon lying within the limits of from about 0.1 to 5 wt.% after the initial period, and adding water to the reaction zone to repress carbon formation in an amount such that the feed to the reaction zone contains 5 to 25 mols of hydrogen per mol of water.
76. Aldridge, C. L. and T. Kalina; Shift process for new catalysts; U.S. Patent 3,850,841, Nov. 26, 1974. **Claim 1:** A process for the preparation of hydrogen and carbon dioxide which comprises introducing a gas mixture containing monoxide and steam at a temperature varying from about 300 to 700°F, and introducing at least a portion of said cooled reaction mixture to at least one additional shift reaction stage and contacting the same therein with a catalyst, the temperature within each said reaction stage being maintained above the dew point temperature of the reaction mixture and the pressure within each said reaction stage being maintained below the dew point pressure of said reaction mixture and ranging from about atmospheric to about 3000 psig, the catalyst in each reaction stage comprising (i) an alkali metal compound derived from an acid having an ionization constant of less than about 1×10^{-3} and (ii) a hydrogenation-dehydrogenation component selected from the group consisting of (a) a metal composition comprising vanadium, molybdenum, tungsten, cobalt, tantalum or niobium materials or mixtures thereof or (b) mixtures of materials comprising vanadium, molybdenum, tungsten, cobalt, tantalum or niobium materials or mixtures thereof with a nickel, iron or chromium material or mixtures thereof, the weight ratio of said hydrogenation-dehydrogenation component to said alkali metal compound, each calculated on the basis of the oxides thereof, being less than 5:1.
77. Vannice, M. A. and R. L. Garten; Catalytic formation of hydrocarbons from CO hydrogen mixtures; U.S. Patent 3,941,819, March 2, 1976. **Claim 1:** A process for producing substantial amounts of dimethyl ether, said process comprising the

step of passing CO and H₂ over platinum supported on alumina, wherein the amount of platinum ranges from 0.3 to 2 wt.% based on total weight of the support including platinum at a temperature ranging from 200 to 300°C and a pressure ranging from 10.10 to 40 atm. and wherein the mol ratio of hydrogen to CO ranges from 0.1 to 2.

78. Kwang, K. K., R. E. Pennington, L. W. Vernon and N. C. Hahas; Methane production, U. S. Patent 3,958,957, May 25, 1976. **Claim 1:** A method for the production of a methane-rich gas which comprises introducing a gaseous mixture of hydrogen and at least one carbon oxide into a reaction zone containing a carbon-alkali metal catalyst at a temperature between about 800°F and about 1500°F and at a pressure between about atmospheric and about 2000 psig, said catalyst being prepared by heating an intimate mixture consisting essentially of a carbonaceous solid and an alkali metal constituent to an elevated temperature sufficient to produce a reaction between the carbon and alkali metal in said mixture and form a carbon-alkali metal reaction product, and recovering a methane-rich gas from said reaction zone.
79. Vannice, M. A.; Method for the direct preparation of halogenated hydrocarbons by the reaction of CO, H₂ and halogen in the presence of a catalyst; U.S. Patent 4,041,087, Aug. 9., 1977. **Claim 1:** method for the preparation of halogenated hydrocarbons of the formula C_AH_{2A+2-B}X_B wherein x is a halogen selected from the group consisting of fluorine, chlorine, bromine and iodine, A is an integer ranging from 1 to 4 inclusive and B is an integer ranging from 1 to 10 inclusive, except that 2A+2-B may not be less than zero, which method comprises the steps of: (1) preparing a system comprising CO, H₂ and a source of halogen wherein the source of halogen is selected from the group consisting of molecular halogen and hydrogen halides; (2) passing said system over a catalyst metal selected from the group consisting of Group VIII metals, rhenium, and platinum-iridium and platinum-rhenium alloys, which catalyst metal is in combination with an acidic inorganic oxide material; (3) heating the system containing the CO, H₂ and halogen source over the catalyst to a temperature in the range of 200-1000°C; and (4) pressurizing the system to a level in the range of 0.1 atm to 500 atm.
80. Vannice, M. A. and R. L. Garten; Hydrocarbon synthesis from CO and H₂ using Ru supported on a titanium oxide; U.S. Patent 4,042,614, Aug. 16, 1977. **Claim 1:** A process for the selective synthesis of olefins from C₂ to C₁₀ chain length inclusive, said process comprising the steps of passing H₂ and CO at a H₂/CO ratio of 0.1 to 10 over a catalyst comprising ruthenium on a titanium-containing oxide support, wherein said titanium-containing oxide support is selected from the group consisting of TiO₂, ZrTiO₄, TiO₂-carbon, TiO₂-Al₂O₃, TiO₂-SiO₂, alkaline earth titanates, alkali titanates, rare earth titanates and mixtures thereof, at a space velocity of from 100 to 50,000 v/v/hr at a temperature of from 100 to 500°C at a pressure of from 100 to 10⁵ kPa for a time sufficient to effect the generation of the desired olefinic products in the desired ratio wherein the concentration of said ruthenium in said catalyst is from 0.01 to 15% by weight.

81. Yates, D. J. C. and L. L. Murrell; Method for preparing a highly dispersed supported nickel catalyst; U.S. Patent 4,073,750, Feb. 14, 1978. **Claim 1:** A highly dispersed nickel catalyst having a nickel surface area of from 200 to 400 m²/g nickel prepared by the method which comprises slurring a nickel metal precursor dissolved in a nonaqueous organic liquid solvent with a high surface area refractory oxide support, removing the solvent to obtain a composite of said nickel metal precursor and said support, and activating said composite by reducing in hydrogen or hydrogen dilutes with an inert gas at conditions sufficient to convert substantially all of the nickel metal precursor to nickel metal.
82. Tauster, S. J., L. L. Murrell and S. C. Fung; Supported metal interaction catalysts; U. S. Patent 4,149,998, April 17, 1979. **Claim 1:** Improved catalytic composition consisting of a metal selected from the group consisting of iridium, osmium, rhodium, and mixtures thereof and an oxide of titanium support prepared by depositing said iridium, osmium, rhodium and mixtures thereof on the oxide of titanium and pretreating the composition prior to use, the improvement comprising, as a final step before use, reducing the composition in a hydrogen atmosphere at a temperature of at least 200°C, thereby producing a composition which exhibits suppressed hydrogen chemisorption.
83. Wheelock, K. S., Catalyst and a process for its preparation; U.S. Patent 4,219,447, Aug. 26, 1980. **Claim 1:** A catalyst useful for the conversion of a hydrocarbon feed by contact thereof at hydrocarbon conversion conditions which comprises a cluster of titanium metal oxide and a Group VIII noble metal deposited on the surface of an inorganic oxide support.
84. Murrell, L. L., C. J. Kim, and D. C. Grenoble; Acid catalyzed hydrocarbon conversion process utilizing a catalyst comprising a group IVB, VB or VIB metal oxide on an inorganic refractory oxide support; U.S. Patent 4,233,139, Nov. 11, 1980. **Claim 1:** In a hydrocarbon conversion process wherein hydrocarbon fractions are cracked over acid catalysts at elevated temperatures, the improvement comprising using as the catalyst a material comprising a catalytic metal oxide selected from the group consisting of the oxides of tungsten, niobium and mixtures thereof and tungsten or niobium oxides in combination with one or more additional metal oxides selected from the group consisting of tantalum oxide, hafnium oxide, chromium oxide, titanium oxide and zirconium oxide supported on an inorganic refractory metal oxide base selected from the group consisting of alumina, zirconia, boria, thoria, magnesia, zirconium-titanate, titania, chromia, kieselguhr and mixtures thereof, said catalyst being steamed prior to use.
85. McCandlish, L. E. and E. L. Kugler; CO hydrogenation process using molybdenum oxycarbonitride catalyst; U.S. Patent 4,418,154, Nov. 29, 1983. **Claim 1:** A process for preparing paraffinic hydrocarbons including linear and branched C₁-C₁₀ carbon chain numbers comprising contacting a gaseous mixture of CO and H₂ in a CO/H₂ volume ratio of 10:1 to 1:10, respectively, with a catalyst comprised of face-centered cubic molybdenum oxycarbonitride, in which the

interstitial oxygen, carbon and nitrogen atoms are distributed throughout the bulk structure, at a temperature of about 100 to 600°C, a pressure of about 0.1 to 50,000 v/v/hr and recovering product paraffinic hydrocarbons.

86. Hallulin, A. P. and A. E. Burnett; Coprecipitated Si-Al-metal-particle catalyst; U. S. Patent 4,497,907, Feb. 5, 1985. **Claim 1:** A calcined support catalyst comprised of: (a) one or more metals which are catalytically active for the hydrogenation of organic compounds, (b) alumina and silica at a weight ratio of 0.45:1 to 1:0.45, respectively, and (c) solid porous particles, the catalyst being characterized as having a BET total surface area ranging from about 150 to about 350 m²/g wherein the total amount of catalytically active metal in the catalyst ranges from about 10 wt.% to about 70 wt.% and wherein the catalyst has been prepared by: (aa) coprecipitating ions of one or more catalytically active metals, aluminum ions and silicate ions, with the solid porous particles, (bb) drying the coprecipitated catalyst and (cc) calcining the dried coprecipitated catalyst at a temperature from about 300 to 450°C.
87. Mauldin, C. H.; Conversion of methanol to hydrocarbons; U.S. Patent 4,513,161, Apr. 23, 1985. **Claim 1:** A process useful for the conversion of methanol to hydrocarbons which comprises contacting at reaction conditions a feed comprised of an admixture of methanol and hydrogen, in methanol:hydrogen molar ratio equal to or greater than about 2:1 at total pressure equal to or greater than about 160 psig, over a catalyst which comprises ruthenium in catalytically active amount composited with titania or titania-containing support.
88. Soled, S. L., A. Wold and R. Kershaw; Reduction process for forming powdered alloys from mixed metal iron oxides; U.S. Patent 4,525,206. **Claim 1:** A process for producing a powdered metal-based iron alloy comprising the steps of: (a) heating a mixture comprised of a powdered mixed metal iron oxide, being difficulty reducible in hydrogen gas, with at least a stoichiometric amount of calcium metal, in a non-oxidizing atmosphere, at a temperature below the melting point of the mixed metal iron oxide for a time sufficient to substantially reduce all the metal oxide present, and form said product metal-based iron alloy, as determined by X-ray diffractometry, (b) contacting said reduced mixed metal iron oxide with aqueous acid to remove calcium impurities and by-products; and (c) recovering said product metal-based iron alloy.
89. Payne, V. L. and C. H. Mauldin; Cobalt catalysts for the preparation of hydrocarbons from synthesis gas and from methanol; U.S. Patent 4,542,122, Sept. 17, 1985. **Claim 1:** A catalyst composition useful for the conversion of methanol or synthesis gas to hydrocarbons which consists essentially of cobalt, or cobalt and thoria in catalytically active amount composited with titania or a titania-containing support, wherein the titania support is one having a rutile:anatase ratio of at least about 2:3.
90. Wachs, I and C. C. Chersich; Catalysts comprising tantalum supported on titania; U.S. Patent 4,544,649, Oct. 1, 1985. **Claim 1:** A catalyst composition comprising

an oxide of tantalum support on titania wherein at least a portion of the supported tantalum metal oxide is in a non-crystalline form.

91. Madon, R. J.; Liquid hydrocarbon synthesis using supported ruthenium catalysts; U.S. 4,477,595, Oct. 16, 1984. **Claim 1:** A process for selectively producing paraffins comprising: (a) first contacting a mixture of H_2 and CO for at least 10 hours with a reduced and supported ruthenium catalyst, said ruthenium catalyst comprising ruthenium on a support selected from the group consisting of TiO_2 , $ZrTiO_4$, TiO_2 -carbon, $TiO_2-Al_2O_3$, TiO_2-SiO_2 , alkaline earth titanates, alkali titanates, rare earth titanates, V_2O_3 , Nb_2O_5 , Ta_2O_5 , $Al_2O_3-V_2O_3$, $Al_2O_3-Nb_2O_5$, $Al_2O_3-Ta_2O_5$, $SiO_2-V_2O_3$, $SiO_2-Nb_2O_5$, $SiO_2-Ta_2O_5$, V_2O_3 -carbon, Nb_2O_5 -carbon, Ta_2O_5 -carbon, alkaline earth Group VB oxides, alkali-Group VB oxides, rare earth-Group VB oxides, Group IVB-Group VB oxides, and mixtures thereof, at FT conditions such that the temperature ranges from about 100 to 400°C, the pressure ranges from about 0.2 to 10 mPaA, the gas hourly space velocity, GHSV, ranges from about 100 to 50,000 v/v/hr and wherein the ratio of GHSV/pressure is below about 24,000 v/v/hr/mPaA, and at least about a 20% CO conversion is effected; and (b) continuing said contacting as in step (a) at a H_2 /CO molar ratio from about 0.1 to 4 and thereafter recovering a hydrocarbon mixture comprising C_5 - C_{40} hydrocarbons, containing C_5 - C_{20} paraffins and olefins in a paraffins to olefins weight ratio of at least 1.5
92. Fiato, R. A. and E. L. Kugler; Production of alkanes from mixtures of CO and H_2 ; U.S. Patent 4,548,953, Oct. 22, 1985. **Claim 1:** A process for producing hydrocarbons, including alkane hydrocarbons, from gaseous mixtures of CO and H_2 comprising contacting said mixture, at a temperature ranging from about 200 to 350°C and for a time sufficient to convert at least a portion of said feed to alkane hydrocarbons, with a catalyst comprising a mixture of iron carbide and ilmenite supported on titania wherein the amount of said supported iron present in said supported iron carbide and ilmenite, calculated as Fe_2O_3 , is at least about 2×10^{-3} grams per square meter of titania support surface.
93. Arcuri, K. B., C. H. Mauldin and D. H. Shaw; Ruthenium catalysts, and use thereof for Fischer-Tropsch synthesis; U.S. Patent 4,567,205, Jan. 28, 1986. **Claim 1:** A process useful for the synthesis of hydrocarbons at reaction conditions from a feed constituting an admixture of carbon monoxide and hydrogen, which comprises contacting said feed with a catalyst which comprises ruthenium in catalytically active amount composited with titania, or titania-containing support, having a rutile:anatase ratio of at least about 2:3 and rhenium in amount sufficient to provide a weight ratio of rhenium:ruthenium which ranges from about 2:1 to about 1:4, sufficient at corresponding reaction conditions to obtain improved activity maintenance vis-a-vis a ruthenium catalyst otherwise similar except that it does not contain rhenium.
94. Halluin, A. P. and A. E. Barnett; Catalyst support compositions; U.S. Patent 4,593,014, June 3, 1986. **Claim 1:** A catalyst support composition consisting essentially of alumina and titania at a weight ratio of about 0.3:1 to 1:0.3

respectively, and solid porous particles selected from the group of kieselguhr, infusorial earth, diatomaceous earth and siliceous earth.

95. Fiato, R. A. and E. L. Kugler; Improving activity of iron carbide and ilmenite on titania Fischer-Tropsch catalyst; U.S. Patent 4,594,331, June 10, 1986. **Claim 1:** A process for improving the activity of a FT catalyst present in a FT reaction zone wherein said catalyst comprises a mixture of iron carbide and ilmenite supported on a titania support wherein the amount of iron present in said supported iron carbide and ilmenite mixture, calculated as Fe_2O_3 , is at least about 2×10^{-3} grams per square meter of titania support surface and wherein said reaction zone contains a FT feedstream comprising a mixture of H_2 and CO, said process comprising reducing or eliminating the hydrogen content of the FT feedstream, raising the temperature in said reactor between about 50 to about 150°C above the FT reaction temperature for from about 1 to 6 hrs. and then lowering the temperature back to the reaction temperature and reestablishing the hydrogen content of the feedstream.
96. Payne, V. L. and C. H. Mauldin; Preparation of hydrocarbons from synthesis gas; U.S. Patent 4,595,703, June 17, 1986. **Claim 1:** A process useful for the conversion of synthesis gas to hydrocarbons which comprises contacting at reaction conditions a feed comprised of an admixture of carbon monoxide and hydrogen, in H_2 :CO molar ratio equal to or greater than about 0.5:1 at total pressure equal to or greater than about 80 psig, over a catalyst which comprises cobalt, or cobalt and thoria in catalytically active amount composited with titania or titania-containing support, wherein the titania support is one having a rutile:anatase ratio of at least about 2:3.
97. Wachs, I. E., R. A. Fiato and C. C. Chersich; Iron carbide on titania surface modified with Group VA oxides as Fischer-Tropsch catalysts; U.S. Patent 4,608,359, Aug. 26, 1986. **Claim 1:** A catalyst comprising iron carbide supported on a surface modified titania support wherein said support comprises an oxide of a metal selected from the group consisting of niobium, vanadium, tantalum or mixture thereof supported on said titania wherein at least a portion of said supported oxide of niobium, vanadium, tantalum or mixture thereof is in a non-crystalline form, wherein the amount of said supported oxide ranges from about 0.5 to 25 wt.% metal oxide on the titania support based on the total support composition and wherein the catalyst contains at least about 2 milligrams of iron, calculated as Fe_2O_3 per square meter of support surface.
98. Fiato, R. A., G. B. McVicker and A. A. Montagna; Fe-Co catalyst slurry system for use in alpha olefin production; U.S. Patent 4,624,967, Nov. 25, 1986. **Claim 1:** A process for synthesizing hydrocarbons containing alpha olefins comprising contacting a gaseous feed mixture of H_2 and CO, in a reaction zone, with a slurry catalyst system at elevated temperature for a time sufficient to convert at least a portion of said gaseous feed to said alpha olefins, wherein said catalysts slurry system is prepared by a process comprising the steps of: (a) heating a slurry mixture comprised of: a FT slurry liquid, an iron carbonyl compound, a cobalt

carbonyl compound, or iron and cobalt compounds capable of forming carbonyl complexes in a atmosphere of CO, and mixtures thereof, and a powdered support, wherein said iron and cobalt compounds are present in a total iron:cobalt atomic ratio of about 35:1 to 1:10, taken as free metals, and wherein the cobalt carbonyl compound has a lower melting point/decomposition temperature than the iron carbonyl compound; in a carbon monoxide atmosphere under pressure, at a temperature above the melting point/decomposition temperature of the cobalt compound for a time sufficient to substantially decompose the cobalt compound, (b) heating said slurry mixture from step (a) at a temperature above the melting point/decomposition temperature of the iron compound in said CO atmosphere under pressure, to substantially decompose the iron compound; and (c) heating said slurry mixture from step (b) in an atmosphere of hydrogen gas to substantially reduce said iron and cobalt carbonyl compounds and their decomposition products to form said catalyst.

99. Rice, G. W., R. A. Fiato and S. L. Soled; Promoted iron-carbon-based catalysts produced in the presence laser radiation; U.S. Patent 4,659,681, April 21, 1987. **Claim 1:** A composition of matter comprising finely divided non-pyrophoric iron-carbide catalytic particles comprising iron and carbon in the substantial absence of silicon, a substantial portion of which is cementite, produced in a reaction zone in the presence of laser radiation under such conditions of laser flux density, power adsorption, concentration of iron compound reactants selected from the group consisting of iron carbonyls, iron acetyl-acetonate, and ferrocene and pressure sufficient to produce non-pyrophoric iron-carbon particles having average diameters between 1 and 100 nm, and which particles are subsequently impregnated with at least 2% of a promoter selected from the group of the salts and oxides of alkali and alkaline earth metals.
100. Rice, G. W., R. A. Fiato and S. L. Soled; Iron carbide-based catalyst produced in the presence of laser radiation; U.S. Patent 4,668,647, May 26, 1987. **Claim 1:** A composition of matter comprising finely divided non-pyrophoric iron-carbide catalytic particles comprising iron and carbon in the substantial absence of silicon, a substantial portion of which is cementite, produced in a reaction zone in the presence of laser radiation under such conditions of laser flux density, power adsorption, concentration of iron compound reactants selected from the group consisting of iron carbonyls, iron acetyl-acetonate, and ferrocene, and pressure sufficient to produce non-pyrophoric iron-carbon particles having average diameters between 1 and 100 nm.
101. Mauldin, C. H.; Improved cobalt catalysts, and use thereof for Fischer-Tropsch synthesis; U.S. Patent 4,670,475, June 2, 1987. **Claim 1:** A process useful for the conversion or synthesis gas feed comprised of hydrogen and carbon monoxide to hydrocarbons which comprises contacting said feed at reaction conditions with a catalyst which comprises cobalt, or cobalt and thoria in catalytically active amount composited with a titania or titania-containing support, to which is added sufficient rhenium to obtain, with a similar feed at

corresponding process conditions, improved activity, as contrasted with a catalyst composition otherwise similar except that it does not contain rhenium.

102. Fiato, R. A. and E. L. Kugler; Iron on titania Fischer-Tropsch catalyst; U.S. Patent 4,689,313, Aug. 25, 1987. **Claim 1:** A catalyst composition consisting essentially of catalytic components being selected from the group consisting of a mixture of iron carbide and ilmenite and a mixture of iron carbide and ilmenite containing at least one alkali metal promoter wherein the ratio of supported iron present in said supported iron carbide and ilmenite, calculated as Fe_2O_3 , to the surface area of said titania support ranges between about 2 to 25 milligrams per square centimeter, and wherein said catalyst has been formed by depositing an iron precursor salt of said catalytic component on said titania support, calcining said deposited salt and support to form a calcined composite and sequentially contacting said composite with a hydrogen containing reducing gas free of CO at elevated temperatures of from about 300 to about 500°C for a time sufficient to reduce the calcined composite followed by contacting said reduced composite with CO at a temperature from about 100 to about 200°C lower than the temperature used for said hydrogen contacting.
103. Fiato, R. A., R. Bar-Gadda and S. Miseo; Cerium promoted Fischer-Tropsch catalysts; U.S. Patent 4,719,240, Jan. 12, 1988. **Claim 1:** A hydrocarbon synthesis process comprising contacting a feed stream of CO and H_2 in a molar ratio of about 0.5 to about 4:1 with a catalyst at a temperature in the range of about 200 to 350°C, a pressure in the range of about 1 to 50 atm, a space velocity in the range of about 10 to 10,000 v/v/hr to produce a hydrocarbon product containing ethylene and ethane in which the ethylene/ethane mole ratio is greater than one, and recovering the product; the catalyst being comprised of a sintered composition containing: (a) about 5-80 wt.% Fe oxide; (b) about 4-20 wt.% Zn oxide, (c) about 10-40 wt.% Ti and/or Mn oxide, (d) about 1-5 wt.% of a Group IA metal oxide selected from the group consisting of K, Rb and Cs, and mixtures thereof, (e) about 1-10 wt.% Ce oxide such that said sintered combination comprises a series of spinels of Fe, Zn and/or Ti and/or Mn and said Group IA metal oxide in a cerium oxide matrix.
104. Fiato, R. A.; Slurried CO hydrogenation catalysts; U.S. 4,752,600, June 21, 1988. **Claim 1:** A slurry catalyst composition consisting essentially of: (a) TiO_2 , (b) the decomposition product of a ruthenium carbonyl complex which is $\text{Ru}_3(\text{CO})_{12}$, said decomposition product being formed by the decomposition of said $\text{Ru}_3(\text{CO})_{12}$ in the presence of a gas mixture of $\text{CO}:\text{H}_2\text{N}_2$ at a temperature of about 230°C to about 270°C and a pressure of about 230 to about 270°C and a pressure of about 4 to about 20 atm. for a sufficient period of time to form said decomposition product, said decomposition product being supported on said TiO_2 , and (c) an inert alkane hydrocarbon.
105. Iglesia, E., S. L. Soled and R. A. Fiato; Cobalt-ruthenium catalysts for Fischer-Tropsch synthesis; U.S. 4,822,824, April 18, 1989. **Claim 1:** A hydrocarbon synthesis process which comprises reacting hydrogen and carbon monoxide in

the presence of a catalyst comprised of cobalt and ruthenium on titania, at reaction conditions suitable for the formation of higher hydrocarbons, the catalyst being prepared by impregnating titania with solutions of cobalt and ruthenium salts, drying the impregnating support, reducing the cobalt and ruthenium, treating the reduced metals with an oxygen containing stream at conditions sufficient to form oxides of cobalt and oxides of ruthenium and reducing the cobalt and ruthenium oxides.

106. Wachs, I. E. and D. B. Yang; Catalysts comprising ruthenium on titania surface modified with Group VA oxide of vanadium, niobium or tantalum; U.S. 4,861,747, Aug. 29, 1989. **Claim 1:** A catalyst comprising ruthenium supported on a surface modified titania support wherein said support comprises an oxide of a metal selected from the group consisting of niobium, vanadium, tantalum or mixture thereof, in a non-crystalline form, supported on said titania.
107. Behrmann, W. C., C. H. Mauldin and K. B. Arcuri; Cobalt-titania catalysts. Process utilizing these catalysts for the preparation of hydrocarbons from synthesis gas, and process for the preparation of said catalysts; U.S. Patent 4,962,078, Oct. 9, 1990. **Claim 1:** A catalyst composition useful for the conversion of synthesis gas to liquid hydrocarbons which comprises cobalt dispersed and impregnated as a catalytically active layer upon the surface of a support, the support being at least about 80% by weight titania, the layer ranging in average thickness from about 0.2 mm to about 0.20 mm with the cobalt loading being about 0.04 g/cc to about 0.15 g/cc, calculated as metallic cobalt per packed bulk volume of catalysts, and having a productivity and methane selectivity at 200°C of at least 150 hr⁻¹ and no more than 10 mole %, respectively.
108. Mauldin, C. H. and K. L. Riley; Titania-supported catalysts and their preparations for use in Fischer-Tropsch synthesis; U.S. Patent 4,992,406, Feb. 12, 1991. **Claim 1:** A support composition for forming a catalyst useful for the conversion of synthesis gas to hydrocarbons which comprises titania in which there is incorporated from 0.1 to about 20 wt.% of an inorganic oxide binder selected from the group consisting of alumina and zirconia based on the weight of the titania-binder support, to provide a titania-binder support having a pore volume ranging from about 0.2 cc/g to about 0.5 cc/g, and surface area ranging from about 8 m²/g to about 70 m²/g.
109. Hildinger, H. W. and E. D. Carlson; Process for recycling and purifying condensate from a hydrocarbon or alcohol synthesis process; U. S. Patent 5,004,862, April 2, 1991. **Claim 1:** A process for purifying a condensate stream from a hydrocarbon synthesis or alcohol synthesis process which comprises: (a) contacting the condensate with a hot gaseous mixture comprising methane and steam to strip contaminants comprising lower molecular weight hydrocarbons and oxygenates; (b) recovering a gaseous stream comprising the contaminants and the gaseous mixture; and (c) separately recovering purified water.

110. Hildinger, H. W. and E. D. Carlson; Process for recycling and purifying condensate from a hydrocarbon or alcohol synthesis process; U.S. Patent 5,053,581, Oct. 1, 1991. **Claim 1:** A process for producing heavy hydrocarbons which comprises: (a) reacting CO and H₂ over a catalyst at reactive conditions in a hydrocarbon synthesis to form heavy hydrocarbons and a product condensate; (b) separately recovering the heavy hydrocarbons from the product condensate; (c) contacting the product condensate with a hot gaseous mixture comprising CH₄ and steam to strip the product condensate of contaminants, said contaminants comprising lower molecular-weight hydrocarbons and oxygenates; (d) recovering a gaseous stream comprising the contaminants and the gaseous mixture; and (e) converting the gaseous stream recovered in step (d) to CO and H₂ and utilizing at least a portion of said CO and H₂ in step (a).
111. Fiato, R. A.; Two stage process for hydrocarbon synthesis; U.S. Patent 5,028,634, July 2, 1991. **Claim 1:** A two stage hydrocarbon synthesis process comprising:
- (a) reacting in a first stage, hydrogen and carbon monoxide in the presence of a supported cobalt or ruthenium catalyst and obtaining a CO conversion to C₂+ hydrocarbons of at least 50% at reaction conditions including a pressure of at least 10 atmospheres;
  - (b) recovering a reaction product comprising hydrogen and carbon monoxide and separating liquid therefrom;
  - (c) reacting in a second stage, at a pressure below 10-12 atmospheres and no greater than the outlet pressure of the first stage, the remaining reaction products in the presence of a catalyst comprising catalytically effective amounts of cobalt supported on alumina at reaction conditions and
  - (d) wherein the second stage catalyst is at least as active for CO conversion to C₂+ hydrocarbons as the first stage catalyst at second stage reaction pressure.
112. Iglesia, E., H. Vroman, S. Soled, J. Baumgartner and R. A. Fiato; Selective catalysts and their preparation for catalytic hydrocarbon synthesis; U.S. Patent 5,036,032, July 30, 1991. **Claim 1:** A method for preparing a supported cobalt catalyst particle which comprises: (a) contacting a support particle with a molten cobalt salt, for a period sufficient to impregnate substantially all of the molten cobalt salt on the support to a depth of less than about 200 μm; (b) drying the supported cobalt salt obtained in step (a); and (c) reducing the cobalt of the supported cobalt salt in step (b) to metallic cobalt by heating the salt in the presence of H₂, wherein the heating is conducted at a rate of less than about 1°C/min up to a maximum temperature ranging from about 200°C to about 500°C to produce a supported cobalt catalyst particle.
113. Hsu, E. C. and J. L. Robbins; Catalyst pretreatment method; U.S. Patent 5,070,064, Dec. 3, 1991. **Claim 1:** A liquid phase method for removing sub-1 micron particles adhering to catalyst particles the catalyst containing a Group VIII metal supported on an inorganic refractory oxide as a result of preparation of the

catalyst which comprises: (a) dispersing the catalyst particles to which the sub-1 micron particles adhere within a liquid comprising a FT; (b) agitating the dispersion and separating the sub-1 micron particles from the catalyst particles, and concentrating the sub-1 micron particles in the liquid phase; and (c) separating the sub-1 micron containing liquid phase from the particulate material.

114. Mauldin, C. H. and K. L. Riley; Titania catalysts,. their preparation, and use in Fischer-Tropsch synthesis; U.S. Patent 5,140,050, Aug. 18, 1992. **Claim 1:** A process for the conversion of synthesis gas to hydrocarbons at high activity which comprises contacting at reaction conditions a feed comprised of an admixture of carbon monoxide and hydrogen, in H₂:CO molar ratio equal to or greater than 0.5:1 at pressure greater than or equal to 80 psig, over a catalyst composition comprised of a catalytically effective amount of a Group VIII non-noble metal catalytically active for the conversion of synthesis gas to hydrocarbons dispersed upon a titania support in which there is incorporated from about 0.1% to about 10% of an inorganic oxide binder selected from the group consisting of alumina, and zirconia based on the weight of the titania-binder to support to provide a titania-binder support having a pore volume ranging from about 0.2 cc/g to about 0.55 cc/g and surface area ranging from about 8 m²/g to about 70 m²/g.
115. Soled, S. L., G. B. McVicker and W. E. Gates; Metal on rare earth modified silica alumina as hydrocarbon conversion catalyst; U.S. 5,248,409, Sept. 28, 1993. **Claim 1:** A catalytic hydroconversion process which includes hydroisomerization of at least a feedstream comprising: contacting and feedstream with a catalyst composition comprising an amorphous silica-alumina support having at least about 50 wt. % silica, a rare earth oxide, and a metal selected from the group consisting of Group VIII noble metals, rhenium, and mixtures thereof.
116. Herbolzheimer, E. and E. Iglesia; Slurry bubble column; U.S. Patent 5,348,982, Sept. 20, 1994. **Claim 1:** A method for optimally operating a large diameter three phase (gas, liquid, solid) slurry bubble column having a diameter greater than 15 cm for FT synthesis over a supported cobalt catalyst in which solid particles are fluidized in the liquid phase by bubbles of the gas phase, comprising: (a) injecting the gas phase into said column at an average gas velocity along said column, U_g>2 cm/sec, such that the flow regime is in the substantial absence of slug flow; (b) fluidizing the solid supported cobalt catalyst particles of average diameter, d_p>5 :m, to the height, H>3m, of the expanded liquid in the column by operating with a catalyst settling velocity, U_s, and dispersion coefficient, D, such that

$$0.5 (U_s - U_L) \leq \frac{D}{H}, \text{ where } H > 3m$$

where

$$U_s = \frac{1}{18} d_p^2 \frac{\rho_s - \rho_l}{\mu} g f(C_p), \text{ where } d_p > 5 \mu m$$

and (c) maintaining plug flow in said column by operating with a gas phase velocity, U_g , expanded liquid height, H , and dispersion coefficient, D , such that $U_g \geq 0.2 D/H$, where $H > 3m$, $U_g > 2$ cm/sec, wherein D_s = effective density of the particles; D_l = density of the liquid; η = viscosity of the liquid; $f(C_p)$ = hindered settling function; ϕ = volume fraction of solids in the slurry (liquid plus solids); U_L = liquid velocity along the column; H = height of the expanded liquid in said reactor; g = gravitational constant; d_p = diameter of particles; m = meters.

117. Agesteguia, C. R., S. L. Soled and S. Miseo; Catalysts for iso-alcohol synthesis from $CO + H_2$, U.S 5,387,570, Feb. 7, 1995. **Claim 1:** A catalyst composition consisting essentially of a solid solution or a coprecipitated mixture of a first oxide and a second oxide, wherein said first oxide is selected from the group consisting of yttria, rare earth oxides and mixtures thereof, and wherein said second oxide is a Group IIA oxide and a Group IB metal.
118. Clavenna, L. R., S. M. Davis, R. A. Fiato and G. R. Say; Structurally modified alumina supports, and heat transfer solids for high temperature fluidized bed reactions; U.S. 5,395,406, March 7, 1995. **Claim 1:** A composition of matter which comprises: a support components comprising particulate alpha alumina solids of fluidizable particle size of 30-150 microns modified by compositing a metal therewith to form particles represented by formulas (1) and (2), a composite particle being represented by formula (1), as follows;

with the core of the particle being represented by formula (2), as follows:

where in formulas (1) and (2), M is a Group IIA metal, x is a number ranging from about 0.01 to about 0.4 and is representative of the number of moles of the metal M per mole of Al_2O_3 , y is a number equal to or greater than zero, and x is greater than y .

119. Pruett, R. L. and J. S. Bradley; Transition metal bimetallic clusters of ruthenium with thallium, indium and gallium, U.S. 4,360,475, Nov. 23, 1982. **Claim 1:** A composition of matter comprising a bimetallic cluster compound of the formula $[M]_n[(Ru_6C-(CO)_{16})_2L]$ where M is alkali metal cation, alkaline earth metal cation, $N(RN)4+$, $P(RN)4+$ or $As(R^0)4+$ where RN is C_1 - C_{20} aliphatic, C_3 - C_8 cycloaliphatic, C_7 - C_{14} aralkyl or C_6 - C_{10} aryl, n is a number which satisfies valence requirements and L is Tl , In or Ga .
120. Iglesia, E., S. L. Soled and J. E. Baumgartner; Selective fixed-bed Fischer-Tropsch synthesis with high surface area Cu and K promoted, iron/manganese spinels; U.S. 5,118,715, June 2, 1992. **Claim 1:** A hydrocarbon synthesis process for preparing a product containing C_5+ hydrocarbons and less than about 30% CO_2 comprising contacting in a fixed-bed a pelletized catalyst composition

wherein the particle size is greater than about 200 microns average diameter, at a temperature of 200-240°C, the catalyst comprising at least one unsupported, single phase, iron-manganese spinel dual promoted with both copper and a Group IA or IIA metal, said spinel exhibiting a single phase being isostructural with Fe_3O_4 as determined by powder X-ray diffractometry, and possessing a BET surface area greater than 30 m^2/g and an Fe:Mn atomic ratio of at least 2/1, with a mixture of CO and hydrogen under conditions of pressure, space velocity, and elevated temperature for a time sufficient to produce said C_5+ hydrocarbons.

121. Behrmann, W. C., C. H. Mauldin and K. B. Arcuri; Cobalt-titania catalysts. Process utilizing these catalysts for the preparation of hydrocarbons from synthesis gas, and process for the preparation of said catalysts (C-2448); U.S. 5,128,377, July 7, 1992. **Claim 1:** A process useful for the conversion of synthesis gas to liquid hydrocarbons, which comprises contacting at reaction conditions a feed comprising carbon monoxide and hydrogen, in H_2 :CO molar ratio equal to or greater than about 0.5:1 at total pressure equal to or greater than about 80 psig, over a catalyst composition which comprises cobalt dispersed and impregnated as a catalytically active layer upon the surface of a support containing at least about 80 wt% titania ranging in average thickness from about 0.02 mm to about 0.20 mm, with a cobalt loading of about 0.04 g/cc to about 0.15 g/cc, calculated as metallic cobalt per packed bulk volume of catalyst and with a productivity and methane selectivity at 200°C of at least 150 hr^{-1} and no more than 10 mole%, respectively.

122. Say, G. R., J. H. Taylor, D. C. Long and R. A. Fiato; Synthesis gas generation of startup process (C-2556); U.S. 5,143,647, Sept. 1, 1992. **Claim 1:** A method for starting up a fluidized bed or spouted bed steam reforming partial oxidation process for converting a feed gas comprising methane to a product comprising hydrogen and carbon monoxide and unconnected methane which comprises the sequential steps of: (a) heating to reaction temperature the fluidized bed or spouted bed comprised of essentially inert particles, in the presence of oxygen, in an oxidizing atmosphere, and in the substantial absence of a reforming catalyst; (b) converting to a reducing atmosphere; and (c) introducing into the fluidized or spouted bed sufficient Group VIII metal containing catalyst and converting, in the presence of oxygen, the feed gas to the product.

123. Soled, S. L., E. Iglesia and R. A. Fiato; Copper promoted cobalt-manganese spinel catalyst and method for making the catalyst for Fischer-Tropsch synthesis; U.S. 5,162,284, Nov. 10, 1992. **Claim 1:** A composition of matter comprising a copper promoted cobalt-manganese spinel, the spinel having the formula: $\text{Co}_{3-x}\text{Mn}_x\text{O}_4$, where x is from about 0.5 to about 1.2.

124. Soled, S. L., S. Miseo, E. Iglesia and R. A. Fiato; Iron-zinc catalysts for the conversion of synthesis gas to alpha-olefins; U.S. 5,185,378, Feb. 9, 1993. **Claim 1:** A process for preparing a liquid product containing olefins and paraffins wherein the olefin/paraffin ratio is at least about 2.5/1, and the C_5+ / C_4 -ratio is at least about 4.5/1 which comprises reacting in a slurry liquid, at suitable reaction

conditions, hydrogen and carbon monoxide in the presence of a catalyst comprising: iron, zinc, copper, an alkali metal selected from the group consisting of potassium, rubidium, cesium, and mixtures thereof, wherein the iron:zinc atomic ratio is at least a 5:1, and the alkali:copper atomic ratio is at least 2:1.

125. Soled, S. L., E. Iglesia and R. A. Fiato; Substituted cobalt catalysts for Fischer-Tropsch synthesis; U.S. 5,248,701, Sept. 28, 1993. **Claim 1:** A FT process for the conversion of synthesis gas to hydrocarbons which comprises activating a copper promoted, cobalt-manganese spinel catalyst having the formula $\text{Co}_3\text{Mn}_x\text{O}_4$, where x is from about 0.5 to about 1.2 by contacting the catalyst with a reducing atmosphere and contacting the activated catalyst in a reactor with hydrogen/carbon monoxide synthesis gas.
126. Chang, M. and C. A. Coulaloglou; Enhanced catalyst mixing in slurry bubble columns (OP-3723); U.S. 5,252,613, Oct. 12, 1993. **Claim 1:** A method for improving the axial distribution of catalyst in a hydrocarbon synthesis slurry bubble column which uses rising synthesis gas introduced by means of synthesis gas distribution means located at the bottom of said column to provide the majority of the energy used in distributing catalyst in said column, the improvement in axial distribution of catalyst being achieved by using a secondary fluid introduction means in said slurry bubble column at a location above the synthesis gas distribution means located at the bottom of said column to introduce a secondary fluid stream into said column.
127. Hsia, S. J.; External catalyst rejuvenation system for the hydrocarbon synthesis process; U.S. 5,260,239, Nov. 9, 1993. **Claim 1:** A process for practicing catalytic hydrocarbon synthesis and reactivation rejuvenation of deactivated hydrocarbon synthesis catalyst on a continuous basis, said process comprising combining catalyst and synthesis feed and hydrocarbon liquid in a hydrocarbon synthesis first vessel means to produce a reactor slurry comprising catalyst, synthesis feed and synthesis product, collecting deactivated catalyst from the top of the reactor slurry by means of a first downcomer-conduit means the top of which is fitted with gas disentrainment means and which is located just below the top surface of the reactor slurry, passing the deactivated catalyst down the first downcomer-conduit means from the top of the first vessel means to the bottom of a reactivation-rejuvenation second vessel means, said second vessel means having rejuvenating gas introduction means located at its bottom, forming a reactivating slurry of catalyst in reaction product and rejuvenating gas, wherein the deactivated catalyst is reactivated-rejuvenated in said second vessel means, collecting reactivated-rejuvenated catalyst from the top of the reactivating slurry by means of a second downcomer-conduit means the top of which is fitted with gas disentrainment means and which is located just below the top surface of the reactivation slurry and passing the reactivated-rejuvenated catalyst down the second downcomer-conduit means from the top of the second vessel means to the bottom of the first vessel means, all catalyst downward flows on both the first and second downcomer means occurring solely under the influence of gravity.

128. Pedrick, L. E., C. H. Mauldin and W. C. Behrmann; Draft tube for catalyst rejuvenation and distribution; U.S. 5,268,344, Dec. 7, 1993. **Claim 1:** A method for rejuvenating reversibly deactivated particulate hydrocarbon synthesis catalyst in a slurry phase reactor, said method comprising the use of substantially vertical draft tube means, open at both ends, fully immersed in the slurry containing the catalyst and injecting a hydrogen containing gas at or substantially near the bottom of said draft tube means thereby lifting catalyst in slurry from the bottom of the slurry phase reactor into and through the open bottom end of the draft tube means, rejuvenating catalyst in the presence of said hydrogen containing gas in the vertical draft tube means and ejecting the rejuvenated catalyst into the top of the slurry phase in the slurry phase reactor through the open top of the draft tube means.
129. Mitchell, W. N.; Rejuvenation of hydrocarbon synthesis catalyst; U.S. 5,283,216, Feb. 1, 1994. **Claim 1:** A method for rejuvenating a partially deactivated, Group VIII metal containing Fischer-Tropsch catalyst having an initial catalyst activity which comprises: suspending the catalyst in slurry liquid hydrocarbons and treating the suspended catalyst with hydrogen or a hydrogen containing gas at elevated temperatures and pressures and recovering a substantial portion of the metal catalyst activity.
130. Mitchell, W. N.; Activation of hydrocarbon synthesis catalyst; U.S. 5,292,705, March 8, 1994. **Claim 1:** A method for activating an essentially fresh, reduced cobalt containing Fischer-Tropsch catalyst which comprises treating the catalyst with hydrogen or a hydrogen containing gas in the presence of hydrocarbon liquids for a period sufficient to increase substantially the initial catalyst productivity.
131. Chang, M.; Enhanced gas separation for bubble column draft tubes; U.S. 5,332,552, July 26, 1994. **Claim 1:** A slurry bubble column reactor comprising a double walled vessel defined by an inner vessel wall having a peripheral circumferential top rim and a bottom edge, and an outer main containment vessel wall surrounding said inner vessel wall, said outer main containment vessel having a top and a bottom, and wherein the inner vessel wall and the outer vessel wall are substantially co-axial and have a space between them forming an annulus between said respective walls, the outer main containment vessel wall having a synthesis gas inlet means at the bottom, gas outlet means and product recovery means at the top, and a floor above the gas inlet means which floor is fitted with gas distribution means, the inner vessel wall serving as a main reactor zone, the peripheral circumferential top rim of the inner vessel wall having attached to it an inverted channel having an apex and two edges, the point of attachment of the inverted channel to the inner wall being along a first one of said two edges of said inverted channel, a second of said two edges of said inverted channel extending over the main reaction zone thereby creating a gas space within its inverted contour and which inverted channel has a gas vent extending out of, and upwardly from, said inverted channel, and having a liquid by-pass pipe extending from a point on one side of the inverted channel below the apex

of said inverted channel and between said apex and the edge of attachment to the inner vessel wall, to under said top rim of said inner vessel wall and which by-pass pipe empties into the annulus, and liquid exit means at the bottom of the annulus defined by openings in the bottom edge of the interior vessel wall and above the gas distributor means of the main containment vessel.

132. Clavenna, L. R., S. M. Davis, G. R. Say and R. A. Fiato; Synthesis gas from particulate catalysts, and admixtures of particulate catalysts and heat transfer solids; U.S. 5,348,717, Sept. 20, 1994. **Claim 1:** In a process for the production of hydrogen and carbon monoxide from a low molecular weight hydrocarbon by contact with a fluidized bed of catalyst at elevated temperature in the presence of oxygen, or both steam and oxygen, the improvement wherein the fluidizing bed is comprised of an admixture of a particulate consisting essentially of a non-leachable barium hexaaluminate solids of fluidizable particle diameter in concentration ranging from about 10 percent to about 99.9 percent, based on the weight of the admixture, and a catalyst comprised of a carrier component composited with a metal, or metals, component catalytic for the production of hydrogen and carbon monoxide from low molecular weight hydrocarbons when contacted with a fluidized bed of the catalyst, in concentration ranging from about 0.1 percent to about 90 percent, based on the weight of the admixture.
133. Clavenna, L. R., S. M. Davis and B. E. Beasley; Process for the reactivation of nickel-alumina catalysts; U.S. 5,356,845, Oct. 18, 1994. **Claim 1:** In a process for the production of hydrogen and carbon monoxide from a low molecular weight hydrocarbon by contact with a fluidized bed of nickel-on-alumina catalyst at elevated temperature in the presence of steam and oxygen, in a reaction zone operated in a net reducing atmosphere, the steps comprising: withdrawing a portion of said catalyst and contacting said catalyst with an oxygen-containing gas at a temperature elevated sufficiently to convert the nickel component of said catalyst to nickel aluminate, and disperse said nickel aluminate within the alumina support, without sintering and alumina support; and reducing said catalyst after contact with the oxygen-containing gas to the reaction zone to reduce the nickel aluminate component of the catalyst, and increase the activity of the catalyst vis-a-vis that of the catalyst initially withdrawn from the reaction zone.
134. Davis, S. M., L. R. Clavenna, G. R. Say and R. A. Fiato; High surface purity heat transfer solids for high temperature fluidized bed reactions; U.S. 5,360,778, Nov. 1, 1994. **Claim 1:** In a process for the preparation of a particulate heat transfer solid characterized as particulate refractory inorganic oxide solids containing silicon, or boron, or both silicon and boron impurities, the steps comprising: contracting, and treating, said particulate refractory inorganic oxide solids containing silicon in concentration no greater than about 0.5%, based on the total weight of the solids, and boron in concentration no greater than about 500 parts, per million parts by weight total solids, with an acid sufficient to reduce the concentration of silicon and boron in the outer peripheral surface layer of the

particles to no greater than about 5 atom percent silicon and boron, based on the total number of cations within said outer peripheral surface layer.

135. Behrmann, W. C., C. H. Mauldin and L. E. Pedrick; Hydrocarbon synthesis reaction employing vertical downcomer with gas disengaging means; U.S. 5,382,748, Jan. 17, 1995. **Claim 1:** A method for uniformly redistributing particulate catalyst in a slurry phase reactor, said method comprising using a substantially vertical conduit means open at both ends, fully submerged in the slurry of the slurry phase reactor, the bottom end of the substantially vertical conduit means is near the bottom of the slurry phase reactor and the top of the conduit means is topped by gas disengaging means which are below the top surface of the slurry in the slurry phase reactor and wherein the bottom of the substantially vertical conduit means is shielded by a baffle means which diverts gases rising from the bottom of the slurry phase reactor from entering into the bottom of the substantially vertical conduit whereby catalyst in slurry which passes down the substantially vertical conduit and is ejected from the bottom of said conduit near the bottom of the slurry phase reactor.
136. Koros, R. M., Bubble column, tube side slurry process and apparatus; U.S. 5,384,336, Jan 24, 1995. **Claim 1:** A hydrocarbon synthesis process comprising reacting a gaseous mixture of hydrogen and carbon monoxide at a pressure of 1 to 100 atmospheres and a temperature of about 175°C to about 400°C in the presence of a hydrocarbon synthesis catalyst dispersed in a liquid thereby forming a slurry liquid, wherein the catalyst dispersion is disposed in a plurality of vertically arranged elongated reaction tubes having an L/D (length/diameter) of at least about 10, each tube being surrounded by a common heat transfer medium disposed within the shell of a shell and tube reactor, the heat transfer medium not being in fluid communication with the slurry liquid.
137. Mitchell, W. N.; Activation of hydrocarbon synthesis catalyst; U.S. 5,389,690, Feb. 14, 1995. **Claim 1:** A FT process which comprises activating an essentially fresh, reduced cobalt containing FT catalyst with hydrogen or a hydrogen containing gas, the catalyst being dispersed in hydrocarbon liquids and subsequently using the catalyst in a FT process at FT reaction conditions.
138. Soled, S. L., E. Iglesia, R. A. Fiato and G. B. Ansell; Method for stabilizing titania supported cobalt catalyst; U.S. 5,397,806, March 14, 1995. **Claim 1:** In a FT process, under FT reaction conditions, including contacting with a feedstream comprising a CO and H₂ reaction mixture, a 400-750°C regeneration stable catalyst composition comprising cobalt on a substituted ternary metal oxide of titania having the general formula Co/Ti_{1-x}M_xO₂ wherein x is from 0.01 to 0.14 and M is selected from the group consisting of silicon, zirconium and tantalum, wherein the titania is an anatase polymorph.
139. Stark, T. M.; Pentane energy transfer medium in gas conversion; U.S. 5,409,960, April 25, 1995. **Claim 1:** A method for removing heat from a slurry FT hydrocarbon synthesis process reaction zone which comprises passing a cooling

medium comprising a C₄-C₁₀ normal, iso- or cyclic paraffin liquid in cooling tubes in indirect heat exchange through the slurry reaction zone, thereby vaporizing the cooling medium at its boiling point, the cooling medium being inert for FT processes, condensable, and vaporizing at a pressure greater than the pressure in the reaction zone, and recovering the vaporized cooling medium heat.

140. Wittenbrink, R. J., S. M. Davis and K. L. Riley; Supported Ni-Cu hydroconversion catalyst; Int. Pub. No. WO 97/03750, Feb. 6, 1997. **Claim 1:** A hydroconversion catalyst comprising nickel in an amount of less than about 15 wt.% catalyst and copper in a copper:nickel ratio of less than about 1:2 supported on an amorphous silica-alumina carrier having less than about 30 wt.% alumina, the carrier having a surface area of greater than about 200 m²/gm and a pore volume of less than about 1.0 mL/gm.
141. Davis, S. M. and D. F. Ryan; Distillate fuel production from Fischer-Tropsch wax; U.S. 5,378,348, Jan. 3, 1995. **Claim 1:** A process for producing middle distillate transportation fuel components from the waxy product of a hydrocarbon synthesis process which comprises: (a) separating the waxy product into a heavier fraction and at least one lighter fraction; (b) catalytically isomerizing the heavier fraction in the presence of hydrogen and recovering products with improved cold flow properties; (c) catalytically hydrotreating the lighter fraction and removing hetero atom compounds therefrom; (d) catalytically isomerizing the product of step (c) to produce jet fuel component having a freeze point of -30°F or lower.
144. Behrmann, W. C., K. B. Areuri and C. H. Mauldin; Surface supported cobalt catalysts, process utilizing these catalysts for the preparation of hydrocarbons from synthesis gas and process for the preparation of said catalysts; U.S. Patent 5,545,674, August 13, 1996. **Claim 1:** A process useful for the conversion of synthesis gas to liquid hydrocarbons less than about 10 mole% methane which comprises contacting at reaction conditions a feed comprised of carbon monoxide and hydrogen, in H₂:CO molar ratio equal to or greater than about 0.5:1 at total pressure equal to or greater than about 80 psig, over a catalyst composition having a productivity of at least 150 hr⁻¹ at 200°C and which comprises cobalt dispersed as a catalytically active layer upon the outer surface of an inorganic oxide support of a thickness of less than about 200 microns, with the loading of cobalt at least about 0.04 g/cc in said catalytically active layer, calculated as metallic cobalt per packed bulk volume of catalyst.
145. Davis, S. M., L. R. Clavenna, G. R. Say and R. A. Fiato; High surface purity heat transfer solids for high temperature fluidized bed reactions; U. S. Patent 5,496,531, March 5, 1996. **Claim 1:** In a process for the production of hydrogen and carbon monoxide from a low molecular weight hydrocarbon by contact with a fluidized bed constituted of a catalyst and particulate alpha alumina containing both silicon and boron impurities, at high temperature in the presence of steam, or oxygen, or both steam and oxygen, the improvement wherein the alpha alumina is comprised of particles of alpha alumina the outer peripheral surface

layer of which contains no greater than about 5 atom percent silicon and boron, based on the total number of cations within said outer peripheral surface layer, thereby improving resistance to sintering and agglomeration of the fluidized bed, said particles being produced by acid washing of the alpha alumina.

148. Beadle, S. W., W. H. Summerlin and E. T. A. Van Driessche; Airless cobalt demetalling in the cobalt flash combination catalyst cycle; U.S. Patent 5,410,090, April 25, 1995. **Claim 1:** A method for removing cobalt values from the crude product of a cobalt-catalyzed hydroformylation reaction formed from an olefinic feedstock, said crude product containing cobalt compounds in addition to an organic hydroformylation reaction product, which comprises: (a) contacting said crude product with an organic acid and water, in the absence of any oxygen-containing gases, thereby producing a substantially cobalt-free organic hydroformylation reaction product and a water soluble cobaltous salt aqueous product; (b) separating said substantially cobalt-free crude product from said water soluble cobaltous salt aqueous product; (c) diverting said substantially cobalt-free organic hydroformylation reaction product for further downstream treatment such as distillation or hydrogenation; (d) concentrating said water soluble cobaltous salt aqueous product thereby producing a concentrated aqueous solution of cobaltous salt and a substantially cobalt-free water containing said organic acid, whereby said concentrated aqueous solution of cobaltous salt is separated from said substantially cobalt-free water containing said organic acid; (e) recycling said substantially cobalt-free water containing said organic acid to step (a); (f) contacting said concentrated aqueous solution of cobaltous salt with an alcohol stream and synthesis gas, and passing this mixture to a preformer reactor where said concentrated aqueous solution of cobaltous salt is converted to a cobalt carbonyl; (g) contacting said cobalt carbonyl with a stream of stripping gas to entrain volatile cobalt compounds in said stripping gas and to generate as bottoms alcohol products and dissolved cobaltous salts, whereby said entrained volatile cobalt compounds are taken out overhead and the alcohol products and dissolved cobaltous salts are taken out as bottoms; (h) separating said alcohol products of step (g) from said dissolved cobaltous salts; (i) recycling said alcohol products from step (h) to step (f); (j) recycling said dissolved cobaltous salts from step (h) to step (a); and (k) contacting said volatile cobalt compounds from step (g) with said olefinic feedstock, whereby said volatile cobalt compounds are absorbed into said olefinic feedstock.
149. Beadle, S. W. and C. A. Poulin; Use of stripper reactor reflux as an initiator for preforming reaction of cobaltous salts to cobalt carbonyls, U.S. Patent 5,457,240, October 10, 1995. **Claim 1:** A method for producing higher aldehydes and higher alcohols which comprises: (a) hydroformylating an olefinic feedstock with synthesis gas in the presence of a cobalt-containing catalyst to form a crude product containing higher aldehyde, higher alcohol, secondary products and dissolved cobalt catalysts; (b) contacting said crude product with an oxygen-containing gas, an organic acid and water, thereby producing a substantially cobalt-free organic hydroformylation reaction product and a water soluble cobaltous salt aqueous product; (c) separating said substantially cobalt-free

crude product from said water soluble cobaltous salt aqueous product; (d) concentrating said water soluble cobaltous salt aqueous product, thereby producing a concentrated aqueous solution of cobaltous salt and a substantially cobalt-free aqueous solution; (e) separating said concentrated aqueous solution of cobaltous salt from said substantially cobalt-free aqueous solution; (f) contacting said concentrated aqueous solution of cobaltous salt with an alcohol and synthesis gas, and passing this mixture to a preformer reactor where said concentrated solution of cobaltous salt is converted to a cobalt carbonyl; (g) passing said cobalt carbonyl to a stripping reactor wherein said cobalt carbonyl is contacted with a stream of stripping gas to entrain volatile cobalt compounds in said stripping gas; whereby said entrained volatile cobalt compounds are taken overhead; and (h) recycling at least a portion of said entrained volatile cobalt compounds taken overhead in step (g) to said preformer reactor.

150. Vanderspurt, T. H. and J.-L. Kao; Noble metal large pore zeolite catalyst for methanol-ethanol coupling; U.S. Patent 5,493,064, February 20, 1996. **Claim 1:** An alcohol coupling process, comprising: contacting a vaporized mixture of starting alcohols of methanol in combination with a second alcohol selected from the group consisting of ethanol, n-propanol, and mixtures thereof with a carrier gas containing CO and H₂ in the presence of an alumina-bound highly dispersed metallic Pd-loaded, alkali metal cation exchanged L zeolite wherein the zeolite and alumina have an essential absence of strongly acidic catalytic sites and wherein said contacting is carried out at a temperature and partial pressure of CO and H of from about 300 to 400°C and from 3000 kPa to about 15,000 kPa at a sufficient pressure to minimize the decomposition of methanol to CO and H₂ and at a space velocity of from about 4000 hr⁻¹ to about 10,000 hr⁻¹ to produce isobutanol and n-propanol in the substantial absence of light gaseous alkanes and C₆₊ oxygenates.
151. Clavenna, L. R., S. M. Davis, R. A. Fiato and G. R. Say; Particulate solids for catalyst supports and heat transfer materials; U. S. Patent 5,395,813, March 7, 1995. **Claim 1:** As a composition, a fluidizable contact mass for the production of hydrogen and carbon monoxide from a low molecular weight hydrocarbon contacted with a fluidized bed of said contact mass at elevated temperature in the presence of steam, or oxygen, or both steam and oxygen, which comprises: an admixture of, a particulate, fluidizable precalcined zirconia heat transfer solid which contains from 0% to about 1% silica, based on the weight of the zirconia, in concentration ranging from about 10% to about 99.9%, based on the total weight of the admixture, wherein the zirconia component of the admixture has a Davison Index measurement of not greater than about 15, and a catalyst constituted of a refractory inorganic oxide support composited with a metal, or metals, component catalytic for the production of hydrogen and carbon monoxide from low molecular weight hydrocarbons, of fluidizable particle size in concentration ranging from about 0.1% to about 90%, based on the total weight of the admixture.

160. Davis, S. M., L. R. Clavenna, R. A. Fiato and G. R. Say; High performance alumina heat transfer solids for high temperature fluidized bed synthesis gas reactions; U.S. 5,360,777, Nov. 1, 1994. **Claim 1:** As a composition of matter, a heat transfer solid resistant to sintering and agglomeration for admixture with a catalyst to form a fluidized bed useful in the conversion of a low molecular weight hydrocarbon to hydrogen and carbon monoxide on contact therewith at high temperature in the presence of steam, or oxygen, or both steam and oxygen which comprises: alumina solids particles: (i) the outer peripheral surface layer of which contains no greater than about 5 atom percent silicon and boron, based on the total number of aluminum cations within said outer peripheral surface layer, while the bulk concentration of silicon in the particles does not exceed about 0.5%, based on the weight of the alumina solids, and the bulk concentration of boron in the particles does not exceed about 500 ppm, based on the weight of the alumina solids; (ii) the outer peripheral surface layer of which contains no more than 20 atom percent impurities based on the sum-total concentration of sodium, iron, calcium, and titanium as impurities; (iii) the tapped bulk density of the particles ranges from about 1.2 g/cc to about 2.5 g/cc; (iv) the Davison Attrition Index of the solids particles is no greater than about 12; and the sum total effect of these relationships between surface purity particle density, and attrition resistance is such as to provide a performance index categorized by the formula:

$$\text{Performance Index} = \frac{1}{(i)x(ii)x(iii)x(iv)} > 20.$$

161. Vanderspurt, T H. and R. J. Koveal; Isoalcohol synthesis; U.S. Patent 5,703,133, Dec. 30, 1997. **Claim 1:** A method for producing isobutanol and methyl butanols from syngas, comprising: (a) contacting a reactant stream containing syngas with a first stage catalyst having alkali promoted La-stabilized, highly dispersed microcrystalline Cu₂O having a particle size of ≤ 6 nm interspersed with metallic copper crystallites having a particle size of ≤ 25 nm, and zinc oxide crystallites having a particle size of ≤ 6 nm in the presence of an alumina structural promoter, wherein on a mol % alkali free metals only basis, Cu is present in from about 45% to about 55%, Zn from about 10% to about 20%, Al from about 10% to about 25%, La from about 5% to about 15% and wherein the alkali is between about 0% to about 1% K and from about 3% to about 6.5% Cs, wherein the first stage catalyst is produced by the process of: coprecipitating at a constant pH of from 0.7 to 11.0 at a temperature of from about 30°C to about 100°C in the essential absence of CO₂ from a solution of soluble metal salts of copper, zinc, lanthanum and aluminum with alkali hydroxide solution selected from the group consisting of LiOH, NaOH, KOH, CsOH and RbOH and mixtures thereof; aging the washed precipitate for from about 1 to 24 hrs at from to 50 to 90°C in the essential absence of CO₂; washing the precipitate in the essential absence of CO₂; drying the washed coprecipitate in air at up to about 120°C; calcining the dried coprecipitate in air for greater than 3 hrs at a temperature of from about 300 to 700°C; contacting the calcined coprecipitate with from 0.01% to 0.91% K and 3% to 6.5% Cs to form a promoted catalyst; drying the promoted catalyst at up to

120°C; recalcining the promoted catalyst at from about 300 to 700°C to produce a catalyst precursor containing highly dispersed CuO crystallites of up to about 10 nm; activating the promoted catalyst in flowing hydrogen for at least 1 hr at 175 to 185°C then for at least 1 hr at 250 to 270°C; wherein said contacting of reactant stream and first stage catalyst is carried out at a pressure of from about 850 psi (5,840 kPa) to about 1500 psi (10,310 kPa) a temperature of from about 240°C to about 340°C for a time sufficient to produce a product stream containing methanol, ethanol, propanol, and methyl butanols; (b) contacting methanol, ethanol and propanol from step (a) with a second stage catalyst having at least a first phase of mixed oxide crystallite containing from about 60 to 74 atomic % zirconium, from about 21 to 31 atomic % manganese and from about 5 to 9 atomic % zinc, and less than about 1 atomic % alkali, a second phase of zirconium doped hetaerolite containing from about 65 to 69 atomic % manganese, about 31 to 35 atomic % zinc, 0.5 to 5 atomic % zirconium, and optionally a trace atomic % alkali, and a third phase containing from about 20 to 55 atomic % manganese, from about 13 to 55% atomic zinc and 13 to 35 atomic % zirconium wherein the first phase mixed oxide crystallites have a zirconium oxide like structure have a particle size of at least about 40 D to about 100 D, the second phase of at least about 200 D to greater than about 2000 D and the third phase of at least about 1000 D to greater than 400 D at a pressure of from about 850 psi to about 1500 psi (10,300 kPa) a temperature of from about 340 to about 380°C to produce additional isobutanol and methyl butanols from the methanol, ethanol and propanol and trace ethylene and propylene.

162. Koveal, R. J and T. H. Vanderspurt; Isoalcohol synthesis catalyst; US Patent 5,691,268, Nov. 25, 1997. **Claim 1:** A syngas-to-alcohol catalyst, comprising: highly dispersed, alkali promoted, La stabilized, microcrystalline Cu₂O having a particle size of ≤ 6 nm in the presence of an alumina structural promoter, wherein on a mole % alkali free metals-only basis Cu is present in from 45% to 55%, Zn from 10% to 20%, Al from 10% to 25%, La from 5% to 15%, and wherein the alkali is from 0.01% to 0.91% K and from 3% to 6.5% Cs.
163. Apesteguia, C. R., S L Soled and S. Miseo; Catalysts for iso-alcohol synthesis from CO+H₂; US patent 5,508,246, Apr. 16, 1996. **Claim 1:** A syngas conversion process, having increased selectivity to methanol and isobutanol and conducted under syngas conversion conditions at pressures of about 20 to about 250 atmospheres, comprising contacting a carbon monoxide and hydrogen feedstream with a catalyst composition consisting essentially of a solid solution or a coprecipitated mixture of a first oxide and a second oxide, wherein said first oxide is selected from the group consisting of yttria, rare earth oxides and mixtures thereof and wherein said second oxide is a Group IIA oxide, and a Group IB metal.
164. Vanderspurt, T H., M A Greaney, D PI Leta, R J Koveal, M M Disko, A V Klaus, S K Behal and R. B. Harris; Isobutanol synthesis catalyst; US patent 5,707,920, Jan 13, 1998. **Claim 1:** A catalyst composition, comprising: a noble metal supported on at least a first phase having a poorly crystalline manganese and

zinc coped zirconium oxide phase containing about 71 to about 91 atomic % zirconium, about 10 to about 16 atomic % manganese and about 4 to about 8 atomic % zinc and a second phase of irregularly shaped hetaerolite crystals containing about 65 to about 69 atomic % manganese, about 31 to about 35 atomic % zinc and 0 to about 5 atomic % zirconium embedded in the first phase.

165. Herskowitz, M., Method for hydrocarbon synthesis reactions; US patent 5,652,193, July 29, 1997. **Claim 1:** A method for making a CO hydrogenation catalyst wherein said catalyst includes a metal selected from the group consisting of cobalt and ruthenium deposited in a porous, inorganic, refractory oxide support, said catalyst having said metal located in a rim on the outer surface of said support, said method comprising: (a) determining the rim thickness by: (i) determining intrinsic kinetic rate data including the intrinsic rate of reaction of carbon monoxide hydrogenation and the rate of CO conversion to methane for said catalyst; (ii) determining the thickness of said rim by relating the rates of diffusion of said carbon monoxide and said hydrogen to the intrinsic rate of reaction in said rim for a support geometry selected from the group consisting of a sphere, a ring, a cylinder, and a semi-circle and combinations thereof, such that said rim thickness optimizes both the rate of carbon monoxide hydrogenation and the reduction in methane selectivity; and (b) making a catalyst having a rim thickness determined in step (a).

166. Davis, S. M. and J. W. Johnson; Process for hydroisomerization of waxy hydrocarbon feeds over a slurried catalyst; EP 0 753 563 A1; 04/07/96. **Claim 1:** A hydroisomerization process for the conversion of a C₅₊ paraffinic feedstock to middle distillates which comprises contacting and reacting at hydroisomerization reaction conditions said C₅₊ paraffinic feedstock, and hydrogen, with a catalyst comprising a Group IB metal component, or a Group VIB metal component, or a Group VII metal component or a mixture of two or more of said metal components, supported on an acidic particulate solid, of average particle diameter in a range of from about 30 microns (30 :m) to about 150 microns (150 :m), dispersed in a paraffinic liquid hydrocarbon.

167. Wittenbrink, R. J., R. F. Bauman, P. J. Berlowitz, and B. R. Cook; Synthetic diesel fuel and process for its production; WO 97/14769, 24 April 1997. **Claim 1:** A material useful as a fuel heavier than gasoline or as a blending component for a distillate fuel comprising: 1 250-700°F fraction derived from a non-shifting FT catalyst process and containing at least 95 wt.% paraffins with an iso to normal ratio of about 0.3 to 3.0, ≤ 50 ppm (wt.) of sulfur and nitrogen less than about 2 wt.% unsaturates, and about 0.001 to less than 0.3 wt.% oxygen.

168. Wittenbrink, R. J., S. E. Silverberg and D F Ryan; High purity paraffinic solvent compositions, and process for their manufacture; WO 97/21787, 19 June 1997. **Claim 1:** A high purity solvent composition which comprises a mixture of paraffins of carbon number ranging from about C₈ to about C₂₀, has a molar ratio of isoparaffins:n-paraffins ranging from about 0.5:1 to about 9:1 and the

isoparaffins of the mixture contain greater than 50% of the mono-methyl species, based on the total weight of the isoparaffins of the mixture.

169. Stark, T M; Heat removal in gas conversion process, EP appl. 0 614 864 A1, 03/03/94. **Claim 1:** A method for removing heat from a hydrocarbon synthesis process reaction zone, which comprises passing a cooling medium through the reaction zone, in indirect heat exchange therewith, thereby vaporizing the cooling medium; the cooling medium being inert, condensible, and vaporizing at a pressure which is at least as great as the pressure in the reaction zone.
171. Hershkowitz, F. and G. Kiss; Unsaturates recovery and recycle process; U.S. patent 5,516,965, May 14, 1996. **Claim 1:** A process for recovering unreacted acetylene from an effluent stream of a process for synthesizing oxygenated hydrocarbons from unsaturated hydrocarbons, said stream containing unreacted unsaturated hydrocarbons, oxygenated reaction products, and low-boiling gaseous components selected from the group including CO, H₂, CO₂, H₂O, C₁-C₅ alkanes, nitrogen, helium, and argon, comprising: (a) absorbing the unreacted acetylene and the oxygenated hydrocarbons of the synthesis process effluent stream in a solvent wherein said solvent is an acetylene-depleted stream of the oxygenated product of said synthesis process; and (b) stripping the acetylene from the solvent to produce a first stream concentrated in acetylene and a second stream of oxygenated product depleted in acetylene, wherein said acetylene-depleted stream is the absorption solvent and the synthesis process product.
172. Clavenns, L. R., R A Fiato and G. R. Say; Particulate solids for catalyst supports and heat transfer materials, U.S. patent 5,476,877, Dec. 19, 1995. **Claim 1:** In a process for the production of hydrogen and carbon monoxide from a low molecular weight hydrocarbon by contact with a fluidized bed of catalyst at elevated temperature in the presence of steam, or oxygen, or both steam and oxygen, the improvement wherein the fluidized bed is comprised of an admixture of a particulate, fluidizable precalcined zirconia heat transfer solid which contains from about 0% to about 1% silica, based on the weight of the zirconia, in concentration ranging from about 10% to about 99.9%, based on the total weight of the admixture, wherein the zirconia component of the admixture has a Davison Index measurement of not greater than about 15 and a catalyst constituted of a refractory inorganic oxide support composited with a metal, or metals, component catalytic for the production of hydrogen and carbon monoxide from low molecular weight hydrocarbons, of fluidizable particle size in concentration ranging from about 0.1% to about 90%, based on the total weight of the admixture.
173. Herfbolzheimer, E., F J Kaiser, Jr and E. Iglesia; Catalyst fluidization improvements; U.S. patent 5,157,054, Oct. 20, 1992. **Claim 1:** A slurry phase hydrocarbon synthesis process for the conversion of hydrogen and carbon monoxide at reaction conditions to products which comprises: injecting a gas comprising hydrogen and carbon monoxide at or near the bottom of a bubble

column containing a slurry liquid, a catalytically active first solid and at least a second solid, dispersing the solids in the slurry liquid, all of the energy thereof being supplied by the gas, in the absence of liquid product recycle, the amount of the second solid being sufficient to increase the bed height of the first catalytic solid by at least 10%, and recovering liquid product.

174. Long, D. C.; Staged hydrocarbon synthesis process; U.S. patent 5,498,638, March 12, 1996. **Claim 1:** A once through hydrocarbon synthesis process which comprises reacting in a first stage or stages, a feed comprising hydrogen and carbon monoxide, and optionally CO₂, in the presence of a non-shifting hydrocarbon synthesis catalyst containing cobalt or ruthenium, recovering the product therefrom, condensing liquids from the product and reacting the remaining gases in a subsequent stage or stages in the presence of a hydrocarbon synthesis catalyst having shifting activity, and recovering the products therefrom.
175. Long, D. C.; Staged hydrocarbon synthesis process; EP appl. 0 679 620 A2, 26/04/95. **Claim 1:** A substantially once-through hydrocarbon synthesis process which comprises reacting in a first stage or stages, a feed comprising hydrogen and carbon monoxide, and optionally CO₂, in the presence of a non-shifting hydrocarbon synthesis catalyst, recovering the product therefrom, condensing liquids from the product and reacting the remaining gases in a subsequent stage or stages in the presence of a hydrocarbon synthesis catalyst having shifting activity, and recovering the products therefrom.
176. Taylor, J. H., and G. R. Say; Production of synthesis gas via fluidized bed/fixed bed process combination; U.S. patent 5,421,840, June 6, 1995. **Claim 1:** In a process for the production of hydrogen and carbon monoxide, the steps comprising: contacting, in a first reaction zone, low molecular weight hydrocarbons comprising methane, oxygen, and steam, at high temperature in a net reducing atmosphere, with a fluidized bed of catalyst, or catalyst and a solids diluent, to convert from about 85% to about 92% of the hydrocarbons to hydrogen and carbon monoxide and form a reaction mixture of hydrogen, carbon monoxide and unreacted hydrocarbons, oxygen and steam, withdrawing said reaction mixture as an effluent from said first reaction zone, and contacting said effluent, in a second reaction zone, with a fixed bed of catalytic metal solids with a void fraction of at least about 0.9 to convert, sufficient of the unreacted hydrocarbons, oxygen, and steam and increase the hydrocarbon conversion to a level ranging from about 0.5% to about 5% above that obtained in said first reaction zone.

ADDENDUM - EXXON FISCHER-TROPSCH WORK

Fischer Synthesis Process

A patent (A.1), a continuation of four prior applications with the first dated October 3, 1989, claimed a method for hydrocarbon synthesis reactions. This patent relates to the use of a catalyst of the "rim" type, as the terminology is used by Exxon. These are catalysts where the active metal(s) are deposited in the outermost layer of the support particle, and in a manner that the interior of the support particle is essentially devoid of the metal(s). This approach is widely used in the manufacture of auto exhaust catalysts that are shaped into spheres, cylinders, etc. The specific experiments were conducted with a 6 wt.% cobalt and 0.5 wt.% ruthenium on silica or titania support; since the surface area of the catalyst used in the example was reported to be about 20 m²/g it is assumed that the support was titania. The description of the preferred embodiment includes a derivation of the theoretical aspects of the determination of the rim loaded thickness needed to optimize CO conversion and/or minimize methane production. This theory has been included in several of the reviews of Fischer-Tropsch synthesis that have recently been published by Exxon workers. It is surprising that the authors of these reviews are not inventors of this method for hydrocarbon synthesis reactions and that the inventor (M. Herskowitz) is not an author of the review articles.

The outer layer containing the catalytic metal has a thickness determined so as to optimize CO conversion to heavy hydrocarbons so that conversion to methane is maintained at a predetermined level. The inventor maintains that it is not possible to simultaneously maximize CO conversion and minimize methane conversion. However it is possible to define a rim thickness so as to optimize one of these products. The

thickness of the rim-loaded catalyst is determined by relating the rate of diffusion of CO and H₂ to a rate of reaction in the porous inorganic oxide for a predetermined support geometry, partial pressures and temperatures.

The fluxes of the two reactants at steady state must be equal since there is no accumulation; thus,

$$\beta D_{e,CO} [dC_{CO}/d\chi] = D_{e,H} [dC_H/d\chi] \quad [A.1]$$

where the flux is expressed as a product of the effective diffusivity, D_e , and the concentration gradient. β is the stoichiometric coefficient and is equal to 2.07 in the reported work. Since hydrogen diffuses more rapidly than CO, the relative concentration of hydrogen should increase from the surface to the center of the catalyst pellet.

The differential mass balance inside the pores of the catalyst pellet of carbon monoxide, the limiting reactant, is

$$[D_{e,CO} (1/\chi^s)] d/d\chi[\chi^s (dC_{CO}/d\chi)] = \rho_p r_{CO} \quad [A.2]$$

where χ is the radial position measured from the external surface toward the center, ρ_p is the pellet density, C_{CO} is the CO concentration in the liquid-filled pores and r_{CO} is the intrinsic rate of reaction on the active sites. The shape factor, s , is equal to two for a sphere and to unity for a cylinder; the treatment can be extended to other pellet shapes.

The boundary condition on the external surface is:

$$C_{CO} = P_{CO,b}/H_{CO} \quad [A.3]$$

where $P_{CO,b}$ is the CO partial pressure in the bulk gas phase and H_{CO} is the Henry's Law constant. The other boundary condition can be defined for two cases as:

$$\text{inert core} \quad dC_{CO}/d\chi = 0 \quad \chi = \chi_i \quad [A.4]$$

$$\text{hollow core} \quad C_{CO} = P_{CO,b}/H_{CO} \quad \chi = \chi_i \quad [A.5]$$

This derivation assumes that external mass transfer resistance is negligible and that the pellet is isothermal. Experimental data verified that these are valid assumptions.

The intrinsic rate expression (small particle, diffusion free case) for cobalt or ruthenium on titania or silica support is

$$r_{CO} = k_1 \exp(-E_1/RT) [P_{CO}^a P_H^b / (1 + k_2 P_{CO} + k_3 P_H)^c] \quad [A.6]$$

where k_1 , k_2 , k_3 , E_1 , a , b , and c are calculated from experimental rate data. [In this and other Exxon patents there are many typos that are usually obvious but sometimes cause concern. Thus, in the above equation we have modified the equation given in the patent by replacing 1 in the original with a and 2 with c to produce equation [A.6].] The inventor indicates that the kinetic parameter, k_1 , usually depends only on the metal concentration on the support; presumably the dispersion must also be included. The inventor indicates that in certain cases such as cobalt on titania, it is also a function of water partial pressure:

$$k_1 = A[(1 + k_4 P_{H_2O}) / (1 + (k_5 P_{H_2O})^2)] \quad [A.7]$$

where A is the activity of the catalyst.

Henry's Law can be used to express equation [A6] in concentrations of CO and H_2 :

$$C_{CO} = P_{CO}/H_{CO} ; C_H = P_H/H_H \quad [A.8]$$

Integrating equation [A1] allows the expression of the hydrogen concentration in terms of the carbon monoxide concentration:

$$C_H = [P_{H,b}/H_H] - [\beta D_{e,CO}/D_{e,H}][(P_{CO,b}/H_{CO}) - C_{CO}] \quad [A.9]$$

or

$$H_H C_H / P_{H,b} = 1 - \gamma [1 - (H_{CO} C_{CO} / P_{CO,b})] \quad [A.10]$$

where

$$\gamma = (\beta D_{e,CO}/D_{e,H})(H_H/H_{CO})(P_{CO,b}/P_{H,b}) \quad [A.11]$$

Substituting equations [A6] and [A7] into equation [A8] and expressing in dimensional-less form yields

$$\phi = (\chi_s - \chi_c)[\rho k_1 \exp(-E_1/RT) [P_{CO}^a P_H^b / D_{e,CO} (k_2 P_{CO,b})^c]^{1.2} \quad [A.12]$$

The Thiele modulus, ϕ , is the ratio between the maximum rate of reaction and the maximum rate of diffusion. Likewise, γ expresses the ratio between the maximum rate of diffusion of the two reactants; when $\gamma = 1$ the ratio C_{CO}/C_H remains constant and when it is less than one the ratio decreases.

Equation [A.2] is solved to yield the concentration profiles in the pores of the catalyst pellet. This concentration profile is then integrated over the volume of the pellet and this is used to calculate the effectiveness factor which is the ratio of the actual reaction rate (global rate) averaged over the pellet and the maximum reaction rate calculated for the surface conditions:

$$\eta_{CO} = [1/V \int_{VP} r_{CO} dV] / [R_{CO}(P_{HP_{CO}} P_{H_2O})] \quad [A.13]$$

The effectiveness factor for methane can also be obtained in a similar manner using the rate of methane production, r_{CH_4} :

$$\eta_{CH_4} = [1/V \int_{VP} r_{CH_4} dV] / [R_{CH_4}(P_{HP_{CO}} P_{H_2O})] \quad [A.14]$$

and r_{CH_4} is obtained from kinetic measurements:

$$r_{CH_4} = k_4 \exp(-(E_2 - E_1)/RT) [P_H / (1 + k_2 P_{CO} + k_3 P_H)] r_{CO} \quad [A.15]$$

Assuming an isothermal reactor for simplicity, η_{CO} and η_{CH_4} are used in a reactor mass balance to calculate the carbon monoxide conversion and methane selectivity:

$$y_{\text{CO},i}(G_f/M_i)(dX_{\text{CO}}/dZ) = \eta_{\text{CO}} \rho_B r_{\text{CO}} \quad [\text{A.16}]$$

$$y_{\text{CO},i}(G_f/M_i)(dX_{\text{CH}_4}/dZ) = \eta_{\text{CH}_4} \rho_B r_{\text{CH}_4} \quad [\text{A.17}]$$

where $Y_{\text{CO},i}$ is the carbon monoxide mole fraction in the feed, G_f is the mass velocity, M_i is the molecular weight of the feed, ρ_B is the bed density and X_{CO} and X_{CH_4} are the carbon monoxide and methane conversion, respectively.

Using a 6% Co/0.5% Re catalyst of different pellet sizes and a feed with $\text{H}_2/\text{CO} = 2$, the CO conversion and CH_4 selectivity were measured. These conversion data were used to estimate the CO and H_2 diffusivities using the following procedure:

- a. values of $D_{e,\text{CO}}$ and $D_{e,\text{H}}$ were assumed;
- b. effectiveness factors η_{CO} and η_{CH_4} were calculated from equations [A.9] and [A.10] and the solution of equation [A.2] given the inlet conditions of the reactor;
- c. the CO conversion and conversion to methane were calculated by integrating equations [A.16] and [A.17]; since the effectiveness factors are functions of the partial pressures of CO, CH_4 and H_2O they must be recalculated along the length of the reactor taking into account of the changes in the partial pressures;
- d. methane selectivity was calculated from the ratio of conversion to methane, X_{CH_4} and carbon monoxide conversion, X_{CO} ;
- e. the calculated carbon monoxide conversion and the methane selectivity were compared with the experimental values for the various pellet sizes; and
- f. the effective diffusivities are adjusted to give the best fit of the experimental data.

An example of the agreement between the calculated and the experimental data for catalysts with a range of diameters is shown in figure A.1.

In one example the experiments were performed in a 3'x0.5" reactor that was packed with 1 mm diameter spherical particles uniformly loaded with 6%Co-0.5%Re. Data were obtained as the reaction temperature and the H_2/CO ratio were varied and the CO conversion and CH_4 selectivity obtained as described above. When the initial H_2/CO ratio is less than 2, the ratio will decrease along the catalyst bed and, since methane selectivity depends upon this ratio, it will decrease down the bed.

Simulations of carbon monoxide conversion and methane selectivity were made for various thickness of the rim loaded metals. As shown in figure A.2, both conversion and methane selectivity increase with increasing rim thickness. However, the important point is that these two factors increase rapidly from a low to high value and that the rim thickness where this increase occurs is different for the two factors.

In another simulation, the carbon monoxide conversion and methane selectivity were determined for two pellet shapes: ring and cylinder. As shown in figure A.3, the rim thickness needed to obtain the maximum CO conversion and a low methane selectivity depends upon the pellet shape. Thus, the cylindrical shape provides a much greater difference between the rapid increase in the two factors than the ring shape does.

The inventor claims a method for making a catalyst by determining the rim thickness which optimizes both the rate of carbon monoxide hydrogenation and the reduction of methane selectivity.

Long (A.2,A.3) claims a substantially once-through hydrocarbon synthesis process which comprises reacting in a first reactor or stages, a feed comprising

hydrogen and carbon monoxide, and optionally CO₂, in the presence of a non-shifting hydrocarbon synthesis catalyst. The effluent is treated to recover the product from the first reactor by condensing the liquids and then reacting the remaining gases in a subsequent stage or stages in the presence of a hydrocarbon synthesis catalyst having shift activity, producing and recovering additional products.

A basis for this invention is that "The shift reaction can, however, be suppressed if the feed contains higher amounts of CO₂ relative to CO, and CO₂ is known to be added to H₂ + CO synthesis gas feeds for hydrocarbon synthesis. Synthesis gas feeds can contain up to 10% CO₂, that is, about 0.1-10% CO₂." The feed to the first stage(s) has H₂/CO in a 1.5:1 to 1.5:1 mole ratio, preferably 1.9: to 2.3:1, and CO₂ in the range 1.0-10 mole%, preferably 5-10 mole%. This mixture is subjected to synthesis with a non-shifting catalyst, preferably cobalt on alumina, silica or titania (preferred), and preferably promoted by metals as Ru, Rh, Ce or Hf, most particularly Rh (A.4). Conversion of CO in the first stage(s) are preferably at least 90%. Following conversion by the non-shifting catalyst, the liquid products, containing C₅+ hydrocarbons, water, oxygenated compounds and small amounts of dissolved gases.

The feed for the stage 2 reactor(s) with shift catalyst is illustrated in Table A.1. Based on our calculations, the mole fraction of water in the feed is 0.0024 (1.83 mm if operating at 20 atm). For a water-vapor saturated stream, we estimate the temperature of the separation to be -10 to -15°C, a surprisingly low temperature. The gas shown in Table A.1 is fed to a stage 2 reactor(s) where subsequent hydrocarbon synthesis produces a product with an olefin:paraffin ratio of 1.5:1 to 4:1, the lower ratios being favored for higher hydrocarbons and the higher ratios favored for the lower carbon number hydrocarbons. The H₂/CO ratio entering the stage 2 reactor(s) will be

essentially the same as the stage 1 reactor(s) because of the non-shifting character in the stage 1 operations. However, because of the conversion in stage 1 reactor(s), less gas will enter stage 2 reactor(s) with the result that the relative concentration of CO₂ will be higher in stage 2 than in stage 1 reactors. Sufficient hydrogen must be present in the feed to stage 2 reactor(s) to react with both CO and CO₂. Reaction conditions in stage 2 reactor(s) will be similar to those in stage 1 reactor(s); e.g., 10-35 bar, 220-340°, SHSV 200-2000 dry feed (water less than 5 vol% of feed).

Slurry Reactor

Herbolzheimer et al. (A.5) claim the use of a second solid in a slurry phase hydrocarbon synthesis process. A gas is injected at or near the bottom of the bubble column containing a slurry liquid, a catalytically active first solid and at least a second solid. The energy to maintain the dispersion of the solids is supplied by the gas in the absence of liquid recycle. The second solid is added in sufficient quantity to increase the bed height by at least 10%.

The authors state that slurry phase reaction, particularly those occurring in bubble columns, are well-known and do not need to be discussed. In column 6, line 23, the authors state that, "Slurry reactors are well known..." This is surprising since it would appear to imply that at the time of filing this patent [February 25, 1991] the use of slurry reactions are well known and, since bubble column reactors are also well known, only specific improvements to the operation of slurry bubble column reactors should be patentable inventions. Catalyst settling is a problem that can be encountered in bubble column reactors. Particles tend to settle to the bottom because of the influence of gravity. Opposing the settling tendency is the dispersion forces created by the rising

bubbles of gas injected at or near the bottom of the reactor. The balancing effect of these two forces results in an exponential distribution of catalyst solids concentration.

The authors utilize the data employing a dispersion coefficient and the settling velocity. D , the dispersion coefficient, depends on the superficial gas velocity through the system and on the effective diameter of the reactor column. The authors do not define this term in more detail, and presumably are considering the dispersion coefficient for the solids. The settling velocity of the catalyst particles, U_s , is given as

$$U_s = U_o(1 - c)^n \quad [A.18]$$

where

$$U_o = d_p^2(\rho_s - \rho)g/18\mu \quad [\rho_s \text{ is given as } \rho_s \text{ in the patent}] \quad [A.19]$$

where c is the volume fraction of solids in the slurry, d_p is the particle diameter, ρ_s is the density of the solids, g is the gravitational constant, μ is the viscosity of the suspending liquid, and n is a constant ranging from 4 to 8.

In the description, they indicate that most reactors operate in a regime somewhere between plug-flow and fully-backmixed (or CSTR) conditions. A plug-flow condition can be attained by using fixed-bed catalyst or a very large L/d (where L and d are the length and effective diameter of the reactor, respectively). In the plug-flow reactor the concentration (or partial pressure) of hydrogen and carbon monoxide, the reactants for Fischer-Tropsch Synthesis, decrease along the path of reactor flow due to reaction, and this decreases the driving force of the reaction. On the contrary, complete backmixing results in the same concentration of reactants along the entire length of the reactor resulting in a constant driving force and reflects the relatively low driving force at exit conditions.

Productivity is generally favored in plug-flow systems and selectivity is favored in backmixed systems. Later Exxon patents pertain to the operating conditions for plug-flow bubble column slurry reactors .

In the preferred mode for this patent, there is an absence of liquid throughput; thus, in the preferred mode, all of the energy from maintaining solids as a dispersion in the liquid is provided by the injection of gas at or near the bottom of the slurry reactor.

The catalysts utilized in the examples are typical of those described in many Exxon, and other, patents. The preferred catalyst is cobalt supported on titania and promoted with rhenium. The preferred catalyst particle size is in the range of 20 to 100 microns.

The data described in the examples were obtained in a 5 meter tall, non-reactive bubble column with 15 cm internal diameter (i.e., the L/d ratio was greater than 20, corresponding to nearly plug-flow conditions). Nitrogen gas was injected vertically into the column through a half inch hole at the bottom of a conical insert. This cone was used to insure fluidization of all the particles charged to the system. Pressure and temperature were monitored at 1 meter intervals along the column length, and slurry samples were withdrawn at these locations. The slurry liquid was C₂₀-C₄₀ paraffinic wax produced by Fischer-Tropsch synthesis using a cobalt catalyst. The solid was either TiO₂ or glass beads. No liquid was added during the measurements.

The solids distribution of 80 micron glass beads in FT product was determined at a temperature of 400°F (204°C) and 280 psig (for gas velocities below 8 cm/sec) or 150 psig (for gas velocities above 8 cm/sec). The decay length of the particle concentration profile was obtained by taking the slope of a line segment joining the data points when plotted as the logarithm of the solids concentration versus height. In figure A.4, the

decay length in each zone is plotted versus the average concentration in the zone for superficial gas velocities of 2-16 cm/sec.

They correlated the data by

$$D/U_s(\text{feet}) = 0.2(1 + 20c^2 + 3000c^4)/U_o(\text{cm/sec}) \quad [\text{A.20}]$$

for $U_g < 4$ cm/sec and

$$D/U_s(\text{feet}) = 1.2(1 + 3c^2 + 500c^4)/U_o(\text{cm/sec}) \quad [\text{A.21}]$$

for $U_g < 4$ cm/sec.

U_o is Stokes settling velocity and c is the volume fraction of solids in the slurry.

The results of the above experiment with glass beads was then used in models to predict solids distribution for several examples of various solids combinations. For catalyst and inert solids of the same density (2.7 g/cm^3) and diameter (50 microns) that are (1) dispersed in a solvent with a liquid viscosity of 0.9 cp and density of 0.7 g/cm_3 , (2) with an average catalyst loading of 0.05 by volume (gas-free basis), (3) an expand bed height of 30 feet, (4) a gas inlet velocity of 8 cm/sec, and (5) an overall conversion of 0.8, they obtained catalyst distributions with 0, 0.05, 0.1, 0.2 and 0.3 volume fraction of inert solids added.

The data in figure 5.A show that with only catalyst the effective bed height is about 13 feet, and with the catalyst more heavily concentrated at the bottom of the reactor. The addition of even a small amount of inerts increase the bed height. As the inert solids content is increased the bed expands further in height and the catalyst concentration profile becomes flatter.

In another example, they use the same catalyst and inert solid except the inerts are 1 micron in size. This example would be approximated by the use of 80 micron iron catalyst spheres made up of 1 micron particles that, because of attrition, produce

individual 1 micron fines. Effects similar to those of equal sized particles are obtained. A similar calculation was made using an active catalyst of density 2.7 g/cm^3 and lower activity catalyst with a density of 1.0 g/cm^3 . They also made calculations for the case when the original activity is decreased by factors of 2, 4, and 6. The use of the less active component also causes the bed to expand.

In the examples provided, the authors do not provide an identification of the meaning of the curves for volume fraction of catalyst vs. height in figures A.2-A.5 of the patent or in the figure legend. Thus, the reader must assume the identity of the curves.

It appears that this patent is the basis for the several patents that pertain to inert solids. For example, a structurally modified alumina prepared by incorporating a Group IIA metal or metals, particularly Mg or Ba, is claimed to have increased resistance to sintering and agglomeration (A.6). These materials are considered as aiding catalyst fluidization, as a catalyst support, and as heat transfer agents in syngas production or utilization in the slurry phase (A.7-A.12).

Stark (A.13,A.14) was issued a patent to cover the use of pentane (or similar light hydrocarbon) to remove the exothermic heat of reaction of the Fischer-Tropsch process and to expand the pentane to recover the energy to drive air plant compressors. Steam/water is the usual material for heat removal, and is utilized in the commercial reactors at Sasol. However, Stark indicates that it is desirable to have a coolant that has a boiling point and vaporizes at a pressure higher than the reaction pressure; this will ensure that no problem will arise if a leak allows coolant to enter the reaction zone. In order for vaporization to occur with pentane, it is necessary that the coolant side be below the critical conditions (197°C ; 44.1 atm. (679 psi)).

Stark (A.13,A.14) claims a method for removing heat from a hydrocarbon synthesis process reaction zone. A cooling medium is passed through the reactor zone in an indirect heat exchange, thereby vaporizing the cooling medium. The cooling medium is chosen so that it possesses the properties of inertness, condensable and vaporizes at a pressure which is at least as great as the pressure in the reaction zone.

Water/steam is frequently employed as the heat transfer medium. However, the authors claim that there is a reasonable expectation of leaks in a F.T. reactor because of the presence of numerous tubes and welds. In the case of water/steam, the reactor pressure is higher than the water/steam side so that F.T. products will leak into the cooling section whenever a leak occurs. The accumulation of products in the cooling side will eventually require the unit to be shut down for cleaning and/or repairs. In this instance, the cooling medium is chosen to have a higher vapor pressure than inside the reactor so that any leakage will be from cooling side to reactor. An appropriate cooling medium is n-pentane, a product of the F.T. synthesis.

The high pressure energy is recovered from the cooling medium through an expander. Preferably a substantial portion of the energy recovered from the expander is used to drive compressors for an air plant which separates oxygen from nitrogen.

The U.S. patent, but not the European patent application, indicates that the F.T. synthesis is carried out in a slurry phase system.

Hydrocracking and Hydroisomerization

Davis et al. (A.15) claim a hydroisomerization process for the conversion of a C₅₊ paraffinic feedstock to middle distillates. This involves contacting and reacting the feedstock and hydrogen at hydroisomerization reaction conditions with a catalyst comprising a Group IB, VIB or Group VIII metal component, or two or more metals,

supported on an acidic particulate solid with an average particle diameter of the size range 30 to 150 μm which is dispersed in a paraffinic liquid hydrocarbon.

Davis et al. (A.15) report that in normal hydrocracking with large catalyst particles, secondary reactions, arising from diffusional limitations, produce large amounts of gas and naphtha, and decrease the yield of the desirable middle distillate fractions. To overcome this limitation, staged fixed-bed reactors are operated at relatively low space velocities. They cite an earlier process [U.S. Patent 5,378,348] utilizing a separation into two boiling range fractions (500°F^- and 500°F^+) and separately hydroisomerizing to make middle distillates.

The hydroisomerization of the present invention is conducted in a slurry phase, preferably with greater than 25% catalyst slurry of particles in the micron size range (preferably 40-60 micron). The catalyst is bifunctional, possessing metallic hydrogenation and acidic functions. The metal oxide support, preferably a silica-alumina material, is prepared as described in reference -[U.S. Patent 3,843,509].

It is reported that one slurry reactor can be used to obtain approximately as much conversion as in three packed bed reactors in series under similar reaction conditions. An additional advantage of the slurry reactor is that a water-steam cooling coil can be used to remove the exothermic heat of reaction and to control the temperature. Using a packed fixed-bed reactor, a complex system of traps and quenching techniques are required to control the heat that is released during the reaction.

Data for the conversion of n-hexane show that the conversion decreases with increasing hydrogen pressure. At a given temperature, the fraction of single methyl branches decreases with increasing feedstock conversion; significant amounts of multi-methyl branched compounds appear at higher feedstock conversion. In contrast, in a

fixed bed reactor undesirable cracked products result at higher conversion levels. Even with the slurry technology, the fraction of cracking increases with feedstock conversion at levels above about 80%.

The kinetics of the Fischer-Tropsch wax cracking with a Pd/silica-alumina catalyst was obtained to design a reactor for a commercial scale process. They report that conversion followed zero order kinetics with an apparent activation energy of 30-35 kcal/mole for the conversion range of 30-70%.

Davis and Ryan (A.16) claim a process for producing middle distillate transportation fuels from a waxy product of a hydrocarbon synthesis process. The process consists of:

1. separating the product into a heavier (500°F^{+}) and at least one lower (500°F^{-}),
2. catalytically isomerize the heavier products in the presence of hydrogen,
3. catalytic hydrotreat the lighter fraction to remove heteroatoms (primarily O), and,
4. catalytically isomerize the product from step (3) to a product with a freeze point of -30°F or lower.

The authors indicate that a cobalt catalyst tends to produce heavier products, e.g., containing C_{20+} , whereas ruthenium tends to produce more distillate type products, e.g., $\text{C}_5\text{-C}_{20}$. A typical product slate for a cobalt catalyst is given as (the values may vary by $\pm 10\%$ for each fraction) is given in Table A.2.

Surprisingly, they found that hydrotreatment of the heavier fraction (containing about 0.45 wt% oxygen) prevents the production of a product with the excellent cold flow properties that was formed by hydroisomerization of the untreated material. They indicate the need to limit the conversion for the 700°F^{+} to the 700°F^{-} products to the 35-

80% range as a measure to limit cracking to produce gases and thereby a lower yield of distillates.

The lighter fraction can be the 320-500°F or, preferably, the entire liquid fraction boiling below 500°F. Following a conventional hydrotreatment, the naphtha is flashed off and the remaining material is hydroisomerized using a catalyst appropriate for light fractions, such as the ones described in reference A.17.

The most active catalysts were those materials containing a surface silica additive. However, it is stated that selectivity is more important than activity. Activity was improved when a 4% surface $\text{SiO}_2/\text{CoNiMo}/10\%\text{SiO}_2\text{-Al}_2\text{O}_3$ catalyst was used at 700 psig rather than 1,000 psig. Increasing the LHSV to 3.0 and increasing the temperature to provide activity similar to that of LHSV = 0.5 to 1.0 dramatically effected the products; the yield of jet fuel was decreased in favor of gas and naphtha production and the jet fuel had an increased freeze point. The cause for this was not understood but it was speculated that diffusional problems were the major factor.

An international patent application (A.18) claims the production of a high purity solvent composition which comprises a mixture of paraffins of carbon number ranging from about C_8 to C_{20} . The solvent has a molar ratio of iso-/n-paraffins ranging from about 0.5:1 to 9:1 and the isoparaffins of the mixture contain greater than 50% of the mono-methyl species. This patent application employees catalysts and processing schemes that are included in reference (A.19).

The Fischer-Tropsch product was obtained from the conversion of a synthesis gas ($\text{H}_2:\text{CO} = 2.11\text{-}2.16$) with a titania supported cobalt-rhenium catalyst. The reaction conditions were in the range of 422-428°F, 287-289 psig and feed linear velocity of 12 to 17.5. The alpha of the Fischer-Tropsch synthesis was 0.92.

The 700°F+ boiling fraction was hydroconverted over a Pd-silica-alumina catalyst (0.5 wt.% Pd, 38 wt.% Al₂O₃) to produce 39.4 wt.% conversion of the 700°F+ to 700°F- materials (Table A.3).

Wittenbrink et al. (A.20) describe a processing scheme whereby some oxygenates (primary alcohols) remain in the finished fuel. These oxygenates function to improve the lubricity of the diesel fuel.

The process scheme illustrated in their figure A.6 leads to some confusion. Shown leaving the Fischer-Tropsch reactor (vessel 2) are two streams: 3 (700°F+; 370°C) and 4 (700°F-). It is reported that the reactor is operated in the range 422-428°F (217-220°C) and 287-289 psig using a titania supported cobalt/rhenium catalyst (A22). The syngas had a composition of H₂/CO = 2.11-2.16. The alpha for FTS was 0.92. The FTS products were separated into three fractions having approximate boiling ranges: (1) C₅-500°F (designated F-T cold separator liquids); (2) 500-700°F (F.T. hot separator liquids) and 700°F+ (F.T. reactor wax). It appears that streams 3 and 4 in figure A.6 must be sent to a fractionator (not shown in the figure) to generate three streams.

The hydroisomerization and recombining of fractions are the same, or essentially the same, as described by Davis et al. (A.15) above.

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- A.3. D. C. Long, European Patent Office Publication No. 0 679 620 A2, April 26, 1995.

- A.4. See, for example, U.S. 4,637,993; U.S. 4,717,702; U.S. 4,477,595; U.S. U.S. 4,663,305; U.S. 4,822,824; U.S. 5,036,032; U.S. 5,140,050; U.S. 5,292,705.
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- A.17. U.S. Patent 5,187,138]
- A.18. WO 97/21787
- A.19. U.S. Patent 5,378,348
- A.20. R. J. Wittenbrink, R. F. Bauman, P. J. Berlowitz and B. R. Cook, International
Publication No. WO 97/14769, April 24, 1997.
- A.21. U.S. Patent 4,568,663.

Table A.1			
Reactor Simulation Results			
		Stage 2 Product	
	Stage 2 Feed	Shifting Catalyst	Non-shifting
Component Rates, Moles/Hr			
H ₂	11584	3021	6781
CO	2823	564	524
CO ₂	16324	15065	16326
H ₂ O	113	4887	2400
Hydrocarbon + Alcohol	13701	14045	13924
Inert	2434	2434	2434
Moles Converted			
CO		2259	2299
CO ₂		1259	-2
Total		3518	2297
% (CO+CO ₂) Converted		18.4	12.0
Hydrocarbon + alcohol		344	223
Yield, Moles/Hr			

Table A.2	
Typical Product Slate from FT Process Liquids Produced with a Cobalt Catalyst (from ref. A.17)	
Fraction	Wt.%
IBP-320°F	13
320-500°F	23
500-700°F	19
700-1050°F	34
1050°F+	11
TOTAL	100

Table A.3	
Fischer-Tropsch Synthesis conditions	
Operating Conditions	
Temperature, °F	638
LHSV, v/v/h	1.2
Psig	711
H ₂ treat rate, SCF/B	2,100
Yields, Wt.%	
C ₁ -C ₄	0.97
C ₅ -320°F	10.27
320-500°F	14.91
500-700°F	29.99
700°F+	43.86
TOTAL	100
700°F Conversion, Wt.%	39.4
15/5 Distillation Yields, Wt.%	
IBP-650°F	50.76
650°F+	49.24

Figure A.1. Model predictions for methane selectivity as a function of pellet radius compared to experimental data (6% CO-0.5% Re catalyst; $T = 200^{\circ}\text{C}$; $(P_{H_2}/P_{CO})_{\text{feed}} = 2.0$; $P_t = 19 \text{ atm}$) (from ref. A.????).

Figure A.2. CO conversion and methane selectivity as a function of rim thickness for spherical particles ($d_p = 1.0 \text{ mm}$; $T = 200^{\circ}\text{C}$; GHSV = 770 v/v/hr; --- $A = .6 \times 10^{-5} \text{ mole/s/s}\cdot\text{g}\cdot\text{atm}^2$;)) $A = 1.2 \times 10^{-5} \text{ mole/mole/s/s}\cdot\text{g}\cdot\text{atm}^2$) (from ref. A.1).

Figure A.3. CO conversion and methane selectivity as a function of rim thickness for ring (---) and cylinder (—) pellets ($d_p = 1.0$ mm; $T = 200^\circ\text{C}$; GHSV = 770; $A = 1.2 \times 10^5$ mole/s $\cdot$ g $\cdot$ atm² (from ref. A.1).

Figure A.4. Plot of decay length versus volume fraction solids concentration (#, 2 cm/sec; G, 8 cm/sec; +, 4 cm/sec; X, 12 cm/sec; *, 6 cm/sec; $\diamond$, 16-18 cm/sec).

Figure A.5. A plot of volume fraction versus bed height when a second inert solid to a first catalytically active solid in a bubble column, the inerts being of the same density and diameter as the catalytic solid.

Figure A.6. Schematic of the process (from ref. A.21).

ATTACHMENT XI

Listing of Open Literature Description of Exxon FT Work

A listing of papers by Exxon personnel, and including two by E. Iglesia identified by * that were published after he left Exxon but covering work that was conducted at Exxon. The synopsis will be brief since the results and conclusions in these papers are reviewed in papers XI.1, XI.12, XI.15 and XI.26.

The polymerization of the C_1 monomer produces a distribution described by the Anderson-Schulz-Flory (ASF) distribution. Thus, each carbon number surface species has a probability of continuing the chain growth or terminating the polymerization to produce a product. The ASF mechanism assumes that the ratio of chain propagation r_p , and termination, r_t , are independent of the hydrocarbon chain length. The resulting hydrocarbon selectivity predicted is described as:

$$m_i = \alpha m_{i-1} = (1 - \alpha) \alpha^{i-1} \quad [1]$$

where m_i is the mole fraction of hydrocarbon containing i carbon atoms and α is the probability for chain growth and is related to the probability for chain growth and termination as

$$\alpha = r_p / (r_p + r_t). \quad [2]$$

According to the ASF mechanism, a plot of the logarithm of the mole fractions of the hydrocarbons produced versus the number of carbon atoms in the hydrocarbon should result in a straight line with a single slope given by the chain growth probability, α . Much of the data generated, both in small and large reactor systems, exhibit two values of α . Recently an explanation has been given for this deviation of the hydrocarbon selectivity from that predicted by the ASF reaction mechanism has been

offered by workers at Exxon (XI.1,XI.15,XI.18,XI.26). The explanation termed as the Transport-Enhanced Olefin Re-adsorption (TEOR) model is briefly outlined below.

The normal ASF chain growth scheme is outlined in Figure 1. This mechanism for hydrocarbon production has been modified by the Exxon workers first as shown in figure 2 and later as shown in figure 3. The modified mechanism is claimed to be applicable for iron, cobalt and ruthenium catalysts, although data for iron has not been included.

This mechanism distinguishes between paraffins and olefins formed by termination of the hydrocarbon chain on the catalyst surface. Further, the olefins formed can re-adsorb back onto the catalyst surface and re-enter the chain growth process. This process of re-adsorption is quantified by a re-adsorption rate (r_R). Finally, the olefins formed can be hydrogenated, at least partially on other catalytic sites (rate given by r_S) to paraffins. The effective rate of chain termination is then

$$r_t = r_o + r_H - r_R \quad [3]$$

where r_o is the rate of termination to olefins and r_H is the rate of termination to paraffins. Thus olefin re-adsorption serves to decrease the effective rate of termination.

The rates of chain growth, olefin termination, paraffin termination, hydrogenation and olefin re-adsorption are assumed to be independent of chain length, i.e., the number of carbon atoms in the hydrocarbon. The value of the chain growth parameter, α , is then

$$\alpha = r_p / (r_p + r_o + r_H - r_R) \quad [4]$$

Note that due to the independence of the rates with chain length, this modified mechanism by itself cannot predict two or more values of the chain growth probability with increasing number of carbon atoms in the hydrocarbon.

The pores inside a catalyst particle are filled with the heavier hydrocarbon products (presumably liquid under reaction conditions) from the FTS. In the TEOR model it is assumed that this limits or exerts a strong influence on the diffusion of the FTS hydrocarbon products (both olefins and paraffins) out of the pores. The effect of diffusion resistance is to increase the time spent in a catalyst pore by the FTS hydrocarbon products. The diffusivity of individual hydrocarbons is dependent on their molecular weight or chain length or the number of carbon atoms. In the TEOR model, the dependence of diffusivity is assumed to be an exponential function of the number of carbon atoms:

$$D = D_0 e^{-0.3i} \quad [5]$$

where D_0 is a constant.

As the diffusivity increases with chain length, the time spent inside a catalyst pore is longer for a hydrocarbon containing, for instance, 20 carbon atoms than for a hydrocarbon containing 10 carbon atoms. Thus the olefins containing 20 carbon atoms have a greater chance to re-adsorb on to the catalyst surface and re-enter the chain growth process than olefins containing 10 carbon atoms. Hence, the rate of re-adsorption for a C_{20} olefin is greater than the rate of re-adsorption of a C_{10} olefin, i.e., the re-adsorption rate for heavier olefins is enhanced by transport limitations. Then, according to equation [4], the probability for chain growth, α , should increase with the number of carbon atoms in the hydrocarbon.

The diffusivity of light olefins (C_2 - C_{10}) in the liquid-filled catalyst pores is fairly high so that the re-adsorption rate of these olefins is relatively unaffected. Thus, a single value of the chain growth probability, α , is obtained for these hydrocarbons. For hydrocarbons containing higher than 10 carbon atoms, the rate of diffusion becomes

increasingly significant. Hence, the rate of re-adsorption, and thus the chain growth probability (α), increases with the hydrocarbon chain length. The increasing rate of olefin re-adsorption with hydrocarbon chain length finally reaches the rate of olefin termination, i.e.,

$$r_R = r_o \quad [6]$$

at a sufficiently high value of the number of carbon atoms (C_{25} or greater) in the olefin. At this point no more olefins are desorbed from the catalyst surface and the resulting probability for chain growth becomes

$$\alpha = r_p/r_p + r_H \text{ for } C_{25}+ \text{ olefins} \quad [7]$$

Thus, for $C_{25}+$ hydrocarbons, the chain growth probability does not depend on the hydrocarbon length and once again approaches a constant value.

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ATTACHMENT XII

Review of Fischer-Tropsch Work by Gulf Oil

The Gulf-Badger process leads from the catalysis research work on Fischer-Tropsch synthesis work and the reaction engineering analysis conducted by Gulf Oil, and later the process and engineering design provided by Badger (XII.1). A simplified process scheme is shown in Figure XII.1 (XII.2). The process was first discovered from exploratory work conducted by Gulf in the early 1970s. As Gulf continued to discover large reserves of natural gas, the need to convert remote natural gas to transportation fuels became important (XII.1). Since the exploratory research was successful, fundamental engineering and development work were undertaken, in the early 1980s. Because of its experience with others in the Fischer-Tropsch Synthesis, the Badger Company was invited to participate in some of the experimental work on reactor development and later provided the process engineering as well as the basis for the process economics (XII.2).

The initial involvement by Badger was because they had experience with fluid bed reactors and already had two of them set up in their lab. Gulf management wanted rapid development and did not want to delay to build their own reactors. Gulf researchers apparently advised against using the cobalt catalyst in a fluidized bed reactor but the work progressed to the point where 100 g batches of catalysts were prepared. The catalyst proved to be so active they had to strip insulation off the reactors when the reaction started to go out of control.

More money was spent on the fluid bed work in six months than Gulf had spent in the previous six years. With the result, of course, that the catalyst behaved just as Gulf researchers had predicted. The unit ran fine for half a day or so but then it began

to be difficult to keep the catalyst suspended. The catalyst had to be hydrogen-stripped once or twice a day, and the methane make was so high during those stripping periods that the overall selectivity to liquids was rather poor.

At the same time, the go-ahead for fixed bed development was given, and Gulf continued with Badger because they were already familiar with the catalyst and process. The scale-up of the fixed bed process of the catalyst manufacture by Davison were successfully accomplished.

Two types of reactors - two fluid-phase fixed bed and fluidized bed - were seriously considered. Because of the high molecular weight products that are produced by Gulf's most promising catalysts and thermal instability of the reactor, the fluidized bed reactor design concept presented real problems. Therefore, the Gulf Oil reaction engineering staff selected a fixed bed reactor. Its design and operation were critical, but success was quickly achieved.

The proprietary catalyst (in 1983) was inherently stable when combined with the proper reactor design and operation. Catalyst activity decay was avoided when stable, parametrically insensitive conditions and operation were achieved. The catalyst could be regenerated to the original activity by controlled oxidation and reduction.

The catalyst activity is an important property. It has a direct impact on the reactor design and operation as well as on capital and operating costs. The catalysts activity and selectivity in the developed reactor determine the reactor size that is required to produce a given quantity of desirable product, and to convert a given volume of synthesis gas, per day.

Operating conditions also influence the catalytic conversion and selectivity, and thereby the product distribution. An increase in temperature increases the reaction rate

whereas decreasing the H_2/CO ratio at constant temperature and pressure decreases the rate with the Gulf catalyst (XII.2). It was found that a $10^\circ C$ increase in temperature would just about compensate the rate loss for a decrease in H_2/CO ratio from 2 to 1.5. A substantial increase in reaction rate results from increasing the total pressure. The results for increasing pressure and temperature are illustrated in Figures XII.2 and XII.3 (XII.2). Representative data are summarized in Table XII.1 (XII.2). The Gulf-Badger reactor design has a constrained range of performance and acceptable operation.

Production of C_5+ products depends upon both the activity and selectivity of the catalyst, and is a product of these two factors. Thus, some of the effects that increase activity may decrease productivity.

Pilot plant data for a reactor, consisting of a single, commercial-size reactor (1" x 40') tube show that reasonable temperature control can be achieved. Conditions that are representative of those used at Gulf are (XII.2):

Temperature	200-225°C
Pressure	250 psig
H_2/CO feed ratio	1.5-2
Feed space velocity	500-1,000/hr.
CO conversion	40-60% per pass
Selectivity to C_5+	<u>ca.</u> 70-75% of carbon converted

A typical product make from a reactor operating under such conditions are illustrated in Table XII.2.

Two reactor concepts were tested during the pilot plant work - a tubular fixed bed and a fluidized bed at Badger. The latter was not satisfactory. Details on only the fixed bed reactor were given in reference XII.2. Gulf's pilot plant consisted of two reactor

sections in series (Figure XII.4, ref. XII.2). After initial operation, temperature of the hot spot in the Gulf Oil reactor did not exceed that of the average temperature by more than 5°C. The illustrated CO conversions depended linearly upon temperature, as did the relative rate (Figures XII.5 and XII.6; ref. XII.2). The productivity of C₅+ hydrocarbons did not increase linearly with temperature due to the relative increased production of light (C₁ - C₄) gaseous products (Figure XII.7; ref. XII.2).

A demonstration unit was designed (in 1983) that would produce approximately 15 b/d of naphtha, 15 b/d of diesel fuel and 7 b/d of wax from 350,000 scf of natural gas (Figure XII.7; ref. XII.2). Natural gas was compressed to the reformer pressure and mixed with recycle CO₂, heated and passed through a zinc oxide bed to remove sulfur compounds. The natural gas was obtained by drilling a well at the laboratory site. It then entered a steam-methane reformer and was converted to synthesis gas. Carbon dioxide was removed in an amine scrubber after the gas was cooled and compressed. The gas then passed through a membrane separation system to adjust the H₂/CO ratio. Hydrogen would be used as fuel in the demo plant but could be utilized for upgrading in a commercial operation.

Gulf-Badger Process - Patent Literature

A series of catalysts was prepared that demonstrated a beneficial effect of a minor amount of ruthenium on a catalyst containing a major amount of cobalt for the low pressure synthesis of higher hydrocarbons from synthesis gas (XII.3).

A standard reference cobalt catalyst was prepared according to a published procedure (XII.4) whereby solution I (49.4 g. Co(NO₃)₂•6H₂O; 11.0 g. Mg(NO₃)₂•6H₂O and 1.5 g. Th(NO₃)₄•4H₂O dissolved in 250 ml water) and solution II (35 g. K₂CO₃ in 250 ml water) were heated to boiling. Solution I was added rapidly with vigorous stirring to

solution II, and immediately thereafter, 20 grams of dry powdered kieselguhr was admixed with stirring which continued for 10 minutes. The mixture was filtered and washed with distilled water until no evidence for nitrate ion was observed in the wash water. The solid was dried at 120°C for 16 hours, calcined in air at 350°C for 16 hours, then reduced in flowing hydrogen at 350°C for 3 hours. A second catalyst was prepared following the same procedure except that 0.35 g. of RuCl_3 was added to solution; this catalyst had the following composition: Co (31.6 wt.%); Mg (3.25 wt.%); ThO_2 (1.98 wt.%); Ru (0.53 wt.%); and kieselguhr (62.64 wt.%).

These two catalysts were subjected to synthesis runs using the same experimental conditions ($\text{H}_2/\text{CO} = 2$; upflow reactor with preheater for feed gas; atmospheric pressure; gas hourly space velocity based on the total amount of charge gas was 250; g.c. analysis). A series of experiments were conducted at various reaction temperatures with the CO conversion levels shown in Figure XII.9. It is seen that a measurable conversion is obtained only at a temperature of about 125°C or higher. On the other hand, the same catalyst except that it contains Ru, exhibits appreciable conversion at 50°C and maintains this superiority with increasing reaction temperature. The products from the runs at 220°C with the standard Co catalyst and the Ru containing catalyst were analyzed. The products from the standard catalyst exhibited an ASF distribution, with an alpha value of 0.85 (Figure XII.10). The products from the Ru containing catalyst exhibited a product distribution that contained significantly heavier hydrocarbons; the alpha value, based on the curve in Figure XII.10, was 0.98. Thus, the addition of Ru to the standard catalyst resulted in a significant increase in the catalytic activity as well as producing a significantly heavier products. The data indicated that the presence of Ru essentially eliminated the production of

methane and ethane (however, this conclusion is on a relative basis). In addition, the C_{9+} product from the standard catalyst contained 29% of olefinic product compared to 4% with the Ru containing catalyst. The gaseous products were found to contain about 15 volume percent CO_2 for the standard cobalt catalyst but only traces of this gas were obtained with the Ru containing catalyst. While it is not stated how the samples were collected, the low value for the C_{9-11} product fraction, relative to lower and higher carbon number products (Figure XII.10), suggests that the products consisted of gaseous and liquid fractions that were subsequently analyzed separately, resulting in loss of some C_{9-11} hydrocarbons.

Similar catalysts were prepared. For catalyst 3, about equal amounts of alumina and magnesia were added to replace kieselguhr in the above Ru containing catalyst (31.6 wt.% Co, 2.0 wt.% thoria, 0.5 wt.% Ru, 32.9 wt.% alumina and 32.9 wt.% magnesia). The other catalyst (4) contained a lower amount of Co and no thoria; at the same time alumina was substituted for the kieselguhr and the amount of magnesium oxide was increased. This catalyst (XII.4) contained 17.77 wt.% Co; 0.70 wt.% Ru, 40.77 wt. % alumina and 40.77 wt.% MgO .

The three catalysts were compared for methane production at various reaction temperatures; these results are compiled in Table XII.3. Referring to Table XII.3, it is apparent that the presence of Ru significantly decreased the amount of methane produced at all reaction temperatures. All Ru containing catalysts produced only traces of CO_2 . Substituting gamma-alumina for kieselguhr had little, if any, effect on methane production; likewise, the removal of thoria and an increase in magnesia had little effect on methane production.

As shown in Table XII.4, it is noted that the "% selectivity for C₉₊ fraction" increased, and the % olefin in the fraction decreased, when Ru was present in the catalyst.

It appears that another Gulf worker later repeated Kobylinski's work with precipitated Co and CoRu catalysts, as well as one with the 20Co-0.5Ru-1La₂O₃ composition. Ru was found to confer better dispersion and activity, just as it did for the impregnated catalysts, but that there was no appreciable change in product distribution in standard week-long tests. Apparently a problem with the GC analysis, such as getting drops of liquid product in with the vapor phase products impacted the reported data. The precipitated catalysts were found to have activities per unit weight of metal that were intermediate between those of catalysts made by aqueous impregnation and those made by nonaqueous impregnation.

High octane gasoline and diesel fuel are produced from synthesis in a two stage process (XII.5). In the first stage, synthesis gas is converted to straight chain paraffins that have a boiling range that falls mainly in the diesel fuel range. A cobalt catalyst, preferably containing a Group IIIB or IVB metal oxide, is supported on gamma- or eta-alumina, or a mixture of these two aluminas. The C₅-C₉ straight chain portion of the product from the first stage is converted in the second stage to highly aromatic plus branched chain paraffinic gasoline using a platinum group metal catalyst. The most preferred metal oxide for use in the catalyst for the first stage is thoria. The support should have low acidity, meaning a Brønsted acidity with H₀ ≤ 1.5, which is less than 5 micromole per gram (about 10¹⁶ acid sites per m² of surface area). The deleterious effect of acidity is the isomerization and cracking of intermediate alkenes, removing them from chain growth and producing a low molecular weight product. **This latter**

statement implies that higher molecular weight alkenes readsorb on the catalyst to react with synthesis gas (or other alkenes) to produce higher alkenes. In addition, the production of low molecular weight products requires either that low molecular weight alkenes do not readsorb to undergo subsequent chain growth or that the low molecular weight products produced by cracking are alkanes, and not alkenes.

The catalyst for the first stage was defined by hydrogen chemisorption and should adsorb at 25°C from 125 to 300 micromole per gram of total catalyst. The chemisorption of hydrogen is illustrated in Figure XII.11 and shows a maximum for a catalyst that is receded in flowing hydrogen at 350°C. The maximum hydrogen adsorption corresponds to a dispersion, d , of cobalt of 0.066; that is, 6.6% of the Co atoms are located on the surface of cobalt metal crystallites.

The support must be of high purity and have a surface area in excess of 50 m²/g, and preferably in the range of 150 to 225 m²/g. High purity means that the support will contain negligible amounts of sodium, sulphate, silicon, phosphates or other material having a deleterious effect on the metal dispersion or the production of high molecular weight hydrocarbons.

The preparation of the catalyst was accomplished using a nonaqueous, organic impregnation solution containing the soluble cobalt and Group IIIB or IVB salts in order to achieve the necessary metal loading and distribution. The alumina was calcined in air prior to impregnation, preferably in 5h 400 to 600°C range. Suitable solvents include ketones, such as acetone or methyl ethyl ketone; the lower alcohols; amides, amines, ethers, hydrocarbons or mixtures thereof. A mixture of ethanol and acetone (4 parts

acetone; 1 part ethanol) is preferred and is used in an amount that will fill the pore volume; a maximum amount would be equivalent to five times the total pore volume.

The impregnated material is dried (25 to 45°C) to remove solvent to "dryness" and the material is then calcined in air, preferably 225 to 275°C. The impregnation, drying and calcination steps are repeated until the desired metal loading is obtained. The catalyst is slowly reduced in hydrogen. In the first reduction step, the catalyst is heated slowly (0.5 to 5°C/min) to a maximum temperature of 180 to 220°C and held at this temperature for about 24 hours. The second reduction step is accomplished by heating at a rate of 5 to 20°C per minute to the optimum temperature. Initially the reduction step is accomplished in a diluted hydrogen stream (e.g., 5% hydrogen in nitrogen); gradually the hydrogen concentration is increased to provide pure hydrogen.

While it is stated that the reactor type utilized is not critical, a fixed bed, with gas downflow, was preferred.

The catalyst for the second stage could be a typical naphtha reforming catalyst; that is, a platinum group metal supported on alumina using halogen to impart acidity.

The catalyst which gave the hydrogen adsorption data that is shown in Figure XII.11 contained the following composition by weight: 100Co/18ThO₂/200Al₂O₃. This catalyst was evaluated for activity using a flow of 240 cm²/g/hr of CO and the same flow of H₂. Data were obtained for the above catalyst and are summarized in Tables XII.5 and XII.6.

The conversion depends upon temperature as is shown in Figure XII.12 (the numbers in parentheses are the total gas flow rate (cm²/g/hr)). Thus, at a flow rate of 1:1 synthesis gas of 1.22 NL/g/hr; the conversion of CO was 6.5%. The activation energy was calculated using the data in Figure XII.12 to be 15 kcal/mole. The product

distribution changed slightly to favor lower weight products as the temperature increased (Figure XII.13). The product distribution did not adhere to the ASF plot except perhaps for the lowest temperature run; in all instances the C₂-C₄ products were much too low to approach fitting an ASF plot. It was not possible to fit the data in Table XII.2 with an ASF distribution.

This patent covers the activation of a promoted or unpromoted supported cobalt catalyst (XII.6). The catalyst is prepared using cobalt carbonyl and the support is either silica or alumina. The activation procedure comprises three steps: (1) reduction in hydrogen, (2) oxidation in an oxygen-containing gas, and (3) reduction in hydrogen, all three steps conducted at temperatures less than 500°C. This activation comprising reduction, oxidation and reduction has been called "ROR". It has been found that the addition of promoter, such as lanthanum or manganese (and oxides of the lanthanides and actinides), reduces the activity of the unpromoted catalyst. However, if in addition to the above promoters, ruthenium is also incorporated the ROR activation results in an increase in activity above that of the unpromoted cobalt catalyst.

The cobalt carbonyl is added by an impregnation technique using a non-aqueous solvent. If desired, the addition of promoter can be accomplished by co-impregnation along with cobalt. In the preferred procedure, the promoters (metal oxide and/or ruthenium) are added prior to the cobalt carbonyl.

Thus, the promoter is added to the calcined support as described in ref. XII.5. The impregnated catalyst, preferably using the incipient wetness technique, is dried slowly in air. The slow drying procedure is used so as to spread the metals over the entire support. After drying in air, the catalyst is calcined by heating slowly in flowing air to, preferably, 250 to 300°C. The drying and first calcination can be accomplished

separately, or done in a combined step. The calcination step is accomplished at a slow heating rate, preferably 0.5 to 1.0°C/min., and held at the final temperature for up to 20 hours (2 h. is preferred). If necessary, the impregnation, drying and calcination steps are repeated to provide the optimum metals loading.

Following the calcination, the catalyst is impregnated with an organic solution containing cobalt carbonyl. Prior to impregnation, the catalyst is not exposed to the atmosphere sufficiently for the support to be rehydrated. If more than one impregnation is required, the catalyst must be subjected to a reduction-reoxidation treatment, the first two steps of the ROR procedure.

The preferred procedure for the ROR process is:

- (1) Slowly heat to about 200°C and hold at this temperature for about 20 hours (starting with about 5% H₂ in nitrogen and increase gradually to pure H₂), then heat to the optimum reduction temperature (about 350°C) and hold for about 24 h. Reduction should be slow enough to prevent the volatilization of cobalt carbonyl and to prevent the water vapor from exceeding 1% in the exit gas.

Passivation is effected at room temperature using diluted air.

- (2) The oxidation step is conducted as described in ref. XII.5.
- (3) The oxidized catalyst is reduced as described in step (1) above.

The advantage of the ROR technique was illustrated by the preparation of three catalysts: (A) cobalt carbonyl was impregnated onto Ketjen gamma-alumina; (B) impregnating gamma alumina with cobalt and ruthenium nitrates (20 wt.% Co and 0.5 wt.% Ru); and (C) impregnating gamma-alumina with nitrate salts to give a material containing 25 wt.% Co, 0.5 wt.% Ru and 1.0 wt.% lanthanum oxide. The three catalysts

were tested at 185°C; $H_2/CO = 1.85$ (atmospheric pressure), producing the results shown in Table XII.7.

The ROR treatment of the cobalt carbonyl catalyst provided a more active catalyst than the other two preparations and the selectivity of the cobalt carbonyl catalyst for C_5+ hydrocarbon is comparable to the ruthenium-promoted cobalt catalyst.

Hydrogen adsorption studies showed that the ROR treatment produced lower dispersions of Co than just hydrogen reduction. Thus, catalyst A had a metal dispersion of 0.29 following a reduction in hydrogen, but only 0.13 following the ROR treatment. Thus, the activity per metal site increased rather than the number of sites.

The activity of a silica-supported catalyst prepared using cobalt carbonyl is higher than that of an alumina-supported catalyst; however, the selectivity for C_5+ hydrocarbons is lower. The ROR treatment of the silica-supported material improves the C_5+ hydrocarbon selectivity.

This patent provides additional data to support the view that the reduction-oxidation-reduction, "ROR", technique provides superior activity over the same catalyst when it is just treated with hydrogen (XII.7). Data is also presented to show the improvement in activity when ruthenium is incorporated into the cobalt catalyst. The data shown in Table XII.8 was obtained at 1 atm pressure with [the patent gives the gas composition as weight percent but it surely is molar percent] a 35% CO and 65% H_2 synthesis gas mixture.

As shown in Table XII.8, the use of ruthenium significantly improved the catalyst activity as compared to the test of a catalyst that did not contain ruthenium. Even when the Co/Ru molar ratio exceeded 200/1, the catalyst activity increased in excess of 100

percent over that in which ruthenium was absent. Likewise, the ROR activation led to a catalyst that exceeded the activity of a hydrogen treated material by 24-34 percent.

Data were also presented to show the benefit of Ru for a catalyst prepared by precipitation of cobalt, ruthenium and lanthanum oxide onto an alumina support by the addition of potassium carbonate. In this case the use of the ROR treatment improved the catalyst activity. However, when the amount of ruthenium exceeded 0.5 wt.%, the activity showed a decline of 4%.

A method of catalyst preparation is given which consists of an aqueous impregnation using a solution of a cobalt salt, drying the impregnated material and then employing a nonaqueous, organic impregnation solution of salts of ruthenium and a Group IIIB or IVB metal (XII.8).

A supported catalyst was prepared using a microspheroidal gamma-alumina commercially available from Harshaw; this alumina had an average particle diameter of about 60 microns. After calcination at 600°C, the alumina was impregnated with a cobalt nitrate solution. The material was dried at 120°C and then impregnated with thorium nitrate and ruthenium acetylacetonate dissolved in an acetone-ethanol (=2:1 ratio) solution. Excess solvent was removed at reduced pressure at room temperature in a rotary evaporator. The catalyst was then dried by heating to 90°C with the nitrate salt melting with evolution of water in the temperature range of 50-60°C. Prereduction and passivation was conducted using a hydrogen flow of 720 ml/g/hr. The catalyst was heated to 100°C at 1°C/min and maintained at this temperature for 1 hr and then heated at the same rate to 200°C. After holding at the latter temperature for 2 hr., the catalyst was heated at 10°C/min to 360°C and held at this temperature 16 hrs. After cooling below 200°C, the catalyst was flushed with nitrogen and the temperature lowered to

room temperature. Air was then bled into the nitrogen (1:50 air:nitrogen with flow of 50 mL per minute per 5 g catalyst for 16 hr). The final reduced catalyst contained 21.9 wt.% Co, 0.5 wt.% Ru, 2.2 wt.% ThO_2 and 75.4 wt.% alumina.

The activity of the catalyst was obtained using a 1/2" fluid bed reactor where 50 grams of catalyst was heated to a temperature of 350°C in a flow of hydrogen (N L/g/hr) and held at this temperature overnight. The hydrogen flow was reduced to 0.3-0.4 L/g/hr and an equal flow of CO was introduced (if $\text{H}_2/\text{CO} = 2$, the hydrogen flow was doubled). The results of runs are summarized in Table XII.9.

The results show that, for similar conditions, an increase in the H_2/CO ratio from 1 to 2 caused a decrease in the C_5+ hydrocarbon yield and an increase in the amount of methane. An increase in pressure from 15 to 30 psia caused an even greater decrease in the C_5+ hydrocarbons and increase in methane; an increase in temperature had a similar effect.

A recent paper by Haddad and Goodwin (XII.16) on the CoRu catalyst claimed to obtain no change in activity from a ROR treatment. Looking at their catalyst preparation, they claimed to add 20% Co as the nitrate apparently in one step. This would appear to require the use of a supersaturated cobalt solution. In most catalysts, the alumina does not have enough pore volume to accommodate that much cobalt nitrate. The fact that they saw no ROR effect could be taken to mean that they had not produced an alloy catalyst whereas measurements of Curie point changes showed that the Gulf workers had done so. Goodwin reports TGA studies after a wide range of precalcination and reduction temperature, but none for an RO-treated catalyst. Gulf workers usually found a 100°C lowering in the reduction temperature for an RO-treated catalyst, compared to a fresh one - more evidence of a drastic change in properties.

The best proof of the advantage of ROR was obtained on a large scale - after one year of operation and several hydrogen strippings, the catalyst in the demo plant was regenerated (mainly for experience with recalcination). It was then 50% more active than it had been after initial startup and this made operation with the regenerated catalyst even more difficult. After the plant was shut down Gulf workers tested catalysts from about 20% of the reactor tubes and the catalysts, except for one tube, had the expected catalytic properties.

This patent relates to the use of a mixture of a catalyst active for the Fischer-Tropsch synthesis and one that effects alkene isomerization and/or cracking to produce gasoline from synthesis gas (XII.9). The Fischer-Tropsch synthesis catalyst is any one of the many examples that are comprised of cobalt alone or promoted by ruthenium and/or Group IIIB or IVB metal oxides. The acid cracking/isomerization catalyst is a silicalite-1 type (see XII.10 - XII.12).

An example utilized a catalyst containing 50 wt.% silicalite and 50 wt.% of a catalyst with the composition $100\text{Co}/18\text{ThO}_2/200\text{Al}_2\text{O}_3$ (example of conversion data given above). The particles were separately ground to give a particle size 100 mesh, mixed and then wetted, and then comminuting and sieving the resultant mixture to provide uniform 30-40 mesh particle size. Tests were conducted using 0.5 g samples of the prereduced catalyst by reducing in hydrogen at 360°C in hydrogen 2.4 L/g/hr at one atmosphere. The hydrogen flow was then reduced to 0.48 L/g/hr and an equal flow of CO ($\text{H}_2/\text{CO} = 1:1$). The tests were effected at 185°C and one atmosphere pressure to provide the data in Table XII.10.

The impact of the addition of silicalite to the Fischer-Tropsch catalyst is apparent (Figure XII.14). The ASF plot shows that $\alpha = \sim 1$ for the C_3+ hydrocarbons; however

the amount of methane is much above and the C_2 products much below the values expected for conformity to the ASF plot. When silicalite is added to the Fischer-Tropsch catalyst, the data do not fit the ASF distribution. Methane and the C_2 -products are slightly higher than was obtained with the Fischer-Tropsch catalyst alone. More importantly, the C_3 - C_{10} hydrocarbon products significantly deviate from the ASF distribution. Thus, it is apparent that the acid catalyst has effected a significant amount of isomerization and cracking of heavier hydrocarbons to lighter, gasoline range hydrocarbons.

The fraction of n-alkane in each carbon number hydrocarbon fraction provides a surprising distribution (Figure XII.15). When the catalyst contains only the Fischer-Tropsch component, the amount of n-alkane drops from about 75% for C_2 to about 20% for C_3 and then slowly increases with increasing carbon number to approach 60% for the C_{10} carbon number fraction. In this respect, the cobalt catalyst, when operated at 1 atmosphere, exhibits a distribution that is very similar to the one obtained for an iron catalyst at 1 atmosphere or at intermediate pressure levels (XII.13). However, when the silicalite catalyst is present, the alkane fraction deviates from the one obtained for Fischer-Tropsch synthesis. Up to carbon number 6, a similar trend is obtained for both catalysts; however, above carbon number 6 there is significantly less n-alkane when the silicalite is present. The apparent explanation for this is that the products have increasing fractions of isoalkanes, isoolefins and internal olefins as the carbon number increases above C_4 , thus lower fractions of n-alkanes and 1-olefins. Isomerization to iso or internal olefins is not possible with C_2 and C_3 . The degree of olefin reincorporation may be strongly influenced by the degree of substitution at the double bond. Ethylene readsorbs the most readily because it has two free CH_2 groups. Among the 1-olefins,

readsorption and chain initiation declines slowly with carbon number. Internal olefins readsorb poorly because they have no free CH₂ group, but they can isomerize back to 1-olefins and that gives them a small path towards readsorption. Isoolefins are also relatively unreactive. Although some have a free CH₂, if they have two substituents on the adjacent carbon that appears to be enough to make readsorption difficult.

All that is needed then to lower the effective chain growth probability among C₄+ chains is for the 1-olefins, produced as primary products, to be isomerized to internal olefins or isoolefins. That removes them from the F-T reaction. With a catalyst that does this (almost any acidic catalyst), one can observe a large drop in chain growth probability between C₃ and C₄.

The isomerization to isoolefins requires a strong acid site and it was found that this reaction declined fairly quickly with time over silicalite or ZSM-5. However, the isomerization to internal olefins, which requires only moderate acidity, persisted for as long as any of the composites were run, and it was sufficient to alter the ASF distribution.

A layered aluminosilicate (montmorillonite-type structure) containing cobalt substituted into the crystal lattice was activated for the Fischer-Tropsch reaction using a sequential reduction-oxidation-reduction (ROR) technique (XII.14). A Group VIII noble metal, such as ruthenium, is also added by impregnation prior to the final reduction step.

The hydrothermally produced cobalt aluminosilicate has the following general formula prior to its activation:

[it is 3x+y in the patent]

where n is between 0.02 and 4 (prefer 2 to 3); x is up to about 1 (prefer 0.1 to 0.1); $n+x$ between 0.02 and 4 (prefer 2 to 3); y is between 0.05 and 2 (prefer 0.5 to 2); and z is up to about 10. In the above the predominant amount of Al, Co, OH, and F are in the octahedral layers, and the Si and minor amounts of Al are in the tetrahedral layers. Ammonia and water are located between the layers. Water and ammonia are lost in the pre-activation calcination. The reduction is carried out in hydrogen (or other reducing gas) and the oxidation process is preferable accomplished in air or diluted air. The activation is accomplished in three steps - the ROR process described earlier.

A catalyst is prepared using a saturated aqueous solution of 161 g of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ in two liters of water that is slurried with 1.84 g of a silicic acid solution providing a $\text{Si/Al}=4.7$ ratio. The silica-alumina gel was precipitated by adding the slurry to 1 L of ammonium hydroxide with a pH of 8. The gel was washed with distilled water to remove chloride. A 50 g sample of the washed gel was slurried with 225 ml of water containing 60 g of cobalt acetate, 0.78 g of ammonium fluoride, and 0.42 g of HF while stirring and maintaining the pH at 8.0 by adding ammonium hydroxide as needed. The mixture was heated at 300°C in an autoclave (1,240 psig) for four hours. After drying at 120°C , the gel was calcined at 500°C for 4 hrs and produced a hard, wine-red solid with $\text{SiO}_2/\text{Al}_2\text{O}_3 = 0.30$. The catalyst was reduced at 400°C for 2 hr in hydrogen and then reoxidized at 500°C . A hydrogen reduction at 600°C (16 hr.; 8.5% wt. loss) then reoxidized in air at 500°C (8.1% wt. gain). A final reduction was effected at 400°C for 16 hours.

This catalyst was utilized at 1 atm. in a 0.5 g. catalyst bed using a hydrogen:carbon monoxide = 1:1 with a feed of 0.48 l/g/hr. Three temperatures were utilized following activity stabilization to produce the results shown in Table XII.11.

The major products in the C₅+ hydrocarbons were found to be isoalkanes and isoalkenes. The alkenes contained a high fraction of internal alkenes.

The catalyst is a rare earth promoted layered complex metal silicate composition characterized as having repeating units with a structural formula

where x is a number from 0 to 1 (fraction of Ru in Ru+Ni); a is the valence of nickel, b is the valence of ruthenium; n is a number defined by

$$6/[a(1-x) + bx]$$

and w is a number ranging from 0 to 4 (XII.15). The preferred catalyst is a rare earth promoted nickel chrysotile.

These catalysts produce much methane in addition to higher carbon number hydrocarbons. Typical examples, using H₂/CO = 2.5; 350 GHSV; 210°C; and atmospheric pressure, are shown in Table XII.12.

Low concentrations of thoria are needed but higher (30% or more) are not beneficial, and may have a slight detrimental effect. The inclusion of low concentrations of thoria greatly increase the amount of C₂+

Typical examples, using H₂/CO = 2.3; 400 GHSV; 204°C; and atmospheric pressure, to define the differences in rare earth promoters, if any, are shown in Table XII.13.

The results show that there is a synergistic benefit in conversion when a mixture of two rare earth promoters are used. Thus, thoria incorporation provides a CO conversion of 31.5% and lanthana 25%; rather than the expected intermediate value for CO conversion when a mixture of thoria and lanthana are incorporated, the CO conversion is 71.5%. A similar result is obtained when thoria and praseodymium is utilized.

Slurry Phase Synthesis

A patent (XII.17) claimed a process for the conversion of synthesis gas using a finely divided catalyst (ca. 10-110 microns) dispersed in a fluid medium. The catalyst consisted essentially of cobalt and ruthenium on a support. In subsequent claims the support was identified as alumina or silica. Another subclaim indicated that the fluid is a liquid medium which could be a synthetic hydrocarbon liquid or a hydrocarbon conversion product. The activation known as ROR (reduction in hydrogen, oxidation, reduction in hydrogen) was claimed. A promoter could be selected from the group consisting of Rh, Pt, Pd, Ir, Os, Ag and Au. The use of these catalysts produced a product with less than 16 wt.% methane. The catalyst cobalt concentration covered was from about 5 to about 25 wt.% and the promoter in an amount from about 0.01 to 0.5 wt.% based upon the total catalyst weight.

The patent contains examples of conversions in fixed-bed reactors with a catalyst prepared to have various particle sizes. A catalyst was prepared that had a particle size that one normally encounters in fixed-bed operations (1/16th inch (0.16 cm) extrudate) and then this catalyst was ground to produce average particle sizes of 0.28 and 0.54 mm. The found that both catalyst activity and product selectivity changed with particle size. In particular, the fraction of methane decreased and the amount of C₅+ increased with decreasing particle size of the catalyst (Figures XII.16 and XII.17); over the particle sizes tested it appears that both selectivities change linearly with particle size. It appears that the methane production of the three catalyst sizes extrapolates to a common value of about 4 wt% at very small particle size (Figure XII.16). Likewise, the C₅+ selectivity appears to approach about 87 wt.% at very small particle size. This means that the C₂-C₄ yield is about 9 wt.% for the very small particle size catalyst. As

expected, the rate of reaction increased as the particle size was decreased (Figure XII.18). For the smallest particle size (0.24 mm) the reaction rate increased by a factor of 1.94 for an increase in temperature of 10.5°C, a factor close to the rule of thumb of a doubling in reaction rate for every 10°C increase in temperature. At 195°C, the rate decreased by 27% when the H₂/CO ratio was decreased from 2.0 to 1.5.

The authors indicate that the catalyst prepared using an organic solvent has higher activity than one prepared in the same manner but using an aqueous solution. The authors indicate that the catalyst may contain Group IIIB or IVB metal oxide as a promoter, with oxides of the actinide and lanthanide series being preferred. Especially preferred metal oxides are La₂O₃, CeO₂, ZrO₂, TiO₂, HfO₂, or ThO₂. MnO₂ and MgO are also listed as preferred promoters. The amounts of these promoters can be from about 0.05 to 100 parts by weight to 100 parts by weight of cobalt. It appears that the patent covers only catalysts using these oxides as promoters, and not as the support material.

The support should have low acidity. Its surface area should be at least about 40 to 50 m²/g but not so high that "permit reactant materials to enter the interstices of the catalyst." A preferred surface area is in the range of 150 to 225 m²/g. The support should be high purity, meaning having low concentrations of components having deleterious effects on the cobalt catalyst.

The process is outlined in figure XII.19 and does not differ significantly from one used by Kölbel and coworkers (XII.18). In the reactor, the catalyst particles are suspended in a liquid medium having sufficient viscosity to ensure that the particles remain in suspension and having a volatility that is low enough to avoid loss due to vaporization within the reactor. The catalyst is present from about 2 to 40 wt.%. The catalyst density can be in the range of 0.25 to 0.90. The gas flow enters at a rate

sufficient to suspend all of the catalyst particles in the system without settling. The gas flow rate will be selected depending upon the slurry concentration, catalyst density, suspending medium density and viscosity, and particular particle size utilized. Suitable gas flow rates include, for example, from about 2 to 40, preferably from about 6 to 10 cm/sec. The pressure range covered is from about 1 to 70 atm. Light hydrocarbon products, such as C_{20} and below, are withdrawn overhead through a line designated 32 in Figure XII.19. A portion of the heavier products and catalyst slurry is withdrawn through line 38 and is passed to a separation zone. A concentrated catalyst/slurry fraction is returned to the reactor while a portion of the catalyst/slurry may be passed through a regeneration zone (54) before being returned to the reactor. Heavy products with low catalyst concentration are revolved through line 44. Separation by filtration can be utilized for separating catalyst from the suspending liquid (vessel 40).

The data obtained in the slurry reactor were compared to a run in the fixed bed reactor with the same catalyst formulation. The catalyst for the fixed bed reactor was supported on 1/16 inch extrudate alumina which contained about 20 wt.% Co, 0.5 wt.% Ru and 1.0 wt.% of a rare earth oxide composite containing 66 wt.% La_2O_3 , 24 wt.% Nd_2O_3 , 0.7 wt.% CeO_2 , 8.2 wt.% PrO_2 and 1.1 wt.% other rare earth oxides. The synthesis gas ($H_2/CO = 2.03:1$ with methane diluent of 19.1 mole %) passed through the 1" i.d. reactor at a maximum stable temperature of 215°C with a pressure of 275 psi (18.7 atm., 1895 kPa). For the slurry reactor, alumina which contained about 12 wt.% Co, 0.3 wt.% Ru and 0.6 wt.% of a rare earth oxide composite containing 66 wt.% La_2O_3 , 24 wt.% Nd_2O_3 , 0.7 wt.% CeO_2 , 8.2 wt.% PrO_2 and 1.1 wt.% other rare earth oxides was in the form of 20-105 microns (less than 140 mesh; average particle size 52 microns). A liquid with a viscosity of 8 centistokes ($8 \times 10^{-6} \text{ m}^2/\text{s}$) was composed mainly

of C₄₀-C₅₀ isoparaffins. Gas entered at the bottom through a stainless steel screen in the form of small bubbles. Hydrocarbon was removed from the top through a heated line. The pressure was 160 psig (10.7 atm) and the gas flow with H₂/CO = 1.95 was 1826 cm/s. Initially the temperature was 225°C but was increased and held at several higher temperatures to obtain additional conversion data.

The increase in conversion with increasing temperature gives an activation energy of 20.5 kcal/mol (85.7 kJ/mol) (Figure XII.20). This value of the activation energy is surprisingly close to that reported for a fused iron catalyst (20.0 kcal/mol; 83.6 kJ/mol) and a precipitated iron catalyst (20.9 kcal/mol; 87.4 kJ/mol) (XII.19). At 225°C, methane is 8.4 wt.% of the product and increases to 15.6 wt.% at 240°C. As the temperature increases, the C₅+ fraction gradually decreases (Figure XII.21) and the C₅-C₂₀ fraction increases, indicating that the alpha value decreases with increasing temperature; however, there is not sufficient data to obtain reliable values of alpha (Table XII.14).

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Table XII.1						
Evaluation of G-B Catalyst in Pilot Fluid Bed Reactor Data Taken at 25 Hours on Stream (from XII.2)						
Run	Temp., °C	Pressure, (psig)	H ₂ /CO	Syngas Space Velocity, cm ³ /g/h	Per Pass CO Conversion, %	Selectivity to C ₅ + ^a
First	195	15	2.0	600	25	74
Second	195	30	2.0	1200	22	82
Third	195	30	2.0	1200	16	74
	215	30	2.0	1200	44	71
Fourth	215	60	2.0	1950	41	72
Fifth	205	30	1.5	1200	17	72
Sixth	215	30	3.0	1200	76	55
Seventh	205	30	2.0	1200	23	67
Eighth	205	30	2.0	1800	25	73
Ninth	215	40	1.5	1600	25	72
a. C ₅ + expressed as percent of carbon selectivity basis. b. At some point, every run had one or more reactor "run aways." They all failed.						

Table XII.2	
Typical Data from Fixed Bed Pilot Plant (XII.2)	
Temperature, °C	210
Yields, Wt.% of Hydrocarbon Product	
CH ₄	13.7
C ₂ H ₄ to C ₄ H ₁₀	11.6
C ₅ -C ₈ (naphtha)	25.4
C ₉ -C ₂₀ (distillate)	33.4
C ₂₁ + (wax)	14.2
Oxygenates	1.7

Table XII.3					
Influence of Ru on Catalyst Performance (from ref. XII.3)					
Experimental Conditions:			H ₂ :CO = 2:1, GHSV = 380		
		% Selectivity to CH ₄ Catalyst from Example			
Ex. No.	Temp., °C	1 (Co)	2 (Co + Ru)	3 (Co + Ru)	4 (Co + Ru)
18	200	9.8	0 ^a	0	0
19	300	27.5	0	0	0
20	400	48.0	0	1.2	0.5
21	450	87.0	10.1	21.0	25.0
a. The low selectivities (zero) are most likely not real.					

Table XII.4									
Influence of Ru on the Production of C ₉ ⁺ (from ref. XII.3)									
		% Selectivity to C ₉ + Fraction Catalyst from Example Number in Table XII.3				% Olefins in C ₉ + Fraction Catalyst from Example Number in Table XII.3			
No.	Temp., °C	1	2	3	4	1	2	3	4
22	200	41	88	87	--	29	4	5	3
23	300	30	75	71	73	32	10	9	7
24	400	18	41	38	34	48	30	26	21

Table XII.5					
Products Using a Prerduced Co-Th-Alumina Catalyst (from ref. XII.5)					
Example No.	2	3	4	5 ²	6 ³
Temp., °C	175	185	195	205	194
H ₂ /CO	1:1	1:1	1:1	1:1	2:1
CO Flowrate (cm ³ /gram/hour)	155	155	270	610	270
CO Conversion Rate (cm ³ /gram/hour)					
To CO ₂	0.2	1.1	1.6	2.9	(1.3)
To Hydrocarbons	19	41	61	79	(120)
CO Conversion (Percent)	13	27	23	13	44
Product Distribution (Carbon Atom %)					
CH ₄	4	5	6	8	9
C ₂ -C ₄	6	7	8	10	9
C ₅ -C ₈	23	25	29	34	24
C ₉ -C ₂₀	62	59	50	44	49
C ₂₁ +	5	4	7	4	9
2. Separate run. 3. Not aged at 205°C.					

Table XII.6	
Alpha Values for Runs Shown in Table XII.5 (From ref. XII.5)	
Run Number	Alpha, Based on C ₅ -C ₈ /C ₉ -C ₂₀
2	0.89
3	0.82
4	0.83
5	0.79
6	0.74

Table XII.7				
Impact of ROR (reduction-oxidation-rereduction) of a Co Catalyst (from ref. XII.6)				
	CO Conversion Rate (cc/gram Co/hour)		C ₅ + Liquid (Wt.%)	
Catalyst	R350	ROR	R350	ROR
A	1230	1485	73	81
B	790	1190	80	79
C	690	960	81	--

Table XII.8					
Influence of Ru on Activity of a Co Catalyst (from ref. XII.7)					
		Co/Ru Ratio		195°C CO Conversion Rate (cc/gram metal/hour)	
Test No.	Ru (Wt.%)	(Wt.)	(Molar)	R350 (F)	ROR (G)
1	0.0	---	---	382	476
2	0.05	400	693	780	968
3	0.10	200	346	879	1093
4	0.50	40	69	1034	1415
5	1.00	20	35	930	1286

Table XII.9 Influence of Temperature on a Co-Th-Alumina Catalyst (from ref. XII.8)					
Example No.	2	3	4	5	6
Temp., °C	195	195	195	205	215
Pressure, psia	15	15	30	30	30
H ₂ /CO	1:1	2:1	2:1	2:1	2:1
CO Flowrate (cm ³ /gram/hour)	310	310	735	735	735
CO Specific Rate (cm ³ /gram/hour)	70	95	102	200	257
C ₅ + Synthesis Rate (mg/gram/hour)	38	48	47	83	97
Product Distribution Carbon (Atom %)					
CH ₄	6	10	15	19	22
C ₅ +	88	79	73	64	58
C ₉ -C ₂₀	57	45	41	32	25
C ₂₁ +	9	5	6	4	1
CO ₂	2	2	1	2	2

Table XII.10 Influence of Silicalite on the Product Distribution (from ref. XII.9)				
	Co/ThO ₂ /Al ₂ O ₃		Co/ThO ₂ /Al ₂ O ₃ + Silicalite	
Carbon No.	Carbon Atom %	Wt.% n-Paraffin in Fraction	Carbon Atom %	Wt.% n-Paraffin in Fraction
1	4.7	(100)	11.3	(100)
2	0.7	50	1.8	75
3	2.5	15	8.4	24
4	3.5	20	23.2	25
5	5.0	25	23.1	35
6	6.1	33	14.9	45
7	6.8	46	9.0	38
8	7.5	56	4.8	22
9	8.5	58	2.3	13
10	9.4	62	0.9	5
11+	45		1	

Table XII.11			
Products from the Conversion of Syngas with a Co-Silica-Alumina Catalyst (from ref. XII.14)			
	Temperature, °C		
	175	185	195
Yield, Wt. %			
C ₁ -C ₄	22	25	34
C ₅ -C ₁₁	54	60	57
C ₁₂ +	24	15	9
Relative Rate, mg/g/hr ^a			
C ₁ -C ₄	0.3	0.5	1.1
C ₅ -C ₁₁	0.7	1.2	1.8
C ₁₂ +	0.3	0.3	0.3
a. The units or the numerical values are probably in error. They may be specific rates (mg/g cat/hr) but if this is the case, the magnitude of the values are questionable. In any event, it appears that the rates are only about one-tenth that of a good Co-Al₂O₃ catalyst. The low activity may be due to the difficulty of reducing Co in the above catalysts.			

Table XII.12				
Effect of Thoria Concentration on Product Composition (from ref. XII.15)				
			Mol % Selectivity to	
Example No.	Wt. % ThO ₂	% CO Conversion	CH ₄	C ₂₊
30	0.5	31.1	92.0	8.0
31	1.5	29.0	55.0	45.0
32	2.0	30.5	57.0	43.0
33	3.0	33.2	57.5	42.5
34	5.0	31.0	54.3	45.7
35	10.0	28.6	55.5	44.5
36	20.0	21.4	58.2	41.8
37	30.0	11.2	50.3	49.7

Table XII.13				
Relation of Catalyst Composition to Conversion and Product Selectivity (from ref. XII.15)				
Exempl e No.	Catalyst	Wt.% Rare Earth	% CO Conversion	% Selectivity to C ₂₊
11	Ni-Chrysotile	0	17.0	0
38	Th-Ni Chrysotile	2	31.5	43.0
39	La-Ni Chrysotile	2	25.0	39.0
40	Ce-Ni Chrysotile	2.5	32.5	32.1
41	Pr-Ni Chrysotile	2	35.3	35.0
42	Th + La-Ni Chrysotile	2 + 2	71.5	49.0
43	Th + Pr-Ni Chrysotile	2 + 2	69.1	48.0

Table XII.14					
Conversion Data for Syngas Conversion Using Fixed-Bed and Slurry Reactors (from ref. XII.17)					
Test Number	1	2	3	4	5
Reactor Type	fixed-bed	slurry	slurry	slurry	slurry
Temperature, °C	215	225	230	235	240
CO Conversion rate (ccCO/g/h)	215	649	808	992	1210
CO Conversion, %	45.3	8.4	10.4	12.8	15.6
Product Yields, Methane, wt. %	26.6	10.5	11.5	12.5	14.0
C ₅ -C ₂₀ (mg/g/h)	67	325	400	478	560
C ₅ +, wt. %	60.0	79.0	78.0	76.0	73.0

Figure XII.1. G.B. process, remote natural-gas conversion (from ref. XII.2).

Figure XII.2. Effect of pressure on catalyst activity (relative rate based on data as given in Table XII.1) (from ref. XII.2).

Figure XII.3. Effect of temperature on catalyst activity (relative rate) (from ref. XII.2).

Figure XII.4. Schematic diagram of the pilot plant remote-gas-to-diesel fixed-bed process (from ref. XII.2).

Figure XII.5. Effect of temperature and H_2/CO on carbon monoxide conversion (from ref. XII.2).

Figure XII.6. Catalyst activity (from ref. XII.2).

Figure XII.7. Catalyst productivity (specific rate) (from ref. XII.2).

Figure XII.8. G.B. demonstration plant, block-flow diagram (from ref. XII.2).

Figure XII.9. The impact of Ru (# data points) on a Co (MgThO_x) catalytic conversion as a function of temperature (data from XII.3).

Figure XII.10. Anderson-Schulz-Flory plot of the products from the synthesis using a Co catalyst and one also containing Ru, Mg and Th) (data from XII.3).

Figure XII.11. Co dispersion measurements as a function of temperature (data from XII.5).

Figure XII.12. Dependence of CO conversion on the temperature (numbers in figure are the GHSV) (data from ref. XII.5).

Figure XII.13. Hydrocarbon product distribution for a cobalt catalyst as a function of temperature (data from XII.5).

Figure XII.14. Anderson-Schulz-Flory plot of the products from the Fischer-Tropsch synthesis with a cobalt (Th, Al₂O₃) catalyst alone (F) and physically admixed with a silicate zeolite catalyst (G) (data from XII.9).

Figure XII.15. Wt% N-alkane in the carbon fractions of the products from Fischer-Tropsch synthesis with cobalt (Th, Al_2O_3) catalyst (F) and physically admixed with silicate zeolite (G) (data from XII.9).

Figure XII.16. Methane production for synthesis in fixed-bed reactor with different particle size catalysts (from XII.17).

Figure XII.17. C_5+ product selectivity for three particle size catalysts in fixed-bed reactor (! , 185°C, $H_2/CO = 2$; ▲, 195°C, $H_2/CO = 2$; G, 195°C, $H_2/CO = 1.5$) (from XII.17).

Figure XII.18. Reaction rate for CO conversion in fixed-bed reactor for three particle size catalysts (! , 185°C, $H_2/CO = 2$; ▲, 195°C, $H_2/CO = 2$; G, 195°C, $H_2/CO = 1.5$) (from XII.17).

Figure XII.19. Process schematic for slurry reactor system using cobalt catalyst (from XII.17).

Figure XII.20. Arrhenius plot for CO conversion in slurry reactor with Co catalyst (data from XII.17).

Figure XII.21. CO conversion and C₅+ product selectivity for FTS using slurry reactor and cobalt catalyst (data from XII.17).

ATTACHMENT XIII

Review of Fischer-Tropsch Work by Statoil

Three patents on Fischer-Tropsch synthesis catalysts assigned Den Norske Stats Olijeselskap A.S., Norway by Norwegian and U.S. investigators are summarized below (XIII.1-XIII.3). These individuals summarize the background for their invention. Anderson's book (XIII.4) is taken as the main background for the inventions and consider this book to indicate that the common Fischer-Tropsch (FT) catalysts are nickel, cobalt and iron. Nickel is considered to be active but it produces mainly methane. Among the Group VIII metals (old U.S. Periodic Table nomenclature), ruthenium is a very active catalyst and produces mainly hydrocarbons. Ruthenium is considered to have higher activity than Fe, Co or Ni at low temperatures. Other metals which possess high activity are considered to produce oxygenates and the patentees cite rhodium as an example (XIII.5). Osmium is considered to have moderate activity and Pt, Pd and Ir to have low activity (XIII.4,XIII.6,XIII.7).

These investigators recognize that others have used various combinations of metals for Fischer-Tropsch Synthesis (FTS). For example, nickel-doped cobalt has a higher productivity of methane than cobalt alone (XIII.8). On the other hand, Kobylinski taught that the addition of small amounts of ruthenium to a cobalt catalyst provided a material with a higher activity and with lower methane production than a similar catalyst comprised of cobalt without the ruthenium (XIII.9). Other work has documented that the activity is higher when ruthenium is added to the catalyst but the lower methane make is not as well documented.

These investigators indicate that, "In general, the catalysts [of combinations of metals] of these [prior] teachings have activities and selectivities which are within the

ranges of the individual components." They also note that the combination of a metal with certain oxide supports may lead to higher productivity of products, presumably due to the increase in surface area of the active metal component. The authors cite the case of using titania to support cobalt or cobalt-thoria (XIII.10) with a resulting increase in activity for the production of hydrocarbons and, by implication, attribute this beneficial effect to strong-metal-support-interactions (SMSI) (XIII.11).

Statoil investigators also indicate that a patent (XIII.12) teaches that combinations of cobalt, rhenium and thoria or cobalt and rhenium supported on titania are useful for hydrocarbon production. The patent indicates that similar improvements in activity can be obtained when using other inorganic oxide supports; however, the inventors indicate that titania is the only support specifically discussed in reference 12. These workers indicate that, "The typical improvement [reported in reference 12] in activity gained by promotion of cobalt metal supported on titania with rhenium is less than a factor of 2."

The major teaching of the Statoil patent is that the choice of support for Co is critical, "and the addition of a small amount of rhenium to an alumina—supported cobalt catalyst gives a much greater improvement in activity than the addition of rhenium to cobalt supported on any other inorganic oxide. To be effective as a support for cobalt, the alumina should possess low acidity, high surface area and high porosity. The method of adding the active metals to the alumina support is, according to the inventors, not critical.

Included in inventions by the Statoil investigators is the finding that it is beneficial to include a small amount (0.1 - 5%, preferably 0.1 to 2 wt.%) of a metal oxide promoter

in addition to cobalt and rhenium. The inventors conclude that the most preferable metal oxide is La_2O_3 or a mixture of lanthanides rich in La.

After preparation, the catalyst is calcined in a specified manner ultimately to attain a preferred temperature between 250 and 350°C for 2-5 hours. To activate the catalyst, it is reduced in hydrogen, again using a specified heating ramp to attain a preferred temperature of 300-400°C and holding at this temperature for 6-24 hours. Catalyst passivation and rereduction cycles may be carried out.

Catalyst testing was accomplished with a $\text{H}_2/\text{CO} = 2$ synthesis gas. A fixed-bed reactor (0.5 g catalyst) was utilized at atmospheric pressure and temperatures of 185, 195 and 205°C [a standard testing procedure involved 9.82 hr at 195°C, 4.3 hr at 205°C, 4.5 hr at 185°C and 9.5 hr at 195°C]. The flow rate of synthesis gas was 1.68 L/g catalyst/hr. Catalysts were compared using results obtained during the period of 10 and 30 hours-on-stream.

A series of identical catalysts (12 wt.% Co, 1 wt.% rare earth oxide), except for the content of rhenium, were prepared. For the alumina supported catalyst, there was a greater than 3-fold increase in CO conversion as Re content increases to about 1 wt.% and then a gradual decline in CO conversion was noted for further increases in Re content Figure XIII.1). The incorporation of these amounts of Re did not substantially increase the production of either methane (10-14%) or CO_2 (0.6-1.3%).

Two series of catalysts were prepared in which the Co loading was increased, one series with and one without rhenium. Re was added so as to keep the wt.% Co/wt.% Re constant at 12 for 3, 6 and 9 wt.% Co; for the 20 and 40 wt.% Co formulations, the ratios were 0, 4, 20 and 0, 8, 20 and 40, respectively. The impact of Re is evident in Figure XIII.2 (apparently the data for the 20 and 40% Co are for Co/Re

ratio of 20 samples in Table V of reference XIII.1). This patent indicates that the improvement in activity due to the addition of rhenium increases as the cobalt content increases.

The Statoil investigators report that,

"The catalysts in Table VII (Table XIII.1 of this report) were prepared to test the teaching that various inorganic supports are acceptable for preparing cobalt plus rhenium F-T catalysts. An examination of the data in Table VIII (Table XIII.2 of this report) leads to the surprising conclusion that the type of support is extremely important and that vast differences in activity exist between catalysts prepared on one support and catalysts of the same catalytic metals content on another support. More surprisingly, only cobalt plus rhenium on alumina showed a commercially attractive activity level and selectivity."

Some may question the conclusion that a selectivity that includes 13-18 wt.% methane is a commercially attractive catalyst.

The MgO and Cr₂O₃ supports provide catalysts with very low activity. The zirconia and silica-alumina supported catalysts showed improved but low activity and poor selectivity for C₂⁺. For silica and titania supports, the cobalt only catalysts exhibited activities similar to an alumina supported cobalt catalyst. However, for the addition of rhenium to the alumina, titania and silica cobalt catalysts, a significant improvement was observed **only** for the material employing alumina as a support. The authors report that, "This [latter] result is surprising and would not have been predicted based on teachings in the prior art." [This does not appear to be in complete agreement with some Exxon patents.]

The "Weisz Window" provides a rule-of-thumb estimation of the productivity needed for commercial operation as $10^{-5} - 10^{-6} \text{ mole sec}^{-1} (\text{cm}^3 \text{ reactor})^{-1}$ (XIII.13). In the following we assume: (1) a fixed-bed reactor, (2) the density of the alumina supported catalyst as 2 g/cm^3 , (3) the flow of syngas as 1.88 NL/hr/g and (4) $\text{H}_2/\text{CO} = 2$. From Table XIII.2 for the Re containing catalyst (example 8), the CO conversion is 33%. Thus we calculate that the conversion of CO is 0.209 NL/hr/cm^3 . Using this value, we calculate that the conversion of CO is $0.52 \times 10^{-5} \text{ mole/cm}^3/\text{sec}$; this is close to the value of the Weisz Window. If the rate increases directly with pressure, then the conversion is in the Weisz Window at 10 atm.

The incorporation of alkali in the cobalt catalyst impacts both the activity and hydrocarbon product distribution. For a catalyst containing Co, Re and rare earth oxide, the incorporation of alkali caused (1) a decrease in CO conversion and (2) an increase in the alpha value of the products (Tables XIII.3 and XIII.4; Figures XIII.3 and XIII.4). However, the conclusion that the alpha value depends upon the K/Co ratio depends entirely upon the two data points obtained for the lowest to K/Co ratios. If these two points are not reliable (or are not considered), the K/Co ratio has no impact upon the value of alpha. The question of promotion changing activity and selectivity is complicated for a cobalt catalyst. Anderson pointed out that selectivity changes can be effected by changing reactor pressure (XIII.14).

van Berge and Everson (XIII.15) point out that the data in reference 1 were obtained at different conversion levels, and thus different reactor partial pressures, and that the chain of chemical promotion by K, Na, Cs and Rb could not be regarded as conclusive. Studies performed at Sastech (XIII.16) are reported to confirm the ineffectiveness of chemical promotion of cobalt Fischer-Tropsch catalysts.

The loss of activity with increasing alkali content allows one to calculate, assuming one K eliminates 1 site, that only 4.5 atomic % of the Co is catalytically active. At first glance, it appears that the data are consistent with each potassium eliminating one catalytic site, or some constant fraction of a site (Figure XIII.4). However, it must be realized that the addition of alkali causes an increase in $\ln \alpha$, and a corresponding increase in the average molecular weight of the products. The average number of growing chains, and the average number of catalytic sites, is directly proportional to the average molecular weight of the growing chains (e.g., the average molecular weight of the products). Hence,

$$\overline{\text{No. of Sites}} \propto \overline{M.W.} = 1/(1 - \alpha).$$

When this is taken into account, the catalytic sites decrease more rapidly than the increase in K, or at least those catalytic sites that initiate chain growth must do so (Figure XIII.5).

During the past few years, Statoil has obtained patents related to a catalytic multi-phase reactor, and specifically to catalyst wax separation (XIII.17-XIII.21). An example of such a reactor is illustrated in Figure XIII.6 (XIII.17). "This is a solid/liquid slurry reaction apparatus which comprises: a reaction vessel **(11)**, a filter member **(13)** in contact with the slurry **(16)** defining a filtrate zone which is separated from the slurry and having an outlet **(23)** for filtrate product **(32)**; means for establishing a mean pressure differential across the filter member; means for causing fluctuations or oscillations about the mean pressure differential; and means for introducing gaseous reactants or other components in the form of gas bubbles into the slurry (XIII.17)."

One of the claims is for a filter element **(22)** which comprises a fine meshed screen, helically wound threads, fine vertical threads or sintered metal particles (XIII.17). The hydrostatic pressure preferably results from the filter member being submerged in the slurry.

The pulsating pressure can be applied directly to the filtrate or to the gas space above the filtrate, preferably by the action of a reciprocating piston in a cylinder. The pressure fluctuation may be of the order of 10 to 200% differential (preferably 2 to 5 mbar).

The filter element material and catalyst are preferably selected so that the maximum hole or pore size of the filter element is of the same order of the catalyst particle size. It might be expected that catalyst would plug the filter but this is found not to be the case. Of course, the particle size of the catalyst may be much larger than the maximum hole or pore size of the filter.

In operation, products pass through the filter element **(12)** to form a product filtrate **(32)** which is free of catalyst. Any gaseous products and unconverted reactants that pass through the filter element can be vented through outlet **(31)** and subsequently through **(17)**. The product filtrate **(32)** leaves through level device **(23)** and outlet **(24)** to collect in **(25)** for regulated continuous or periodic removal.

In an example, a reactor of 4.8 cm x 2 m dimensions was filled with approximately 10 wt.% of a Co on alumina catalyst (30 to 150 μm). The gas (H_2 , CO and N_2) was fed at a superficial gas velocity of 4 cm/s. The temperature was 230°C and pressure was 30 bar.

The filter unit was located in the upper part of the reactor and comprised of Sika stainless steel sintered metal cylinder Type R20 produced by Pressmetall Krebsöge

Gmbh. The filter had an outer diameter of 2.5 cm, a height of 25 cm and an average pore diameter of 20 μm .

The slurry was effected using a poly- α -olefin liquid. Fischer-Tropsch product **and a poly- α -olefin that was fed to the reactor** were both withdrawn through the filter unit (ratio of Fischer-Tropsch and poly- α -olefin not specified). Liquid withdrawal rate varied from 2.5 to 320 g/hr, depending on Fischer-Tropsch synthesis rate and feed rate of poly- α -olefin. The experiment lasted for about 400 hrs and approximately 30 liters was withdrawn through the filter unit. Most would therefore conclude that the test was of a short duration compared to the length of time that a commercial unit must operate. Furthermore, the product was diluted with start-up solvent that was added during the run. Thus, it appears that this example is applicable to a limited process scheme, and not for all process schemes.

A solid/liquid slurry reaction apparatus with a filtration section has been submitted for patent coverage (XIII.22) and is illustrated in figure XIII.7. The teachings of this patent application is based upon a recent report identified only as "a report issued by the United States Department of Energy." The DOE report addressed the question of catalyst/wax separation in Fischer-Tropsch slurry reactor systems and concludes:

"Internal filters immersed in the reactor slurry, as used in some bench-scale or pilot-scale units, do not work successfully due to operational difficulties. A reactor with a section of its wall as a filter may be operable for a pilot plant but is not practicable for commercial reactors. Internal filters are subject to plugging risks, which may cause premature

termination of the run, and commercial plants are not allowed to take chances."

The patent applicants have discovered that, contrary to the teachings of the DOE report, "...it is possible to provide a continuous reaction system for a Fischer-Tropsch synthesis in which it is not necessary to perform the solid/liquid separation in an external filter unit. Furthermore, a sufficiently high flow rate of filtrate for commercial operation can be achieved."

The description in the patent application indicates that the filter screen and the catalyst are similar, or identical, to those described in the previous patent application (XIII.17). In this instance, however, the filter screen has been made a part of the slurry reactor wall or, as shown in figures XIII.8 and XIII.9, it may be incorporated in multiple locations of the slurry reactor wall. In the example shown in figure XIII.7, a conical section **(15)** is included as an expansion chamber to prevent the slurry from foaming over and to define a gas space **(16)** above the reaction zone. The cone-shaped portion **(15)** may contain additional means (that are not shown nor specified) for breaking up or reducing foam formation.

The invention was described and was then further illustrated with the following example. Experiments in a laboratory using an apparatus similar to that shown in figure XIII.7 were carried out. The length and diameter of the unit were 1250 mm and 55 mm, respectively. The filter member had a mean pore size of 30 μm and a length of 200 mm. A heat transfer oil (diethyl benzene (95%) and minor amounts of other alkyl benzenes) and 20 wt.% alumina were used as the slurry phase. The alumina particles initially had a cut-off at 53 μm . The experimental conditions in the example were: 1 bar pressure, 20-25°C and 6 cm/s superficial gas velocity. After an initial start-up period,

the separation capacity became approximately constant at a level of 750-800 kg/m²h. The calculated pressure differential was approximately 5 mbar. After 40 days of operation, there was only a slight decrease in separation capacity.

The section of the DOE report that was quoted above was concerned with an operating slurry bubble column reactor for Fischer-Tropsch synthesis at a commercial scale operation. The example provided by the patent applicants was for a cold model with only an alumina solid and without Fischer-Tropsch synthesis. It would appear that the patent applicants have not shown by their example anything that would be contrary to the teachings of the DOE report since the patent applicants did not operate at any of the conditions necessary for a commercial Fischer-Tropsch plant that is currently being operated successfully.

Another patent application (XIII.19) relates to a vessel that contains a number of vertical reaction tubes, each suitable for multi-phase catalytic conversions (figure XIII.10). In this application, the above DOE report is quoted and the teaching that the applicants have provided a means of accomplishing this. Each reactor tube has essentially the features of the reactor described in the previous reference XIII.ref. 18). In operation, the gas is preferentially fed to each multi-phase catalytic reactor. These reactors are held in place by plates **(18)** and **(14)**; in effect these two plates and the vessel wall **(12)** provide the vessel to hold the heat transfer liquid/vapor.

The filter section of each reactor tube is located above the top plate **(14)**, which serves to hold a level of the wax following separation from the catalyst slurry. In another version, a sieve **(34)** surrounds each filter and is utilized to maintain a minimum wax level for each reactor tube so that the tube does not lose liquid level so that the

reactor tube is depleted of liquid. Thus, the sieve extends above the level of the wax filtrate that is maintained on plate **(14)**.

The heat exchange medium is preferably a liquid at its boiling point; water is the preferred medium since the heat of reaction can be recovered as steam to be used to generate electricity or provide heat for plant operations.

In the only example of the patent application, a slurry bubble column Fischer-Tropsch reactor **is simulated** using a two phase quasihomogeneous one dimensional model. They use typical catalyst performance data contained in US 4,801,573. The simulations are utilized to **calculate** optimum values for the reactor and its operation. **Experimental data of an operating Fischer-Tropsch reactor are not provided in the application.** Since the DOE report was for an operating reactor that actually effects a separation of wax and catalyst, it is difficult to understand how the applicants can show that they have provided a solution to the problems enumerated in the DOE report.

A patent application (XIII.20) describes a separation device that has as its main object the prevention of gas from being entrained in the liquid phase in cases where it is desirable to separate gas and liquid or immiscible liquids.

A recent patent application describes a method of regenerating a catalyst in a Fischer-Tropsch synthesis reaction (XIII.21). Examples of regeneration procedures are reviewed and the conclusion is that "These arrangements all suffer the drawback that a separate source of H₂ gas must be provided to achieve regeneration." The present invention (XIII.21) is to overcome this drawback. While the use of hydrogen could be a drawback, it would appear to be so only from an operational viewpoint. For example, Sasol produces a nearly pure hydrogen stream by a pressure swing adsorption process.

It would be a disadvantage to utilize a stream of pure CO since this stream is not available in a normally operating Fischer-Tropsch plant.

Schematic sections through a slurry reactor (figure XIII.12) and a slurry reactor with a separate regeneration vessel (figure XIII.13) are shown. Details of the slurry reactor (figures XIII.12 and XIII.13) are not provided in this patent. To effect regeneration, the feed parameters of the synthesis gas are adjusted to increase the conversion of CO in the synthesis gas until the H_2/CO ratio of the gas leaving the reaction zone exceeds 10:1 and then maintaining this conversion level during the regeneration mode for some period of time to effect regeneration to a desired level. Preferable, the CO conversion is between 95 and 100%, most preferable 100%. Thus, the preferred H_2/CO ratio is 20/1, and most preferably, greater than 30/1. To achieve this high hydrogen/CO ratio, the flow is decreased, preferably slowly, so that the conversion increases to attain the desired level. Alternatively, hydrogen could be increased in the synthesis gas by modification of the generation step of the synthesis gas.

At the high conversion level, the reaction changes from synthesis to a regeneration mode. The regeneration mode is characterized by: high H_2/CO ratio, low C_{5+} selectivity and high CO_2 selectivity. This is taken to indicate a high water gas shift rate due to the high hydrogen partial pressure. Experimentally, it has been found that a few hours of regeneration is normally sufficient; however, it may take longer for more severely deactivated catalysts.

When a separate regeneration vessel is used, "normal" conditions for synthesis are maintained on the synthesis side and the high hydrogen (100% CO conversion)

condition is maintained on the regeneration side. Preferably, there is a flow of deactivated and regenerated catalyst between the two sides.

Two examples are given for the regeneration. In the first example, a catalyst containing 12% Co and 0.5% Re on alumina are used at 220°C and 20 bar (2 MPa) total pressure in a continuous slurry stirred tank reactor (CSTR). The reactor volume is 2 L and is half-filled with slurry. The H₂/CO inlet synthesis gas ratio was 2; the exit gas was also close to this value. The initial stable hydrocarbon activity is set relative to 1; note that this is based on hydrocarbon production. The CO conversion was 63% at this hydrocarbon production level of 1.

After the catalyst had operated for a few days, the catalytic activity had declined so that the relative hydrocarbon productivity activity number had declined to 0.69. At the relative activity number of 0.69, the CO conversion was 68% at a flow rate of 2100 NL/kg cat./hr. It is not clear whether this flow rate is for synthesis gas or for CO only; in the following we shall **assume that the flow is for CO only**. The C₅₊ selectivity was 89.4%. At this stage of catalyst deactivation, a decrease of the flow rate to 1050 NL/kg cat/hr resulted in an increase in CO conversion to 88% with a C₅₊ selectivity of 89.9%.

To establish a regeneration mode at this point (0.69 relative activity), the flow rate was reduced to 750 NL/kg cat/hr and the CO conversion was 99%. The exit H₂/CO ratio was 14/1. This regeneration mode was maintained for 10 hours and was then brought back to the Fischer-Tropsch mode by increasing the flow rate to 2100 NL/kg cat/hr. The reaction continued to produce a C₅₊ selectivity of over 88%. The relative activity at these final Fischer-Tropsch conditions was 0.77. This value is above the value of 0.69 for the deactivated catalyst but still considerably below the value of 1.0 for the fresh catalyst.

Example 2 is for a catalyst that contains 20% Co and 1% Re on alumina; however, the data are less extensive than for example 1. They report that the 20 wt.% Co catalyst was brought back to the initial level following 24 hours of the regeneration mode whereas 10 hours for the 12 wt.% Co catalyst only restored the activity to 77% of the initial activity.

The hydrocarbon production of the deactivated catalyst (relative activity of 0.69) in Example 1 corresponds to 0.983 g hydrocarbon/g cat/hr. For the fresh catalyst (relative activity of 1.0) the hydrocarbon productivity is calculated by us to be 1.29 g hydrocarbon/g cat/hr. For the reactivated catalyst (relative activity 0.77) the productivity is 1.16 g hydrocarbon/g cat/hr.

If it is assumed that the catalyst productivity is linear in Co content, the productivity of the deactivated 20 wt% Co catalyst would be 1.49 g hydrocarbon/g cat/hr and that of the fresh and regenerated catalyst would be 2.15 g hydrocarbon/g cat/hr.

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Table XIII.1 (from ref. XIII.1)						
			Weight of Materials in Impregnating Solution, g		Composition of Finished Catalyst, Wt.%	
Example No.	Support	Weight of Support, g	Co(NO ₃) ₂	HReO ₄ *	Co	Re
28	Silica	20	13.47	---	12	---
29	Silica	20	13.62	0.38	12	1.0
30	Titania**	25	16.84	---	12	---
31	Titania**	24.64	16.78	0.46	12	1.0
32	Titania***	25	16.84	---	12	---
33	Titania***	24.64	16.78	0.46	12	1.0
34	Chromia	20	13.47	---	12	---
35	Chromia	21.3	14.51	0.40	12	1.0
36	Magnesia	21.59	14.54	---	12	---
37	Magnesia	14.54	10.67	0.29	12	1.0
38	Silica- alumina	20	13.47	---	12	---
39	Silica- alumina	20	13.62	0.38	12	1.0
40	Zirconia	20	13.47	---	12	---
41	Zirconia	20	13.62	0.38	12	1.0
* Weight of 82.5% perrhenic acid solution. ** Calcined at 500°C. *** Calcined at 600°C.						

Table XIII.2 (from ref. XIII.1)

Example No.	Co %	Re %	Support	CO Conversion %	C ₂ ⁺ Selectivity %	CH ₄ Selectivity %	CO ₂ Selectivity %
1	12	---	Al ₂ O ₃	12	90.0	8.9	1.1
8	12	1	Al ₂ O ₃	33	87.7	11.4	0.9
28	12	---	SiO ₂	11	90.1	8.7	1.2
29	12	1	SiO ₂	12	88.1	10.7	1.2
30	12	---	TiO ₂ [*]	11	87.6	11.8	0.6
31	12	1	TiO ₂ [*]	17	86.5	12.8	0.7
32	12	---	TiO ₂ ^{**}	11	87.6	11.7	0.7
33	12	1	TiO ₂ ^{**}	17	85.8	13.5	0.7
34	12	---	Cr ₂ O ₃	1	83.5	15.5	1.0
35	12	1	Cr ₂ O ₃	2	80.8	12.3	6.9
36	12	---	MgO	0.3	20.0	30.0	50.0
37	12	1	MgO	0.3	19.1	30.9	50.0
38	12	---	SiO ₂ /Al ₂ O ₃	5	76.3	22.2	1.5
39	12	1	SiO ₂ /Al ₂ O ₃	6	78.6	19.8	1.6
40	12	---	ZrO ₂	4	80.9	16.3	2.8
41	12	1	ZrO ₂	7	78.8	18.7	2.5

* Support calcined at 500°C.

** Support calcined at 600°C.

Table XIII.3 (from ref. XIII.1)										
Example No.	Wt. of Al_2O_3 , g	Type of Alkali	Weight of Material in Impregnation Solution, g				Composition of Finished Catalyst, Wt. %			
			(a)	(b)	(c)	(d)	Co	Re	RE	Alkali
42	300.0	---	1039.65	17.21	13.99	---	40	2.0	1.0	0.0
43	75.0	K	260.46	4.31	3.50	0.34	40	2.0	1.0	0.1
44	75.0	K	256.36	4.25	---	0.67	40	2.0	---	0.2
45	175.0	K	609.03	10.08	8.20	1.59	40	2.0	1.0	0.2
46	100.0	K	349.50	5.79	4.70	1.83	40	2.0	1.0	0.4
47	100.0	K	354.03	5.86	4.76	4.64	40	2.0	1.0	1.0
48	60.0	Na	205.49	3.40	---	0.93	40	2.0	---	0.24
49	60.0	Cs	209.55	3.47	---	2.12	40	2.0	---	1.36
50	65.0	Rb	225.38	4.23	---	1.71	40	2.0	---	0.87
51	20.0	---	13.78	0.38	0.62	---	12	1.0	1.0	---
52	20.0	K	13.80	0.38	0.62	0.06	12	1.0	1.0	0.1
53	20.0	Li	13.64	0.38	---	0.11	12	1.0	---	0.05
54	20.0	Li	13.80	0.38	0.62	0.12	12	1.0	1.0	0.05
55	20.0	Cs	13.67	0.38	---	0.10	12	1.0	---	0.3
56	20.0	Cs	13.83	0.38	0.62	0.10	12	1.0	1.0	0.3
(a) $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (b) 82.5% HReO_4 solution, except for example 50 which was 72.9% HReO_4 (c) Rare earth nitrates (RE) (see example 1) (d) LiNO_3 , NaNO_3 , KNO_3 , RbNO_3 or CsNO_3										

Table XIII.4 (from ref. XIII.1)					
	Alkali				
Example No.	Type	Content Wt. %	CO Conversion %	CH ₄ Selectivity %	Product Alpha*
42	---	---	52.5**	14.2**	0.75**
43	K	0.1	52 50	8.6 11.1	0.86 0.79
44	K	0.2	43	9.3	0.83
45	K	0.2	51 44 41	9.5 11.6 9.4	0.84 0.84 0.81
46	K	0.4	30 35	7.3 7.8	0.87 0.85
47	K	1.0	12 9 6	7.0 7.9 6.2	0.88 0.85 0.87
48	Na	0.24	21	8.3	0.82
49	Cs	1.36	14	8.5	0.86
50	Rb	0.87	11	7.3	0.86
51	---	---	31.7***	10.9***	0.77***
52	K	0.1	19 22	7.6 9.8	0.78 0.84
53	Li	0.05	31	11.7	0.78
54	Li	0.05	27	12.0	0.78
55	Cs	0.3	21	11.1	0.83
56	Cs	0.3	21	10.3	0.84
* Calculated by plotting $\ln(W_n/n)$ vs. n, where n is carbon number and W_n is the weight fraction of the product having a carbon number n, and determining the slope of the line. ** Average of 21 tests. *** Average of 6 tests.					

Figure XIII.1. Effect of rhenium on CO conversion catalysts containing 12% cobalt (from ref. XIII.1).

Figure XIII.2. Effect on conversion of adding rhenium to cobalt on alumina catalyst (from ref. XIII.1).

Figure XIII.3. Alpha versus K/Co (from ref. XIII.1).

Figure XIII.4. Percent CO conversion versus K/Co (from ref. XIII.1).

Figure XIII.5. Percent CO conversion versus K/Co (from ref. XIII.1) and our decrease calculated assuming α is related directly to the site density.

Figure XIII.6. Slurry reactor with internal filter for wax/solids separation from ref. XIII.17).

Figure XIII.9. Slurry reactor incorporating multiple filtration systems into the reactor wall (from ref. XIII.22).

Figure XIII.10. A multi-phase catalytic reactor with multiple tubes for slurry phase reactor systems (from ref. XIII.19).

Figure XIII.11. Schematic of sleeve on reactor tube in Figure 10 to maintain slurry level in each reactor tube (from ref. XIII.19).

Figure XIII.12. Schematic of slurry phase reactor with internal wax/catalyst separation unit that can be used for regeneration of a Fischer-Tropsch catalyst (from ref. XIII.21).

Figure XIII.13. Schematic of slurry phase reactor with external wax/catalyst separation unit that can be used for regeneration of a Fischer-Tropsch catalyst (from ref. XIII.21).

ATTACHMENT XIV

Review of Fischer-Tropsch Work by Rentech

Rentech has obtained eight patents to date [October 10, 1996] [XIV.1-XIV.8].

The drawings, background of the invention and objectives of the invention are identical [except for combining some paragraphs and minor changes in a few paragraphs such as "A further object ..." rather than "It is yet another objective..."]

The background provides a brief description of earlier work [XIV.9-XIV.14]. They indicate that today there are two primary methods for producing syngas from methane: steam reforming and partial oxidation. The primary advantage of partial oxidation over steam reforming is indicated to be that the reaction is self-sustaining and the only heat that must be added is the initial preheating of the reactants. Another advantage is that a lower ratio of H_2/CO is produced, and that it more nearly matches that needed for the FTS. In addition, the CO_2 and/or hydrogen need not be removed from the syngas prior to the synthesis.

The authors indicate that "...the Fischer-Tropsch reactor must typically be able to convert at least 90% of the incoming carbon monoxide."

They discuss the advantages of the two materials they consider to be attracting the most attention: cobalt and iron based catalysts. They indicate that, theoretically, a cobalt catalyst can produce higher conversion yields than an iron based-catalyst since the cobalt catalyst can approach 100% carbon conversion efficiency but that an iron catalyst tends toward 50% carbon conversion to hydrocarbons due to the extent of the water-gas-shift (WGS) reaction. They indicate that cobalt is much higher in cost, and this is likely to increase even further if the demand for cobalt increases to meet widespread development of Fischer-Tropsch synthesis (FTS).

It is indicated that recycle of the tail-gas is usually utilized to achieve 90% conversion of CO. Too much water is considered to be an inhibitor for FTS and the maximum attainable in single-pass operation is 70% CO conversion. On the other hand, the WGS activity of the iron catalyst permits operation at 90% conversion per pass without difficulty. It has been reported, contrary to this view, that even with an iron catalyst, the rate of CO conversion may decline rapidly at CO conversions above about 60% [XIV.15].

The present inventions are claimed to "...include a solution to the problems of reducing the formation of excess hydrogen from the reformer or partial oxidation unit and increasing the conversion efficiency for the entire carbon input to the system when using specifically prepared promoted iron catalysts." The patents demonstrate the use of recycle of the carbon dioxide produced during the FTS to the reformer in order to control the excess hydrogen and to improve the carbon conversion efficiency problems.

It is stated that olefins, alcohols and aldehydes are readsorbed on the catalyst and thereby participate in further chain growth. Naphtha and light diesel fractions are considered to be rich in olefins and to contain relatively large amounts of alcohols. Thus, the authors indicate that it is possible to force the reaction toward higher molecular weight by recycle of olefins, alcohols and aldehydes.

It is also proposed to convert the excess hydrogen as well as the carbon dioxide that is produced through the WGS reaction in a second FTS reactor.

A schematic of one of the process schemes is provided in figure 1. Indicated in this process is the recycle of carbon dioxide and/or recovered gas (streams 9 and 19).

The preferred catalyst is a precipitated iron catalyst that is promoted with a predetermined amount of potassium and copper. The amount of promoters depends upon the desired extent of chain growth and the product molecular weight distribution.

The preferred catalyst is unsupported. To accomplish catalyst preparation, iron and copper metal is dissolved in nitric acid. However, to minimize the emission of oxides of nitrogen, oxygen is bubbled through the solution while the metals are being dissolved.

The catalyst precursor was prepared by precipitation by the addition of ammonium hydroxide (ambient temperature) to the hot (up to 150°C copper/iron solution to produce a pH of 7.4. After cooling to 80°F, the pH is adjusted to 7.2. The slurry is pumped to a holding tank, the solid settles and the solution is removed; subsequent washings to remove ammonium nitrate are with "high quality water free of chloride". A drum filter, with water spray bars, is used to complete the washing and collection of the slurry. Aqueous potassium carbonate of the desired amount is added to the slurry and it is then thoroughly mixed. Drying, such as in a spray drier, is used to produce spherical catalyst in the size range of about 1 to 5 up to about 40 to 50 microns. The last step is heating to 600°F in a fluidized bed to remove residual moisture and to convert the hydrous iron oxide to hematite (Fe_2O_3).

The authors report that "Determining the "best" activating procedure for a catalyst is difficult at best..." In their study, high activity of the catalyst was correlated with the presence of iron carbides after the activation procedure. The most effective procedure used carbon monoxide at 325°C at 0.1 atm. pressure. The authors indicate that it may be preferable to activate in synthesis gas, and give a recipe for doing this in a controlled manner. They heat the catalyst precursor in an inert gas to 500°F and then to 540°F in

synthesis gas until the heat of reaction becomes sufficient to heat the catalyst bed at a faster rate than the applied external heat; at this point heating is terminated and cooling is effected to keep the temperature at 540°F until the CO conversion is 90%. At this point the temperature is lowered to the desired reaction temperature (450 to 525 °F) and the reactor pressure is raised from the activation pressure of 150 psig to below about 450 psig. The flow rate is adjusted to a space velocity in the range of 240 to 300 per hour.

It was reported that the activity and selectivity of the iron catalyst is improved by exposure to a hydrogen-rich synthesis gas at elevated temperature and pressure. The production of water is believed to prevent over-carburization of the catalyst, and thereby inducing the improved activity and selectivity [XIV.16].

The authors prefer a reactor design similar to that utilized by Bureau of Mines workers [XIV.17]. The gas distributor may consist of orifices or of porous metal spargers. Preferably a design using concentric rings of manifolds arranged to conform to the reactor; i.e., the largest diameter ring is at the highest and the smallest diameter at the bottom of the reactor. The reactor diameter should be selected to give a superficial velocity (actual volumetric flow rate of feed gases divided by empty reactor cross-sectional area) between about 0.02 to 0.2 meters per second. This flow should expand the bed by 30 to 45% over that of no flow conditions.

The authors prefer between 5 and 15 wt.% by weight of iron in the slurry, more preferably between 7.5 and 12.5, and most preferably 10 wt.% iron. This corresponds to 30 to 90 grams of iron per liter of expanded bed, and the most preferred is 60 g/L.

Heat removal utilizes heat exchanger tubes that commence about 1 meter above the gas distributor and extends to the top of the expanded slurry. Pressurized steam is the preferred heat transfer medium.

The preferred iron catalyst particle is between 10 and 40 microns, with 30 microns being most preferred. The preferred ratio of potassium (as carbonate) to iron is about 0.010 (0.005 and 0.015). The copper to iron ratio is preferably about 0.010.

The means of removing wax from the catalyst employed a cross flow filter. The advantage of this means is that the flow velocity of the slurry through the porous filter tubes is about 10 feet/sec and this slows down the rate of building a catalyst layer on the tube wall. When the flow has declined to a predetermined level, an inert gas is used to pressurize the shell side to remove the layer of catalyst into the slurry stream, which flows back to the reactor. They described rates for a cross-flow filter from Mott Metallurgical Corp., a filter and procedure which were found to be unsuitable for the operation at the LaPorte, Texas plant.

Catalyst can be removed from the reactor periodically by employing a slipstream.

The gaseous product stream (20, figure 1) can be used directly for process heat.

The quality of the diesel obtained from the Fischer-Tropsch synthesis are illustrated in Tables XIV.1 and XIV.2.

According to the data, the material contains 3.05 wt.% oxygen and the average carbon number is C_{14} . Assuming that the oxygen is distributed on the same basis as the hydrocarbons, then we calculate that the F/T diesel must contain about 38 wt.% alcohols in order to contain 3.05 wt.% oxygen. This value for the alcohol content appears consistent with the composition included at the bottom of Table V of U.S.

Patent 5,324,335. This would appear to be the highest content of alcohols that has been reported for Fischer-Tropsch products.

One of the catalysts utilized in the studies produces a chain-growth probability of 0.73 for carbon numbers from 1 to 9. Like Satterfield and coworkers, the patents reported that two different chain-growth probabilities were obtained.

In example 1, the authors indicate a means of calculating the carbon conversion efficiency for the overall process which is defined as the rate of production of carbon contained in the C_{5+} product in the FTS divided by the carbon atoms in the process feed. The authors state that, "Table VIII lists the product yields and carbon efficiency along with operating parameters for Example 1 and several examples discussed below." However, Table VIII does not contain a column giving efficiencies and the yield given in Table VIII is for C_{7+} rather than C_{5+} as given in the definition. It is not obvious how one can obtain the efficiencies, as defined, from the data in Table VIII. Efficiencies are given in some of the examples together with some indication of the mode of recycle; these are compiled in Table XIV.3 by the reviewer.

The carbon dioxide produced in the FTS can be recovered by absorption from the FTS tail gas and can then be recycled to the gasifier, vented to the atmosphere or stored for later sale or use.

When additional diesel fuel is desired, the wax can be heated to 410°C to effect thermal cracking. It was shown that the diesel from wax cracking contained only 0.16% oxygen whereas the diesel produced in the FTS contained 3.05% oxygen.

After removing the carbon dioxide, the tail gases from the FTS can be recycled to the FTS reactor to "...enable further chain growth of olefins and alcohols."

Examples 2 through 11 were ..."modeled using the conditions listed. The modeling is based on the experience with various conditions used in pilot plant studies and represents the expected results using the conditions employed."

In Example 2, the authors write that, "The large carbon dioxide content (approximately 18%) of the gases leaving the separation vessel is undesirable for the synthesis reactor feed. Therefore, the next step in synthesis gas preparation is reduction of the carbon dioxide content to less than about 5% by volume, and in the example to less than 2%."

Examples 3-10 involve various carbon dioxide and/or light gas recycle and some of these results are summarized in Table XIV.3.

In example 11 it is stated that, "...it was found that the tail gases from the Fischer-Tropsch reactor which consist chiefly of hydrogen and carbon dioxide can be converted to liquid hydrocarbons in a second Fischer-Tropsch reactor... A test was conducted in a small slurry reactor using the same iron-based catalyst that was used in the Fischer-Tropsch synthesis. The temperature, pressure and space velocity were also kept the same. The carbon dioxide conversion was 25% for a feed having hydrogen to carbon dioxide ratios of 2:1 and also 1.5:1. Conversion of the hydrogen was 42%, and 88% of the carbon monoxide produced in the water gas shift reaction was converted to hydrocarbons in the Fischer-Tropsch reaction. The chain growth (α) was the same as in the conventional Fischer-Tropsch synthesis."

Apart from the claims, references XIV.1, XIV.6 and XIV.7 are essentially identical. The patent of reference XIV.1 claims the production of an oxygen containing diesel fuel using FTS. The claims in references XIV.6 and XIV.7 cover a variety of

carbon dioxide and/or light gaseous product recycle schemes that include both stream(s) and the fraction of each stream to be recycled.

Another grouping of three patents are essentially identical except for the claims [XIV.2-XIV.4]. These three patents are to show, "Several Fischer-Tropsch reaction schemes using a promoted iron catalyst in a slurry reactor produce oxygenated naphtha and diesel fractions on distillation that reduce particulate emissions in diesel engines. High carbon conversion efficiencies and optimum chain growth are characteristics of the process."

These three patents are identical to the above three patents up to the Detailed Description of the Invention and, apart from the one difference described below, this section is the same in the two sets of three patents. In references XIV.2-XIV.4 the paragraph in references XIV.1, XIV.6 and XIV.7:

"The steam reforming reactor 5 can be of conventional design employing a commercial nickel catalyst such as obtained from Katalco and designated **23-1**. Preferably, the reactor should be operated at from about 1292°F (700°C) to about 1652°F (900°) at system pressure of about 12 psia (82.7 kPa) to about 500 pais (3447 kPa). The flow of input gases through the reactor catalyst bed should be approximately 300 lbs/hr/ft³ catalyst."

has been replaced by examples of approaches to reduce the amount of carbon monoxide in town gas to a specified level, for example 10% by volume.

It is shown that the water gas shift reaction could be used to reduce the level of CO in the output from the gasifier; however, this approach significantly reduces the heating value of the resulting town gas. It is shown that the removal of the CO₂

produced during the WGS will increase the heat content of the town gas but, in order to have 10% CO in the product, the extent of WGS must be even greater.

The objective of these patents [XIV.2-XIV.4] is to replace the shift reactor with a FTS reactor to remove the excess CO. Thus, a portion of the gas from the gasifier is fed to the FTS reactor while about 20% of the gas bypasses the FTS reactor (Case III in ref. XIV.2-XIV.4). The composition of the blending streams and the town gas are shown in Table XIV.4.

In addition to the town gas, the FTS produces 11.8 barrels of hydrocarbon liquids having five or greater carbon atoms (based on 1.0 MMSCF feed from the gasifier).

Removing the CO₂ will permit the heating value of the town gas of Case III to be increased but this will require a greater fraction of the effluent from the gasifier passing through the FTS reactor (Table XIV.5).

In this instance 12.6 barrels of C₅₊-hydrocarbons will be obtained.

In another scenario, a WGS reactor is included in the process that can be utilized when the FTS reactor is inoperable or, in another scenario, both the FTS and WGS reactors can be utilized in parallel.

The catalyst activation and the test results of this group of three patents [XIV.2-XIV.4] are identical to those in the first group of three patents [XIV.1,XIV.6,XIV.7]. The examples in references XIV.2-XIV.4 are essentially the same as those in references XIV.1, XIV.6 and XIV.7.

Reference XIV.2 claims a method of thermally cracking a wax produced by a FTS reaction using an iron-based catalyst in a slurry reaction at a temperature of 770°F (410°C) for a sufficient period of time to produce diesel and naphtha fractions.

Reference XIV.3 claims a method for preparing and activating with synthesis gas a material that is catalytically active for Fischer-Tropsch synthesis.

Reference XIV.4 claims a FTS method suitable for producing a diesel product that is cleaner than commercially available that is derived from crude oil and having a cetane number which is higher than 45 and aromatics less than 1% and the same product that contains more than 2 wt.% oxygen.

The final two patents [XIV.5,XIV.8] are essentially identical to each other and, except for a section describing the use in conjunction with power generation and the claims, are identical to references XIV.2-XIV.4. The Fischer-Tropsch processes are used in combination with electric power generation. The example considers a 300 MW off-peak power production rate (during 17 hours of the 24 hour day) in a plant with a thermal efficiency of 33%. The feed gas requirements for the peak and off-peak conditions are 14.87 and 11.15 million standard cubic feet per hour (MMSCFH), respectively. This requires a FTS reactor to handle 3.72 MMSCFH of coal gas during off-peak hours. To prevent slurry bed slumping, the FTS reactor would require an additional 0.45 MMSCFH during peak operation. During peak operation, the FTS conditions would be changed from 250 to 100 psi to maintain an adequate superficial velocity in the FTS reactor. The average production of liquid hydrocarbons would be about 2100 barrels per day.

Reference XIV.5 claims: (1) a FTS process for producing liquid hydrocarbons from a synthesis using an iron catalyst in a slurry reactor with recycle of CO₂ to the gasifier, (2) claim 1 using coal derived synthesis gas and (3) the method of claim 2 wherein the FTS is used in combination with an electric power generation system.

Reference XIV.8 has one claim for a diesel fuel additive for reducing particulate emissions by utilizing the oxygenates in the FTS product so that the diesel contains at least 2 wt.% oxygen.

The discussion in the sections of these patents provides an excellent overview of FTS using an iron catalyst and of process concepts to improve the efficiency of carbon utilization. At times it is difficult for the reader to easily discern whether the data is from modeling or produced by experiment. Rentech has operated a 6-inch 8-foot tall slurry reactor both with and without CO₂ removal in advance of the FTS reactor [XIV.8]. In 1992 it was reported that the longest run was for a two-week period but it is understood that subsequent runs have been made for periods of 60 days or more; however, data for these longer runs do not appear to be available in the public domain.

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Table XIV.1			
	No. 1 Diesel ASTM (1)	No. 2 Diesel ASTM (2)	F/T Diesel
Cetane Index ASTM 976-80	45 min.	40 min.	62
Sulfur Wt.% ASTM D129-80 90% Distillation	.50 max	.50 max	<0.0001*
Temperature °F ASTM D56 Viscosity @ 40°C	550°F-max.	540°F-min. 640°F0Max.	556°F
cSt.	1.4 min.	1.9 min.	1.8
ASTM D445-82	2.5 max.	4.1 max.	
Conradson Carbon on 10%; ASTM D189-81 Wt.%	.15 max.	.35 max.	.02
Flash Point °F, min. Corrected to 760 mm Hg ASTM D56-82	100°F	125°F	122°F
Aromatic Content, Vol. %; ASTM D1319	8% min.	33%	less than 1%
API Gravity ASTM D1298	38-41	34.7	48.7
BTU/lb ASTM D240	16,000-17,000	19,810	19,371
Oxygen Content, Wt.%	N/A	N/A	3.05%
* Analyses were below limits of detection. (1) ASTM D975-81, #1 Diesel (2) ASTM D975-81, #2 Diesel			

Table XIV.2			
Test	Method		Results
Flash Point, °F	ASTM D56		122
API Gravity @ 60°F	ASTM D1298		48.7
Sulfur Content, Wt.%	Horiba Analyzer		<0.0001
Kinematic Viscosity @ 40°C, cSt.	ASTM D445-82		1.80
Distillation Range	ASTM D86	IBP 90% FBP	314 566 627
Conradson Carbon on 10% Residuum, Wt.%	ASTM D189-80		0.02
Saturates, Wt.% Alpha-Olefins Internal Olefins Alcohols and Others	NMR/90 MHz		30 45 9 16
Oxygen Content, Wt.%	Elemental Analysis		3.05
Average Carbon Chain Length	GC/FID		C ₁₄
Cetane Index	ASTM D976		62
Heat of Combustion, BTU/lb	ASTM D240		19,371

Table XIV.3			
Efficiencies Taken from Description of Examples Feed 1,000,000 Std. Cubic Feet/Day			
Example	Efficiency	C ₅₊ bbl/day	CO ₂ Recycle
1	58.1	80.7	
2	50		Yes, reactor and reformer
3	36.8	51.8	No
4	43.6	61.3	Yes, from reformer inlet
5	60.5%	85.2	Yes, reformer and 1/2 FT tail gas
6	71.3%	94.6	Yes, ~ all CO ₂ and 1/2 FT tail gas hydrocarbons
7	43.7 ^a	60.0	
a. Same as example 5 except $\alpha = 0.7$.			

Table XIV.4 Stream Compositions for Case III			
Species	From Gasifer (Vol. %)	From F.T. Reactor (Vol. %)	Town Gas (Vol. %)
H ₂	55.7	56.32	56.15
CO	26.9	3.69	10.00
CO ₂	2.0	17.88	13.56
CH ₄	14.1	19.75	18.21
C ₂ H ₆	1.3	2.05	1.84
C ₂ H ₈	0.0	0.19	0.14
C ₄ H ₁₀	0.0	0.12	0.09
LHV (B/ft.3)	388.3	387.1	387.4
Volume (MMSCF)	1.0	0.572	0.786

Table XIV.5 Stream Compositions for Case IV				
Species	From Gasifer (Vol. %)	From F.T. Reactor (Vol. %)	Mixed Gas (Vol. %)	Town Gas (Vol. %)
H ₂	55.7	56.32	56.17	65.34
CO	26.9	3.69	8.59	10.00
CO ₂	2.0	17.88	14.52	0.60
CH ₄	14.1	19.75	18.57	21.57
C ₂ H ₆	1.3	2.05	1.89	2.20
C ₂ H ₈	0.0	0.19	0.16	0.18
C ₄ H ₁₀	0.0	0.12	0.10	0.11
LHV (B/ft.3)	388.3	387.1	387.7	450.9
Volume (MMSCF)	1.0	0.572	0.773	0.664

Figure XIV.1. Recycled water and alcohol.

Task 7. Co Catalyst Preparation

The objective of this task is to prepare a limited number of cobalt-based Fischer-Tropsch catalysts that can be used to obtain baseline data on cobalt-based Fischer-Tropsch synthesis.

A. Fischer-Tropsch Synthesis. Effect of CO pretreatment on a ruthenium promoted Co/TiO₂

ABSTRACT

The effect of pretreatment, using hydrogen or carbon monoxide, on the activity and selectivity of a ruthenium promoted cobalt catalyst [Ru(0.20wt%)/Co(10wt%)/TiO₂] during Fischer-Tropsch (F-T) synthesis was studied in a continuous stirred tank reactor (CSTR). The hydrogen reduced catalyst exhibited a high initial synthesis gas conversion (72.5%) and reached steady state after 40 h on stream, after which the catalyst deactivated slightly with time on stream. The carbon monoxide reduced catalyst reached steady state quickly and showed a lower activity and a good stability. Methane selectivity on the carbon monoxide reduced catalyst was 15 –20 % (carbon base), much higher than that on the hydrogen reduced catalyst (5 – 10%). Carbon monoxide regeneration increased the activity on the hydrogen reduced catalyst; however, it did not have significant effect on the carbon monoxide reduced catalyst.

Key words : Cobalt, Ruthenium, Titania, Fischer-Tropsch synthesis, Synthesis gas conversion, CO pretreatment, Continuous stirred tank reactor.

Introduction

Pretreatment conditions used for supported cobalt Fischer-Tropsch (FT) catalysts often have significant effect on the catalyst activity, selectivity and lifetime (1-9). A number of researchers focused on the study of pretreatment of the catalyst with hydrogen, including the effects of calcination and hydrogen reduction temperatures. Calleja et al. (6) investigated the FT reaction over a Co/HZSM-5 catalyst, and found that the calcination and reduction temperatures did not have an effect on the catalyst activity. The results obtained by Rathousky et al. (8), however, revealed that the calcination and reduction temperatures have a significant effect on the catalytic properties of both Co/Al₂O₃ and Co/SiO₂ catalysts. The turnover frequency (TOF) for the F-T reaction decreased with increasing calcination temperature for both Co/Al₂O₃ and

Co/SiO₂. However, the total reaction rate increased for Co/Al₂O₃ while it decreased for Co/SiO₂ (7-9). Belambe et al. (10) studied the pretreatment effects on the activity of a Ru-promoted Co/Al₂O₃ catalyst for the FT reaction. The calcination temperature was found to have a pronounced effect on the overall activity of the catalyst, but not on the TOF. The reduction temperature had only a negligible effect on the overall activity and TOF. A few studies on the effect of treatment with carbon monoxide or syngas for the supported cobalt catalysts has been reported. It has been reported that the supported cobalt catalyst pretreated with a gas containing carbon monoxide had increased activity and greater selectivity towards producing C₅+ hydrocarbons (11). Older work indicates that Co₂C is formed by low temperature activation with CO (12). Supported cobalt that were reduced in hydrogen, carburized with CO at 208°C and then hydrogenated at 208°C, the carbide was quickly converted to cobalt metal. Below about 240°C, treatment of cobalt catalysts with CO led to Co₂C with little, if any, free carbon.

The present work was undertaken to investigate the effect of carbon monoxide pretreatment on the titania supported cobalt catalyst. The results obtained have been compared with these of catalyst pretreated with hydrogen. The catalyst chosen for the present study is Ru(0.20 wt%)/Co(10 wt%)/TiO₂. Our previous study (13) have shown that this catalyst had good catalyst activity and selectivity for Fischer-Tropsch synthesis.

Experimental

Catalyst preparation

The titania supported cobalt catalyst was prepared by pore volume impregnation of Degussa P-25 TiO₂ (72% anatase, 45 m²/g, calcined at 673 K for 6 h before use) with a cobalt nitrate (Alfa) solution. The sample was dried at 393 K for 16 h and calcined at 573 K for 6 h. The ruthenium promoted catalyst was prepared by impregnating pretreated Co/TiO₂ with a solution containing ruthenium nitrosyl nitrate (Alfa). The sample was dried at 393 K for 16 h and calcined at 573 K for 6 h. The ruthenium and cobalt contents were 0.20 and 10 wt% respectively, corresponding to a atomic Ru/Co ratio of 0.012.

Reaction system and procedure

A 1-liter autoclave, operated as a continuous stirred tank reactor (CSTR), was used for the slurry FT reaction. Analyses of the gaseous, liquid, and solid (at room temperature) products was conducted using a variety of both on- and off-line gas chromatographs.

The catalyst was pretreated with pure hydrogen or with pure carbon monoxide at different temperatures. The hydrogen activation was first conducted *ex-situ* and then *in-situ* according to the following procedure. The catalyst (about 15 g) was put in a fixed bed reactor and pure hydrogen was introduced at a flow rate of 60 NLh⁻¹ (298 K, 0.1 MPa); the reactor temperature was increased from room temperature to 373 K at a rate of 120 Kh⁻¹, then increased to 573 K at a rate of 60 Kh⁻¹ and kept 573 K for 16 h. The catalyst was transferred under a helium blanket to the CSTR to mix with 300 g of melted polyethylene (P.W. 3000). The catalyst was then reduced *in-situ* in the CSTR; the hydrogen was introduced to the reactor at atmospheric pressure with a flow rate of 30 NLh⁻¹ (298 K, 0.1 MPa). The temperature was increased to 553 K at a rate 120 K h⁻¹ and maintained at this activation condition for 24 h.

The carbon monoxide activation was conducted *in-situ* in the CSTR according to the following procedure. Approximately 15 g of catalyst was mixed with 300 g of melted polyethylene (P.W. 3000) in the CSTR. The reactor pressure was increased to 1.68 MPa with carbon monoxide at a flow rate 30 NLh⁻¹ (298 K, 0.1MPa). The reactor temperature was then increased to 523 K at a rate of 120 Kh⁻¹. These activation conditions were maintained for 24 h. In order to void any deposition of refractory carbon residues, a lower carbon monoxide pretreatment temperature (523 K) was chosen for this study.

After the activation period, the reactor temperature was decreased to 483 K and synthesis gas (2H₂/CO) was introduced to increase the reactor pressure to 2.35 MPa. The reactor temperature was then increased to 503 K at a rate of 10 Kh⁻¹. During the entire run the reactor temperature was 503 K, the pressure was 2.35 MPa, and the stirring speed was maintained at 750 rpm.

The space velocity of the synthesis gas was 2 and 3 NL h⁻¹ gcat.⁻¹ and the feed H₂/CO ratio was kept constant at 2. The conversion of carbon monoxide and hydrogen and the

formation of products were measured during a period of 24 h at each condition. Test duration was 210 h on stream for the hydrogen reduced catalyst or 350 h on stream for the carbon monoxide reduced catalyst. A common gas supply and carbonyl removal (using Pb-Al₂O₃) system was used for five CSTR's that were utilized with a variety of cobalt catalysts. Since the methane selectivity and activity stability of the other catalysts utilized in the other four reactors were normal, the feed should not impact the runs. Furthermore, since CO pretreatment has been utilized in similar reactors for more than 100 runs without impact of metal deposition, the CO pretreatment should not impact the results. In this study, a PbO (20 wt.%) - Al₂O₃ trap for metal carbonyls was used. Prior work with an alumina trap led to deposition of iron on cobalt catalysts; however, following installation of the PbO-Al₂O₃ trap, chemical analysis showed that the iron contamination was eliminated.

Results and discussion

Catalyst activity

The synthesis gas conversion is a rough measure of the overall Fischer-Tropsch activity of a supported cobalt catalyst. The synthesis gas conversions (mol%) for RuCo/TiO₂ catalysts reduced with hydrogen and with carbon monoxide as a function of time on stream are shown in Figure 1 to illustrate the effect of pretreatment gas on catalyst activity. The space velocity used were 2 and 3 NL/gcat./h. Firstly, a space velocity of 2 NL/gcat./h was used. The hydrogen reduced catalyst exhibited a higher initial conversion of synthesis gas (73.5%), and it reached a steady state conversion at about 40 h on stream. After steady state, the catalyst deactivated slightly with time on stream. After 120 h on stream, the synthesis gas conversion had decreased to 66.7%, giving a deactivation rate was about 0.6% per day. When the space velocity was changed to 3 NL/gcat./h, the synthesis gas conversion decreased, reaching 45.0% at 140 h on stream.

The carbon monoxide reduced catalyst exhibited a very different catalytic performance compared with the hydrogen reduced catalyst. The synthesis gas conversion was lower and it reached a steady state value (32.0%) quickly. After 40 h on stream, the synthesis gas conversion increased slightly and then remained almost constant (34.0 %) with time on stream during 250 h.

When the space velocity was increased to 3 NL/gcat./h, the synthesis gas conversion decreased to 24.0%, lower than for the hydrogen reduced catalyst.

The rate of hydrocarbon production follows the same trend as the synthesis gas conversion, i.e., the hydrogen reduced catalyst exhibited a higher hydrocarbon production rate than the carbon monoxide reduced catalyst.

Catalyst selectivity

Methane selectivities for the catalysts reduced with hydrogen or with carbon monoxide (calculated as $100 \times (\text{moles of CO converted to CH}_4) / (\text{total moles of CO converted} - \text{moles of CO converted to CO}_2)$) as a function of time on stream are shown in Figure 2. Methane selectivity slightly changed between 15-20% with time on stream on the carbon monoxide reduced catalyst, and the values were higher than the hydrogen reduced catalyst (5-10%). The higher methane selectivity on the carbon monoxide reduced catalyst may be due to some cobalt carbide phase that was produced by the carbon monoxide reduction. However, the methane selectivity varied with synthesis gas conversion, and even a small change on synthesis gas conversion could influence methane selectivity. From Figure 3 it is seen that the same trend can be observed for the catalysts pretreated with hydrogen or with carbon monoxide; i.e. the methane selectivity decreased with increasing conversion for the two catalysts. As shown in Figure 3, the H₂/CO ratio of the exit gas remained essentially constant over the CO conversion range where the methane selectivity underwent significant changes. Thus, the different methane selectivity cannot be due to different H₂/CO ratios. The alpha value, obtained from the Anderson-Schulz-Flory plot for the higher carbon number compounds, was essentially the same for the catalyst whether it was pretreated with H₂ or CO. Thus, the methane selectivity is not the result of widely varying FT selectivity.

One possible explanation is that a product is poisoning the methanation reaction relative to the FT reaction. Since water partial pressure increases with increasing CO conversion, it appears most likely that water selectively poisons the methane production. If this is the case, the most reasonable explanation is that there is a cobalt site that produces only methane, or low alpha FT products, that is poisoned by water. It does not appear that less methane could be

produced as the CO conversion increases in a single conventional pathway that follows Anderson-Schulz-Flory (ASF) kinetics.

Another possibility is that surface cobalt carbide is formed when the catalyst is exposed to only CO. If this is the case, the cobalt carbide sites would produce predominantly methane while the carbide-free cobalt sites would produce typical ASF products. Based on preliminary data produced when adding water to the feed, it appears that the explanation involving surface cobalt carbide is more likely to be valid.

C₅+ selectivity (expressed as a mass fraction of liquid and wax hydrocarbons in total hydrocarbons) exhibited a trend opposite to the methane selectivity. C₅+ selectivity on the hydrogen reduced catalyst was between 71.5 and 77.8%, higher than the carbon monoxide reduced catalyst (57.4 – 63.2%). However, similar alpha values were obtained for the two pretreatments.

Comparing the two pretreatment methods, the hydrogen pretreatment resulted in a higher Fischer-Tropsch activity, a lower methane selectivity and a higher C₅+ selectivity.

CO regeneration effect

In order to investigate the effect of carbon monoxide treatment on the used catalysts, synthesis gas was switched off after 140 h on stream for the hydrogen reduced catalyst (after 280 h on stream for the carbon monoxide reduced catalyst) and only pure carbon monoxide was passed in an attempt to regenerate the catalysts. The regeneration was carried out at reaction temperature of 503 K and a pressure of 1.68 MPa for 24 h. It was found that the carbon monoxide treatment (regeneration) led to a improved catalytic performance in a subsequent FT reaction for the hydrogen reduced catalyst. After regeneration, the synthesis gas conversion increased from 45.0 % to 58.0 % (at 3 NL/gcat./h) during the first 24 h and then gradually decreased to 52%. The methane selectivity firstly decreased from 9.8 to 5.6 % and then gradually increased. However, the carbon monoxide regeneration did not have significant effect on the carbon monoxide reduced catalyst and the synthesis gas conversion remained essentially constant (at 3 NL/gcat./h). The methane selectivity was not influenced by the regeneration (Figures 1 and 2).

Conclusions

The pretreatment gas (reductant) was found to have a remarkable effect on the performance of a ruthenium promoted cobalt catalyst during Fischer-Tropsch synthesis. The hydrogen reduced catalyst exhibited a higher initial synthesis gas conversion (72.5%) and reached steady state after 40 h on stream. The catalyst deactivated slightly with time on stream. The carbon monoxide catalyst reached steady state quickly, exhibiting lower activity and good stability. Methane selectivity for the carbon monoxide reduced catalyst was 15 –20 % (carbon basis), higher than that on the hydrogen reduced catalyst (5 – 10%). However, methane selectivity depends upon CO conversion and this can account for much of the differences in methane selectivity. Carbon monoxide regeneration increased the activity on the hydrogen reduced catalyst; however, it did not have a significant effect on the carbon monoxide reduced catalyst.

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Figure 1. Effect of reduction gas on synthesis gas conversion of RuCo/TiO₂ catalyst

Figure 2. Effect of reduction gas on methane selectivity of RuCo/TiO₂ catalyst

Figure 3. Methane selectivity vs synthesis gas conversion

B. Preparation of Promoted Cobalt Fischer-Tropsch Synthesis Catalysts

Introduction

With the discovery of more and more stranded natural gas resources, the development of cobalt based catalysts with high activity, stability and selectivity has become urgent. The common practice for the future commercial gas to liquid plant is believed to use promoted supported cobalt catalyst in a slurry phase reactor to optimize the diesel and wax productivity, The wax product then can be cracked into middle distillate or sold directly according to the local needs.

Intensive research has been done on the support, precursor, pretreatment and promoter effects on cobalt Fischer-Tropsch synthesis catalyst; however, the majority of these kinds of work were done in a fixed bed reactor. To study the effects of all the preparation parameters in the continuously stirring tank reactors will enable us to predict the behavior of the catalyst in a bubble column slurry phase reactor. Therefore, the effect of promoters on the cobalt catalyst is studied in this work using a 1L CSTR reactor.

According to the results of Iglesia, the hydrocarbon productivity rate of cobalt catalyst only depends on its cobalt dispersion: the higher the dispersion, the higher the productivity rate. The support has no effect on the Fischer-Tropsch synthesis activity. The noble metal promoters' effect of increasing the activity is caused, in this view, by the promotion of reduction of cobalt oxide to cobalt metal. In previous work, we have prepared platinum and rhenium promoted alumina cobalt-catalysts and the activity was increased by the addition of small amount of Pt and Re. In this work, different loading of ruthenium was added to alumina supported catalyst to study the effect of Ru on the activity, deactivation rate and selectivity in 1L CSTR reactor.

Silica was considered to be a support that has a disadvantage for cobalt Fischer-Tropsch synthesis. Because in the presence of water, cobalt and silica can react and form cobalt silicate, thereby causing a rapid deactivation of the catalyst. Zirconia has been impregnated onto the surface of the silica support to retard the formation of the cobalt silicate during the reaction and it was proven to be very effective. Zirconia has also been added to the alumina support to increase the activity; however, the mechanism of the promotion effect has not been explained so

far. In this work, zirconia was added to both silica and alumina support before the impregnation of cobalt and noble metal promoters.

It is mentioned in the patent literature that rare earth promotion of cobalt is beneficial to the Fischer-Tropsch synthesis. Several studies have found improved selectivity for longer chain hydrocarbons upon rare earth promotion of cobalt catalysts. In this report, the La promoted alumina supported cobalt catalyst was prepared and the effect of the La on the catalytic property of the catalyst is going to be defined.

Experimental

1. Co-Ru/Al₂O₃

The catalysts were prepared by the incipient wetness technique using Catalox B alumina (surface area 200m²/g, pore volume 0.4cm³/g). The cobalt precursor is Co(NO₃)₂·6H₂O and the ruthenium precursor is Ru(NO)(NO₃)₃·XH₂O. The cobalt loading is 20wt% and the ruthenium loading are 0.2, 0.5, 1.0wt% respectively. The support was impregnated by a cobalt nitrate solution first, and the catalyst was calcined at 400°C in air. Ruthenium was added to the calcined cobalt-alumina and then the catalyst was dried and calcined again under flow air at 400°C for 4hrs.

2. Co-Ru/ZrO₂-SiO₂

A silica support (Davisil 952) with a surface area of 300m²/g and pore volume of 1.15cm³/g was used. Zirconia was added to the silica surface in the form of ZrO(NO₃)₂ and the obtained catalyst were dried and calcined before the addition of cobalt and ruthenium. The zirconia loading was 10 wt.%, the cobalt loading is 20 wt.% and the ruthenium loadings were 0.2, 0.5, 1.0 wt.%, respectively.

3. Co/ZrO₂-Al₂O₃

The alumina support used was the same as for the Co-Ru/Al₂O₃, the zirconia precursor was ZrO(NO₃)₂ and it was added before cobalt. The obtained material then was dried and calcined before the addition of cobalt (cobalt loading was 15%), zirconia loading was 10%.

4. Co-La/Al₂O₃

Alumina support used was the same as Co-Ru/Al₂O₃, the La was added in the form of lanthanum nitrate hexahydrate with a La loading of 5% and the cobalt loading of 15%.

All of the above catalysts were prepared by the incipient wetness technique and the drying procedure was conducted in a rotary evaporator under vacuum. The catalytic properties of the catalysts are going to be obtained using a 1L CSTR reactor.

C. Fischer-Tropsch Synthesis: Effect of Small Amounts of Boron, Ruthenium and Rhenium on Co/TiO₂ Catalysts

Abstract

The effect of the addition of small amounts of boron, ruthenium and rhenium on the Fischer-Tropsch catalyst activity and selectivity of a 10 wt% Co/TiO₂ catalyst has been investigated in a continuously stirred tank reactor (CSTR). A wide range of synthesis gas conversions has been obtained by varying space velocities over the catalysts. The addition of a small amount of boron (0.05 wt%) onto Co/TiO₂ does not change the activity of the catalyst at lower space times and slightly increases synthesis gas conversion at higher space times. The product selectivity is not significantly influenced by boron addition for all space velocities investigated. Ruthenium addition (0.20 wt%) onto Co/TiO₂ and CoB/TiO₂ catalysts improves the catalyst activity and selectivity. At a space time of 0.5 h-gcat./NL, synthesis gas conversion increases from the 50-54% to 68-71% range and methane selectivity decreases from 9.5% to 5.5% (molar carbon basis) for the promoted catalyst. Among the five promoted and non-promoted catalysts, the rhenium promoted Co/TiO₂ catalyst (0.34 wt% Re) exhibited the highest synthesis gas conversion, and at a space time of 0.5 h gcat./NL, synthesis gas conversion was 73.4%. In comparison with the results obtained in a fixed bed reactor, the catalysts displayed a higher Fischer-Tropsch catalytic activity in the CSTR.

Key words: Cobalt, Titania, Boron, Ruthenium, Rhenium, Fischer-Tropsch synthesis, Synthesis gas conversion, Continuously stirred tank reactor.

1. Introduction

Supported cobalt catalysts have been widely employed for Fischer-Tropsch (F-T) synthesis of long chain hydrocarbons from synthesis gas [1]. Cobalt is claimed to have certain advantages over iron as a catalyst, such as longer catalytic life time, less water-gas shift and production of a modified product. However, the activity of such catalysts still needs improvement. Variation of promoters is being considered as a means to reach this goal. It is well known that the activity of supported cobalt catalysts is increased by the addition of a small amount of ruthenium, and previous studies have indicated that ruthenium addition enhances the

reducibility of cobalt as well as the dispersion [2]. It is claimed to produce a synergistic effect with cobalt [3].

It is also known that many F-T catalysts suffer rapid and substantial loss of activity by poisoning in the presence of sulfur at ppm levels. There is, therefore, considerable interest in the development of more sulfur tolerant catalysts. One approach to remove small amounts of catalyst poisons is by using catalysts containing small amounts of complexes or elements that preferentially react with the poison. Iron, nickel and cobalt borides, which contain small amounts of boron, have been reported to be active and selective catalysts for the Fischer-Tropsch reaction [4-6] and, more importantly, these metal borates have also been shown to be significantly more resistant to sulfur poisoning in F-T synthesis [7].

In the present work, the effect of adding small amounts of boron, ruthenium and rhenium on the Fischer-Tropsch catalytic properties of titania-supported cobalt catalysts was studied. The incipient wetness impregnation (IWI) technique was applied to prepare catalysts and catalytic properties were evaluated in a continuously stirred tank reactor (CSTR). The results obtained in a CSTR were compared with those obtained in a fixed bed reactor.

2. Experimental

2.1. Catalyst preparation

The boron-modified TiO_2 carrier was prepared by pore volume impregnation of Degussa P-25 TiO_2 (72% anatase, 45 m^2/g , calcined at 673 K for 6 h) with a solution containing a small amount of boric acid (Aldrich). The sample was dried at 393 K for 16 h and then calcined in air for 6 h at 673 K.

Cobalt (10 wt%) was deposited on the boron-modified (or boron-free) TiO_2 carrier by pore volume impregnation with cobalt nitrate (Alfa) solution. Samples were dried at 393 K for 16 h and calcined at 573 K for 6 h before they were used.

The ruthenium or rhenium promoted catalysts were prepared by impregnating pretreated (10 wt%) Co/TiO_2 and CoB/TiO_2 with solutions containing ruthenium nitrosyl nitrate (Alfa) or perrhenic acid (Alfa). The samples were dried at 393 K for 16 h and calcined at 573 K for 6 h before they were used. The boron, ruthenium and rhenium contents were 0.05, 0.20 and 0.34

wt% respectively, corresponding to atomic B/Co, Ru/Co and Re/Co ratios of 0.0273, 0.0117 and 0.0108.

2.2. Catalyst characterization

2.2.1. BET Surface Area Measurements

BET measurements were conducted using a Micromeritics Tri-Star system for all catalysts to determine the loss of surface area, if any, following loading of the metal. Prior to testing, samples were slowly ramped to 160°C and evacuated for 4 hrs. to approximately 50 m Torr.

2.2.2. Temperature programmed reduction

Temperature programmed reduction (TPR) profiles of freshly calcined catalysts were recorded using a Zeton Altamira AMI-200 unit which incorporates a thermal conductivity detector (TCD). Calcined fresh samples were first purged in flowing Ar to remove traces of water. TPR was performed using a flow of 20 ccm of 10% H₂/Ar mixture and referenced to Ar. The initial temperature was 323 K and the catalysts was ramped at 10 K/min to a final temperature of 1073K. Resulting profiles were normalized to the height of the main peak so that shifts in the peak positions could be ascertained.

2. 2. 3. Hydrogen chemisorption by temperature programmed desorption (TPD) and percent reduction by reoxidation

Hydrogen chemisorption was also measured using a Zeton Altamira AMI-200 unit. The sample weight in each case was 0.220 g. Catalysts were activated using pure hydrogen at 573 K for 10 hrs and cooled under flowing hydrogen to 373 K. The sample was held at 373 K under flowing argon to prevent adsorption of weakly bound species, prior to increasing the temperature slowly to the activation temperature of 573 K. At that temperature, the catalyst was held under flowing argon to desorb the remaining chemisorbed hydrogen until the TCD signal returned to the baseline. The TPD spectra were integrated and the number of moles of desorbed hydrogen determined by comparing to the areas of calibrated hydrogen pulses. The loop volume, determined by calibration with syringe injections of nitrogen in helium flow, was found to be 52

μL. Dispersion calculations were based on the assumption that the H:Co stoichiometric ratio was 1:1.

After TPD of hydrogen, the sample was reoxidized using pulses of oxygen in a He carrier gas at 573 K. Percentage reduction was calculated by assuming that the metal reoxidized to Co₃O₄.

For each sample, uncorrected dispersions and uncorrected particle size estimates were first determined assuming that the sample was completely reduced. The catalyst was fully oxidized when the peak corresponding to the oxygen pulse was observed in its entirety by the TCD, indicating no additional reaction with cobalt metal. Then, the percentage reduction of the sample was included in the calculation and corrected dispersions and particle size calculations were carried out. For particle size estimation, a spherical cluster morphology was assumed. Additionally, both dispersion and percentage reduction calculations were based solely on cobalt, and the promoter was not taken into account.

$$D_{\text{uncorrected}} = \text{No. of Co}^0 \text{ atoms} / \text{No. of Co atoms in sample}$$

$$D_{\text{corrected}} = \text{No. of surface Co}^0 \text{ atoms} / \text{No. of Co}^0 \text{ atoms in sample} \\ = \text{No. of surface Co}^0 \text{ atoms} / (\text{No. of Co atoms in sample})(\text{fraction Co reduced}).$$

2. 3. Reaction system and procedure

The catalyst (about 15 g) was reduced *ex-situ* in a fixed bed reactor with hydrogen at a flow rate of 60 NLh⁻¹ (298 K, 0.1 MPa); the reactor temperature was increased from room temperature to 373 K at a rate of 120 K h⁻¹, then increased to 573 K at a rate of 60 K h⁻¹ and kept at 573 K for 16 h. The catalyst was transferred under the protection of helium to a CSTR to mix with 300 g of melted Polywax 3000. The catalyst was then reduced *in-situ* in the CSTR; the hydrogen was introduced to the reactor at atmospheric pressure with a flow rate of 30 NLh⁻¹ (298 K, 0.1 MPa). The reactor temperature was increased to 553 K at a rate 120 K h⁻¹ and maintained at this activation condition for 24 h.

A 1-liter autoclave, operating as a continuously stirred tank reactor (CSTR), was used for the slurry FTS reaction. The FTS reactor system has been described earlier [8]. Separate mass flow controllers were used to add H₂, CO and inert gas at the desired rate to a mixing vessel

that was preceded by a lead oxide-alumina containing vessel to remove iron carbonyls. The mixed gases entered the CSTR below the stirrer operated at 750 rpm. Products were continuously removed from the vapor and passed through two traps, one maintained at 373 K and then other at 273 K. The uncondensed vapor stream was reduced to atmospheric pressure through a pressure letdown valve. The flow was measured with a bubble-meter and composition quantified using an on-line GC. The accumulated reactor liquid products were removed every 24 hours by passing through a 2 μm sintered metal filter located below the liquid level in the CSTR. The contents of the 273 K and 373 K were combined, the hydrocarbon and water fractions separated, and analyzed by GC. The reactor wax sample was analyzed by a high-temperature GC to obtain a carbon number distribution for $\text{C}_{20}\text{-C}_{80}$.

After the activation period, the reactor temperature was decreased to 483 K and synthesis gas ($2\text{H}_2/\text{CO}$) was introduced to increase the reactor pressure to 2.35 MPa. The reactor temperature was then increased to 503 K at a rate of 10 K h^{-1} . During the entire run, the reactor temperature was 503 K, the pressure was 2.35 MPa, and the stirring speed was maintained at 750 rpm.

The space velocity of the synthesis gas was varied from 1 to 7 $\text{NL h}^{-1}\text{ gcat.}^{-1}$ at a constant H_2/CO ratio of 2. The conversion of carbon monoxide and hydrogen and the formation of products were measured after at least a 24 h period at each condition.

3. Results and discussion

3.1. Catalyst Characterization

Results of surface area measurements by physisorption of nitrogen are reported in Table 1. Results show that the BET surface area for the 10% loaded Co catalysts on $45\text{ m}^2/\text{g } \gamma\text{-Al}_2\text{O}_3$ were all close to $40\text{ m}^2/\text{g}$. A weight % loading of 10% metal is equivalent to 13.3% by weight Co_3O_4 . If the Al_2O_3 is the main contributor to the area, then the area of the $\text{Co}/\text{Al}_2\text{O}_3$ catalysts should be $0.867 \times 45\text{ m}^2/\text{g} = 39\text{ m}^2/\text{g}$, which matches very well the measured values. Therefore, the results in Table 1 are reasonable.

Figure 1 shows the TPR profiles for unpromoted and promoted Co/TiO₂ catalysts. For unpromoted catalysts, three peaks were observed. Reduction of Co₃O₄ to Co⁰ passes through an intermediate phase, CoO and therefore the two-step reduction proceeds as follows:

Therefore, in producing one mole of Co⁰, one-third of a mole of H₂ is first consumed to produce CoO, and 1 mole of H₂ is consumed to produce the metal. We therefore anticipated that the ratio of the area of the first sharp peak with the remaining broad peak to be close to 0.33:1. Since bulk Co metal is thermodynamically stable after reduction in hydrogen at 623 K, the splitting of the peaks implies that the activation energy for the second reaction is higher. Because reduction is kinetically limited, the second sharp peak will contain, in addition to the first reaction, a small contribution from reduction of CoO to Co⁰. This is most likely the reason why the calculated values in Table 2 are slightly higher than 0.33.

The low temperature peak was therefore assigned to reduction of Co₃O₄ to CoO while the higher temperature peaks corresponded reduction of CoO to Co. The high temperature broad peak was presumably due to reduction of species for which there exists a range of degrees of interaction of the metal oxide with the support. Addition of Ru shifted all peaks to lower temperatures. However, in comparison with the unpromoted catalyst, the promoter more significantly affected the low temperature peak, corresponding to reduction of Co₃O₄ to CoO, as observed in a previous study [3]. While the peak at 753 K for the unpromoted catalyst shifted to 636 K, a difference of 117 K, the low temperature peak shifted remarkably from 603 K to 473 K, a difference of 150 K. However, Re promotion only shifted the high temperature broad peak to lower temperature, while the lower temperature peak position remained unchanged. The enhanced reducibility is likely due to spillover of hydrogen from the reduced promoter to reduce cobalt oxide species, because the spectra are in line with the fact that the reduction of Re occurs at a higher temperature than Ru.

Addition of B did not enhance the reduction property of the catalyst, and in contrast, a notable increase in the reduction temperatures of all peaks was observed. However, addition of

both B and Ru to the catalyst resulted in an even more pronounced decrease in reduction temperature of all peaks to lower temperature than the catalyst with Ru promotion alone.

Addition of Ru lowered the activation energy barriers of both reactions, and shifted both peaks to lower temperatures, while addition of Re catalyzed primarily the second step. A comparison of the degree of reduction with time (Figure 2) supports the view that reduction occurs by nucleation and growth. By comparing the slopes of the lines for the promoted catalyst with the unpromoted catalyst, addition of Ru or Re likely increases the rate of nucleation of reduced sites on the cobalt oxide cluster, presumably by spillover of hydrogen from the reduced promoter metal.

Table 3 shows the hydrogen chemisorption data, where dispersion calculations were based on the assumption that the H:Co stoichiometric ratio was 1:1. Without taking into account the amount of Co left unreduced after reduction, estimates of dispersion are lower than the true value, leading to considerable overestimates of the resulting cluster size. Not surprisingly, percentage reduction values for samples reduced at 573 K were in line with the results of TPR. The boron promoted sample, which reduced at higher temperature in comparison with the unpromoted under TPR, showed the lowest percentage reduction value after treating with hydrogen at 573 K.

Likewise, samples promoted with Ru and Re showed much higher percentage reduction values in comparison with the unpromoted sample. The sample with the greatest fraction of its TPR spectra below 573 K, the RuCoB/TiO₂, sample, exhibited the highest percentage reduction value. The average sizes of the cobalt particles were calculated from the chemisorption data, considering the particles to be spherical and nonporous. The average particle size of the promoted catalysts are slightly smaller (~ 8.5 nm) compared to the unpromoted catalyst (~ 10.6 nm).

3.2. Catalyst activity

The synthesis gas conversion is a rough measure of the overall Fischer-Tropsch activity of a supported cobalt catalyst. A wide range of synthesis gas conversions has been obtained by varying space velocities over the boron and boron-free Co/TiO₂ catalysts. For a comparison, the

synthesis gas conversions have been measured at space velocities of 2 and 3 NL/gcat.h for the ruthenium and rhenium promoted catalysts. The synthesis gas conversions for the five catalysts are shown in Figure 3. At low synthesis gas conversion levels (space time < 0.33 h gcat./NL), Co/TiO₂ and CoB/TiO₂ catalysts exhibited about the same synthesis gas conversions. At higher space times (space time > 0.33 h gcat./NL), CoB/TiO₂ catalyst exhibited slightly higher synthesis gas conversion. The trends of synthesis gas conversion with space time for the two catalysts are very similar. The addition of 0.20 wt% ruthenium onto Co/TiO₂ and CoB/TiO₂ catalysts improved the catalyst activity. At a space time of 0.50 h gcat./NL, the synthesis gas conversions increased from 50.2 and 53.0% to 69.1 and 70.5% for the promoted catalysts, respectively. However, RuCo/TiO₂ and RuCoB/TiO₂ catalysts exhibited a similar synthesis gas conversion. This indicates that small amount of boron does not influence the Fischer-Tropsch activity of Co/TiO₂. The probable reason is that the number of active sites is not influenced significantly by the small amount of boron.

The rhenium promoted Co/TiO₂ catalyst (ReCo/TiO₂) showed the highest synthesis gas conversion among the five catalysts studied. At space times of 0.50 and 0.33 h gcat./NL, the synthesis gas conversions were 73.4 and 61.7%; these are higher than ruthenium promoted Co/TiO₂ and CoB/TiO₂ catalysts, and much higher than non-promoted Co/TiO₂ and CoB/TiO₂ catalysts. The observation that ruthenium and rhenium remarkably increased the activity of supported cobalt catalysts have been reported by other researchers [9-13]. However, few have provided an explanation for this. Kogelbauer et. al [2] investigated the effect of ruthenium on Co/Al₂O₃ Fischer-Tropsch catalysts and indicated that ruthenium enhanced the reducibility of the catalyst and therefore the number of exposed metallic cobalt sites, thus increasing the catalytic activity. A synergy effect for cobalt-ruthenium bimetallic was also used to explain the increased activities of ruthenium promoted Co/TiO₂ and Co/SiO₂ catalysts [3]. A recent paper indicated that ruthenium and rhenium increased the activity of supported cobalt catalysts because of the enhanced catalyst reducibility and dispersion [14]. Our catalytic activity, TPR and hydrogen chemisorption results show that the enhanced activity is due more to the increased reducibility of the catalyst. The average particle size changes very little after correcting for the percentage

reduction of cobalt. The slight decrease in particle size with promoter may be due to the reduction of smaller clusters that have a stronger interaction with the support.

Figure 4 shows that hydrocarbon production rate as a function of reciprocal flow rate. For the Co/TiO₂ catalyst, the hydrocarbon rate increased almost linearly with decreasing space time in the range studied. For the CoB/TiO₂ catalyst, however, the hydrocarbon rate increased first and then remained at a constant level of 0.2 g/gcat.h with decreasing space time. Compared with unpromoted Co/TiO₂ and CoB/TiO₂ catalysts, ruthenium and rhenium promoted catalysts exhibited higher hydrocarbon rates, with the rhenium promoted catalyst exhibiting the highest hydrocarbon rate. These trends are similar to those obtained for synthesis gas conversion as they should be since the impact of the higher conversion is offset by the lower amount of synthesis gas passed over the catalyst per hour..

3. 3. Catalyst selectivity

The hydrocarbon product distributions on non-promoted and promoted Co/TiO₂ catalysts have not been found to obey Flory kinetics (i.e., not a straight line) [3]. The methane and C₅+ selectivities are thus used to describe the Fischer-Tropsch selectivity. The methane selectivity, calculated as: $100 \times (\text{moles of CO converted to CH}_4) / (\text{total moles of CO converted} - \text{moles of CO converted to CO}_2)$, as a function of reciprocal space velocity, is shown in Figure 5. The methane selectivity increased slightly with decreasing space time for Co/TiO₂ and CoBTiO₂ catalysts; however, for all the space times studied, the two catalysts showed very similar methane selectivities. Ru addition onto Co/TiO₂ and CoB/TiO₂ decreased the fraction of methane that was produced. At a space time of 0.5 h gcat./NL, the methane selectivity decreased from 9.5 and 9.6% to 6.1 and 5.5% (mole carbon base), respectively.

The methane selectivity on the rhenium promoted Co/TiO₂ catalyst was very similar to that of the ruthenium promoted catalysts and like the methane selectivity on the ruthenium promoted catalysts, it increased with decreasing the space time. Gaseous hydrocarbon selectivity (expressed as a fraction of C₂-C₄ hydrocarbons in total hydrocarbons, not shown) exhibited the same qualitative trends as methane selectivity.

The C₅+ selectivity (expressed as a mass fraction of liquid and wax hydrocarbons in the total hydrocarbons) of the five catalysts, as a function of reciprocal space velocity, is shown in Figure 6. The Co/TiO₂ and CoB/TiO₂ catalysts showed very similar C₅+ selectivities at all space times studied. At higher space times (> 0.33 h gcat./NL), C₅+ selectivity was constant; at the lower space times (< 0.33 h gcat./NL), C₅+ selectivity decreased with decreasing space time. Ru addition onto Co/TiO₂ and CoB/TiO₂ catalysts shifted the product spectrum to higher molecular weight hydrocarbons. At a space time of 0.5 h gcat./NL, the C₅+ selectivity increased from 64.5 and 66.8% to 74.5 and 78.0%. The rhenium promoted catalyst showed the highest C₅+ selectivity among five catalysts; at a space time of 0.5 h gcat./NL, C₅+ selectivity was 80.5%.

3.4. A comparison of Fischer-Tropsch activity in a fixed bed reactor with that in CSTR

Even though the reactors studied exhibited differences in their flow patterns, temperatures and pressures which will result in different phases present for the same catalyst as well as differences in product distributions, a comparison is displayed in Table 4 which points out the advantages of the enhanced mass/heat transfer characteristics of a CSTR. For Co/TiO₂ and CoB/TiO₂ catalysts, the product selectivities are very similar in the two reactors; however, Fischer-Tropsch reaction rates of catalysts obtained in the CSTR are two times higher than those obtained in the fixed bed reactor. It is emphasized that the results using the two types of reactors were obtained with different batches of catalyst although they were both prepared by the same person. None of the determined catalyst properties could explain the differences observed in the behavior of these catalysts in the two reactor systems. Obviously, less diffusion limitations and better gas solubilities in the liquid medium in the CSTR may explain the differences in the results from the two reactor systems [14]. For ruthenium and rhenium promoted Co/TiO₂ catalysts, the reaction rates obtained by us in the CSTR were higher than those obtained in fixed bed reactors. The methane selectivities obtained in CSTR were lower than those obtained in fixed bed reactors [14]. Iglesia et. al [3] used a low reaction temperature, which favored the formation of heavy products and, thus, they obtained a high C₅+ selectivity in the fixed bed reactor. Because the reaction conditions, especially pressure, are different, we can only make a

qualitative comparison of the catalytic properties of RuCo/TiO₂ and ReCo/TiO₂ in the two reactors.

4. Conclusion

The addition of a small amount of boron (0.05 wt%) onto Co/TiO₂ does not change the activity of the catalyst at lower space times (<0.33 h gcat./NL) and slightly increases synthesis gas conversion at higher space times (>0.33 h gcat./NL). The product selectivity is not significantly influenced by the boron addition for all the space velocities. Ruthenium addition (0.2 wt%) onto Co/TiO₂ and Co/B/TiO₂ catalysts remarkably improves the catalyst activities and selectivities. At a space time of 0.5 (SV=2 NL/gcat.h), CO conversions increase from 50.2 and 53.8 % to 68.4 and 70.5 % and methane selectivity decreases from 9.5 and 9.6% to 6.0 and 5.1% (carbon base). The rhenium promoted Co/TiO₂ catalysts (0.34 wt% Re) exhibits the highest synthesis gas conversion, and at a space time of 0.5 h gcat./NL, synthesis gas conversion is 73.4%. Addition of either Re or Ru improves considerably the percentage reduction of cobalt with only a marginal improvement in the average cobalt particle size. Comparing with the results obtained in the fixed bed reactor shows a higher Fischer-Tropsch catalytic activity in the CSTR.

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Table 1		
BET Surface Areas		
Support/Catalyst	BET SA (m ² /g)	Ave Pore Size (nm)
Degussa P25 TiO ₂	45	-
Co/TiO ₂	38	11
CoB/TiO ₂	40	14
RuCo/TiO ₂	40	11
RuCoB/TiO ₂	42	13
ReCo/TiO ₂	43	12

Table 2	
Ratio of First Peak with Remaining Broad Peak in TPR	
Catalyst	Ratio of Area of First Peak to Remaining Broad Peak in TPR
Co/TiO ₂	0.39
CoB/TiO ₂	0.40
RuCo/TiO ₂	0.36
RuCoB/TiO ₂	0.38
ReCo/TiO ₂	0.35

Table 3

Dispersion and Reducibility of Unpromoted and Promoted Co/TiO₂ Catalysts

Catalyst	$\mu\text{moles H}_2$ Desorb	Uncorrected %D	Uncorrected Diam (nm)	% Reduction	Corrected %D	Corrected Diam (nm)
Co/TiO ₂	42.8	5.05	20	52	9.70	11
CoB/TiO ₂	37.4	4.40	24	38	11.6	8.9
RuCo/TiO ₂	66.6	7.77	13	64	12.2	8.5
RuCoB/TiO ₂	63.1	7.43	14	61	12.2	8.5
ReCo/TiO ₂	65.6	7.73	13	61	12.8	8.1

Table 4

Fischer-Tropsch Synthesis on the Promoted Co/TiO₂ Catalysts

Catalyst	Pressure (Kpa)	Temp., (K)	CO Conv. (%)	Reaction Rate (10 ⁻⁴ molCO/molCo/s)	CH ₄ (wt.%)	C ₅ + (Wt.%)	Reactor
Co/TiO ₂ ^a	800	513	48.6	9.2	21.5	65.2	Fixed bed
CoB/TiO ₂ ^a	800	513	47.7	9.0	17.8	69.0	Fixed bed
RuCo/TiO ₂ ^b	2000	473	61.0	13.1	5.0	91.1	Fixed bed
RuCo/TiO ₂ ^c	100	493	< 5.0	3.3	27.7	---	Fixed bed
ReCo/TiO ₂ ^c	100	493	< 5.0	5.1	45.0	---	Fixed bed
Co/TiO ₂ ^d	2350	503	50.2	22.4	19.1	64.5	CSTR
BCo/TiO ₂ ^d	2350	503	53.8	24.0	16.2	66.8	CSTR
RuCo/TiO ₂ ^d	2350	503	68.4	30.5	13.9	74.5	CSTR
RuCoB/TiO ₂ ^d	2350	503	70.5	31.4	12.5	78.0	CSTR
ReCo/TiO ₂ ^d	2350	503	73.4	32.7	10.5	80.8	CSTR

A. Catalysts: Co/TiO₂, 10 wt.% Co; CoB/TiO₂, 10 wt.% Co, 0.05 wt.% B, from data in ref. [7].

B. Catalyst: RuCo/TiO₂, 11.6 wt.% Co, 0.14 wt.% Ru, from data in ref. [3].

C. Catalysts: RuCo/TiO₂, 12 wt.% Co, 0.5 wt.% Ru; ReCo/TiO₂, 12 wt.% Co, 0.75 wt.% Re, from data in ref. [13].

D. This study.

Figure 1. Temperature programmed reduction (TPR) profiles of promoted and unpromoted TiO₂ supported catalysts.

Figure 2. Degree of reduction versus heating time for promoted TiO₂ supported catalysts (a value of 1.0 represents the extent of reduction after heating to 1073 K).

Fig. 3. Synthesis gas conversion as a function of reciprocal space velocity.

Fig. 4. Hydrocarbon production rate as a function of reciprocal space velocity.

Fig. 5. Methane selectivity vs reciprocal space velocity.

Fig. 6. C₅+ selectivity as a function of reciprocal space velocity.

Task 8. Cobalt Catalyst Testing for Activity and Kinetic Rate Correlations

The objective of this task is to conduct initial screening of the cobalt catalysts prepared in Task 7 to select three baseline catalysts that will then be used to generate a data base on the performance of cobalt-based Fischer-Tropsch catalysts in slurry reactors.

A. Comparison of Fischer-Tropsch synthesis in conventional fixed bed, CSTR and supercritical reactors on unpromoted cobalt catalyst

Introduction

Fischer-Tropsch synthesis has been studied in different reactor systems. Plug flow reactor, continuous stirring tank reactor and fluidized bed reactor have been used. Gas, liquid and supercritical reaction media were used in different reactor systems and under different operating conditions. Fischer-Tropsch synthesis reaction performed in the supercritical phase offers the opportunity to improve the heat transfer property and the ability to extract the heavy wax product from catalyst pores, and therefore extends catalyst lifetime. However, the introduction of the supercritical solvent into the reactor system would increase the operation cost not only because of the consumption of the solvent but also because of the much higher operating pressure. The continuously stirring tank reactor, on the other hand, is another alternative to the rapid catalyst deactivation in plug flow reactor. The heat transfer property is even better than the supercritical media; the disadvantage is that diffusion is slower in the slurry phase than plug flow reactor and therefore the overall reaction rate would be lower. The study conducted on supercritical Fischer-Tropsch synthesis using an unpromoted Co/SiO₂ catalyst prepared in this lab indicated that the lower rate of catalyst deactivation did occur; however, the selectivity of methane decreased by the application of the supercritical solvent. The same catalyst was studied in the continuously stirring tank reactor to compare the activity, selectivity, deactivation rate etc.

Experimental

A 2kg batch Co/SiO₂ catalyst was prepared using an incipient wetness impregnation technique. The support material is Davisil silica 644 (surface area 300m²/g; pore volume: 1.15cm³/g) and the cobalt loading is 15%. The CSTR reactor was loaded with 17.7g of the catalyst. The initial conditions for the reaction were 350psig, 220°C, with the trap temperatures at 200, 130 and 0°C. The feed gas was initially set to 16.03 slph with a percentage composition of 10.73 H₂, 5.03 CO for a H₂:CO ratio of 2.02 and 6.04 WHSV. 300 Grams of startup oil PW3000 was used. The catalyst was pretreated in a fixed bed reactor under hydrogen at 350°C for 15hrs and then added to the startup oil without exposure to the atmosphere.

Results and discussion

Figure 1 shows the change of CO conversion with time on stream in the CSTR at a space velocity of 1.0 sl/g/hr. It shows that, except for the rapid decline of CO conversion in the first 24 hrs of time on stream, the catalyst deactivated at a fairly stable rate of 1.6% CO conversion per day. Figure 2 is the CO conversion curve for the fixed bed and supercritical Fischer-Tropsch synthesis over the same catalyst at the same syngas partial pressure, same temperature and under the same space velocity. The deactivation rate for the fixed-bed operation before using the supercritical solvent is about 9.9%CO conversion per day which is much faster than in the CSTR. The addition of the supercritical solvent into the reactor, on the other hand, decreases the deactivation rate of the catalyst significantly, as one can see from Figure 2. The methane selectivity vs time on stream curves of the CSTR and fixed bed reactors are described in Figures 3 and 4. Similar methane selectivity was obtained at the same level of CO conversion for the fixed-bed reactor and the CSTR. Nevertheless, the methane selectivity for the supercritical Fischer-Tropsch synthesis is much lower than in both conventional fixed-bed and CSTR. The

same trend can be observed for the CO₂ selectivity under these three conditions (Figures 5 and 6).

At the same space velocity, the hydrocarbon productivity rate of the catalyst in the conventional fixed-bed reactor, CSTR and supercritical Fischer-Tropsch synthesis are 0.50, 0.59 and 0.85 (under the most favorable condition), respectively. Therefore, the supercritical Fischer-Tropsch synthesis is still a promising alternative route compared to the conventional fixed-bed synthesis. However, the CSTR is also proved to have a lower catalyst deactivation rate. The choice between CSTR and supercritical reactor depends on the comparison between productivity and the investment and operation cost.

The activity and selectivity of the catalyst were tested in a CSTR at different space velocities, and the CO conversion vs 1/GHSV curve was plotted in Figure 7. It is concluded that the CO conversion changes linearly with the reciprocal of space velocity at the conversion range being studied.

Figure 8 shows the hydrocarbon productivity rate vs the reciprocal of space velocity. One can draw the conclusion that the productivity does not change over the space velocity range being studied. It again supports the idea that at low CO conversion range, Fischer-Tropsch synthesis rate on unpromoted cobalt catalyst in a CSTR is independent of CO concentration, provided the H₂/CO ratio remains constant.

Figure 1. CO conversion vs time on stream in CSTR
(T = 220°C, GHSV = 1.0 SL/hr/g catalyst, P = 295 psig).

Figure 2. CO Conversion vs. time on stream ($T=220^{\circ}\text{C}$, $P_{\text{total}}=8.0\text{ MPa}$, $P_{\text{syngas}}=2.0\text{ MPa}$, $\text{H}_2:\text{CO}=2:1$, (1) $P_{\text{He}}=6.0\text{ MPa}$, $P_{\text{C5+C6}}=0$; (2) $P_{\text{He}}=4.0\text{ MPa}$, $P_{\text{C5+C6}}=2.0\text{ MPa}$; (3) $P_{\text{He}}=2.5\text{ MPa}$, $P_{\text{C5+C6}}=3.5\text{ MPa}$; (4) $P_{\text{He}}=0$, $P_{\text{C5+C6}}=6.0\text{ MPa}$).

Figure 3. CH₄ selectivity vs time on stream in CSTR
(T = 220°C, P = 295 psig, GHSV = 1.0 SL/hr/g-catalyst).

Figure 4. CH₄ selectivity vs time on stream in fixed bed and supercritical reactors ($T=220^{\circ}\text{C}$, $P_{\text{total}}=8.0\text{ MPa}$, $P_{\text{syngas}}=2.0\text{ MPa}$, $\text{H}_2:\text{CO}=2:1$. (1) $P_{\text{He}}=6.0$, $P_{\text{C}_5+\text{C}_6}=0$; (2) $P_{\text{He}}=4.0$, $P_{\text{C}_5+\text{C}_6}=2.0$; (3) $P_{\text{He}}=2.5$, $P_{\text{C}_5+\text{C}_6}=3.5$; (4) $P_{\text{He}}=0$, $P_{\text{C}_5+\text{C}_6}=6.0$).

Figure 5. CO₂ selectivity vs time on stream in CSTR (T=220°C, GHSV=1.0 SL/hr/g catalyst, P=295 psig).

Figure 6. CO₂ selectivity vs time on stream in fixed bed and supercritical reactors (T=220oC, Ptotal=8.0 MPa, Psyngas=2.0 MPa, H₂:CO=2:1. (1) P_{He}=6.0, P_{C5+C6}=0; (2) P_{He}=4.0, P_{C5+C6}=2.0; (3) P_{He}=2.5, P_{C5+C6}=3.5; (4) P_{He}=0, P_{C5+C6}=6.0).

Figure 7. CO conversion vs 1/GHSV at 100hrs time on stream in CSTR (T=220°C, P=295 psig).

Figure 8. STY vs 1/GHSV in CSTR
(T = 220°C, P = 295 psig).

B. CO and CO₂ Hydrogenation Over Co/SiO₂ Catalyst

Summary

CO and CO₂ hydrogenation was studied in a fixed bed reactor using a Co/SiO₂ catalyst. The reaction was carried out at 220°C, 350psig, H₂:CO=2:1, H₂:CO₂ = 2.1, with a total flow rate of 150 mL/min (3NL/hr/g catalyst) and a H₂+CO, H₂+CO₂ or H₂+CO+CO₂ flow rate of 50 mL/min(1NL/hr/g catalyst). CO, CO₂ and CO,CO₂ mixture feed gas was used, respectively, for comparison. The results indicated that in the presence of CO, CO₂ hydrogenation was very small. For the cases of only CO or only CO₂ hydrogenation, the activity of the two were similar but the selectivity was very different. For CO hydrogenation, normal Fischer-Tropsch synthesis product distributions were observed with an α of about 0.80; in contrast, the CO₂ hydrogenation product contained about 70% methane. Thus, CO₂ and CO hydrogenation appears to follow different reaction pathways.

Introduction

Fixation of carbon dioxide has become of greater interest in recent years, primarily because of its impact on the environment through the greenhouse effect. One approach that has attracted attention is to produce synthesis gas through its reaction with methane even though the syngas produced only has a H₂/CO ratio of 1 for the idealized reaction. Another option is to recycle carbon dioxide to a gasification unit; however, there is a limit to the amount of carbon dioxide that can be utilized in this manner. Another approach is to hydrogenate carbon dioxide in Fischer-Tropsch synthesis (FTS) plants; this has become an attractive approach even though one must find a source of hydrogen to accomplish this.

For high temperature (330-350°C) FTS the water-gas-shift (WGS) reaction is sufficiently rapid so that it is nearly at the equilibrium composition. The hydrogenation of CO₂ at high temperatures is possible and occurs in the fluid bed reactors operated by Sasol and Moss gas.

However, the use of a slurry phase bubble column reactor is very attractive since its use allows the FTS reaction to be carried out isothermally. In the liquid phase synthesis, lower temperatures must be utilized (220-240°C) with either a cobalt or iron catalyst. It was of interest to compare the FTS reactions of CO and CO₂ with a cobalt catalyst. In this initial work a simple catalyst formulation has been utilized: cobalt supported on a silica without any promoters.

Experimental

The catalyst was prepared by three incipient wetness impregnations of silica (Davisil 644, 100-200 mesh, 300 m²/g, and pore volume of 1.15 cm³/g) with aqueous cobalt nitrate to produce a final loading of 15 wt.% CO. The material was dried in a fluidized bed and then calcined for 4 hrs. in an air flow at 400°C. Three grams of the calcined catalyst was diluted with 15 g of glass beads and placed in a fixed bed reactor where it was reduced in a H₂(33%)/Ar flow for 10 hours at 350°C. The reaction conditions were: 220°C, 24 atm (2.4MPa), H₂/CO = 2/1, 3 NL/hr/g catalyst total gas flow, 1 NL/hr/g catalyst synthesis gas flow. Analysis of the gaseous products was accomplished using gas chromatography.

Results

The conversion of CO and CO₂ during 10 days on-stream are given in figure 1. Compared to the CO conversions of the same and another similar Co-silica catalyst, it appears that the initial CO conversion is about the same in the CSTR and in the fixed bed reactor; however, the activity decline is more rapid in the fixed bed reactor. The run data and conversions for the fixed bed reactor are compiled in table 1.

There was a decline in activity during the period between collecting the first two samples. The exit gas from the CO₂ conversions contained more CO₂ than the calibration gas so that CO₂ conversions were calculated from the mass balance for the other gaseous and liquid products; thus, there is some uncertainty in the absolute CO₂ conversion data but the trend shown

in Table 1 and figure 1 is certainly valid. Thus, with the cobalt catalyst the conversion of CO and CO₂ occur at about the same rate. This is in contrast to the observations with an iron catalyst under low temperature FTS conditions where the rate of conversion of CO₂ is considerably lower than for CO (1-6).

A striking difference for the cobalt catalyst is the formation of methane. Under the same reaction conditions, the amount of methane produced is much higher for the CO₂ reactant (figure 2). Whenever CO₂ was the reactant, methane accounted for greater than 70% (based on carbon) of the products. However, under the same reaction conditions and with the same catalyst, methane accounted for less than 10% of the products with CO as reactant. Similar results are reported by Riedel et al. (6). This requires that methane be formed by two pathways or that a common reaction intermediate and reaction pathway does not occur with CO and CO₂.

During period 9, the feed was changes so that equal amounts of CO and CO₂ were present in the feed and the flows of Ar, H₂ and (CO + CO₂) were the same as when either pure CO or CO₂ was converted. Under competitive conversions, CO was converted much more rapidly than CO₂, clearly showing that CO is adsorbed on the Co catalyst to a much greater extent than the CO₂. Whereas the total carbon oxide conversion is about the same expected from the trend of the previous runs, the conversion of CO accounted for more than 90% of the total conversion of the carbon oxides. A similar result was obtained following the conversion of methanol except that there was not as dramatic a difference as would be expected from the trend of the previous conversions. The CO conversion following the period of methanol feed was lower than expected from the trend of the prior periods. Since the water partial pressure was much higher during the conversion of methanol, it is anticipated that irreversible, or slowly reversible, damage of the catalyst occurred during the exposure to the high water partial pressure conditions.

Following the first conversion of the mixture of CO and CO₂, methanol was substituted for the carbon oxides feed. Because of the limitations of the liquid pump, the feed during this period was only H₂ and methanol. The total flow was 4 NL/hr/g catalyst and the H₂/methanol molar ratio was 2/1. Thus, the H₂/carbon ratio in the feed was the same as when CO and/or CO₂ was the feed but the flow rate of methanol was four times that of the carbon oxide. Under the reaction conditions used the conversion of methanol was about 50% whereas the conversion of CO or CO₂ was slightly less than 25%. Thus, considering the higher flow rate (4 times higher) and higher conversion (2 times higher) of methanol, the total carbon converted with the methanol feed was about 8 times greater than for the carbon oxides. Thus, the relative rate is rapid enough that any methanol intermediate could be converted to methane so that methanol would not be detected in the liquid sample; unfortunately, in this preliminary run the analysis of the gas sample did not provide a measure of the amount of methanol in the gas phase. The only significant products from the conversion of methanol under the FTS conditions were methane and water; thus, any methanol formed during the reaction could have been converted to methane.

Discussion

The difference in the product distributions obtained from the hydrogenation of CO and CO₂ preclude a common reaction pathway for FTS unless there is a second reaction pathway for the conversion of CO₂, but not CO, to methane. Furthermore, if there is a second pathway, then the FTS with CO₂ occurs at about only 20% of the rate for CO.

Based on the preliminary data, it is proposed that the conversion of CO and CO₂ occurs by different reaction pathways. It is assumed that the hydrogenation and breaking of the two C-O bonds of the CO₂ provide the source of the different pathways. In this proposal, the breaking of the C-O bond, presumably by the addition of adsorbed H to form C-O-H, competes

with, and probably leads, the addition of adsorbed H to form the C-H bond. Thus, for CO the following reaction pathway could apply:

In the case of CO₂ the reaction is more complex since there are two C-O bonds that must be broken prior to, or simultaneous with, the formation of the C-H bond. If it is assumed that similar rates apply for the formation of the first O-H and C-H bonds as in the case of CO we would have a different situation, idealized in reaction [2]:

If reaction [2] is valid, it is then a matter of the hydrogenation of the adsorbed oxygen species to produce the adsorbed intermediate (methanol) and its subsequent hydrogenation:

Based on the carbon mass balance, about 75% of the hydrogenation of CO₂ would proceed by reaction [3] and the remainder would involve the breaking of the second C-O bond to continue along the normal FTS reaction pathway that is followed by CO hydrogenation. At this time, while the above mechanism accounts for the products that are produced from the hydrogenation of CO₂, it is very speculative. ¹⁴C-tracer studies are planned that should provide some evidence to establish whether the speculation has merit.

The results to date for the hydrogenation of CO₂ indicate that it will not be commercially attractive using typical FTS catalysts based on iron or cobalt.

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Table 1			
Run Conditions and Results from the Conversion of CO and CO ₂ with a Cobalt-silica Catalyst			
Sample No.	Time on Stream(hrs)	Feed Gas	Conversion(%)
1	17.3	CO	52.2
2	39.47	CO	45.8
3	44.47	CO ₂	31.2
4	61.97	CO	24.4
5	70.47	CO ₂	23.1
6	90.97	CO ₂	20.5
7	109.97	CO	18.6
8	117.22	CO ₂	24.5
9	134.47	CO+CO ₂	CO, 53.5% CO ₂ , 3.98%
10		methanol	
11	206.22	CO+CO ₂ (different flow rate)	CO: 9.86% CO ₂ : 6.1%
12	226.89	CO ₂	22.8

Fig.1 CO and CO₂ conversion as a function of time on stream

Fig. 2 Methane selectivity as a function of time on stream

C. CO and CO₂ Hydrogenation over Co-Pt/Al₂O₃ Catalyst

Introduction

The feed syngas from natural gas contains a small amount of CO₂, the effect of CO₂ therefore should be studied to determine the necessity of separation of CO₂ from syngas. Study of CO₂ hydrogenation will also help us understand the mechanism for methane formation. CO₂ methanation is important in production of substitute natural gas, since it contributes additional methane needed to meet heating value specifications. Two categories of mechanisms for CO₂ hydrogenation has been proposed based on the early work done on nickel catalysts, (1) conversion of CO₂ to CO via the reverse water gas shift reaction followed by CO methanation, and (2) direct hydrogenation of CO₂ to methane by a mechanism distinct from CO methanation.

Previous works on CO and CO₂ hydrogenation of our group leads to the conclusion that CO hydrogenation rate is much higher than CO₂ over cobalt catalyst and CO₂ methanation goes through methanol as an intermediate.

The purpose of this investigation is to determine the deactivation rate for CO₂ hydrogenation at different H₂:CO ratio and different conversion level, as well as the deactivation rate of CO hydrogenation. We would probably have a better understanding of the mechanism of deactivation.

Experimental

Preparation of Co-Pt/Al₂O₃

Condea vista B alumina with a surface area of 300m²/g, pore volume of 1.15m³/g was used as support materials and the cobalt loading was 15%. A multi-step incipient wetness impregnation method was used to add cobalt nitrate solution to alumina with a drying procedure after each impregnation at 80°C in a rotary evaporator. Following cobalt addition, tetramineplatinum nitrate solution was added by an incipient wetness impregnation method and

the platinum loading was 0.5%. The catalyst was then dried in a rotary evaporator at 80°C again and calcined at 400°C for 4hrs.

Fixed-bed Fischer-Tropsch Synthesis Study

3g of Co-Pt/Al₂O₃ catalyst was diluted by 15g of glass bead and then loaded in a two inch diameter reactor, a three zone furnace was used to control the temperature of the reactor. Four Brooks mass flow controllers were used to control the flow rate of CO, CO₂, H₂ and He. Fischer-Tropsch synthesis was conducted at 210°C, 350psig with H₂:CO=2:1 and GHSV=5.0SL/hr/gcatalyst(H₂:CO:He=2:1:2). CO₂ hydrogenation was tested at same temperature and pressure but with H₂:CO ratio of both 2:1(H₂:CO:He=2:1:2) and 4:1(H₂:CO₂:He=4:1:4). The space velocity was changed from 9.0SL/hr/gcatalyst to 5.0 SL/hr/gcatalyst.

Results and Discussion

Since we use H₂:CO ratio of 2:1 as the feed gas, the highest CO₂ conversion is 50%. At time on stream 48hr, CO₂ conversion observed was 45% which is close to equilibrium. The fact that the conversion decreased at 0.81% CO₂ conversion per day indicated that the catalyst is reasonably stable for CO₂ hydrogenation. In order to investigate the stability of catalyst far from equilibrium, we increased the flow rate from 5.0SL/hr/gcatalyst to 9.0SL/hr/gcatalyst. The deactivation rate became even lower(from 0.81% to 0.69% CO₂ conversion per day) and the activity range maintained at about 20% CO₂ conversion range.

One of the assumptions for the deactivation mechanism of cobalt Fischer-Tropsch synthesis catalyst is the oxidation of surface cobalt to oxide or cobalt aluminate by water. Our assumption of the oxidation mechanism is that when H₂O/H₂ partial pressure ratio goes up to certain point, the oxidation of the cobalt cluster starts to occur. For CO₂ hydrogenation when the conversion level is at 40%, the H₂O/H₂ partial pressure ratio is about 2.0 and is much higher than CO hydrogenation (0.3 at 40% CO conversion). But for CO₂ hydrogenation, the deactivation is

not so obvious (figure 1 is the CO_2 conversion as a function of time on stream). One explanation is that the oxidation only occurs to the small clusters and the methanation of CO_2 is catalyzed by the larger cobalt clusters. The other explanation is that the surface oxidation did not occur as fast as CO hydrogenation. That makes the assumption of $\text{H}_2\text{O}/\text{H}_2$ partial pressure ratio as the decisive factor for the oxidation invalid. It also brings up another explanation of the deactivation of CO hydrogenation, which is $\text{H}_2\text{O}/\text{CO}$ ratio is a more important factor. One possibility is that the adsorption of H_2O and CO are competitive and since more H_2O has been formed, the less CO can be adsorbed. But the results of CO_2 hydrogenation eliminate that possibility; therefore, one can conclude that H_2O and CO has formed some kind of intermediate which caused the oxidation or crystal growth of cobalt clusters.

Since the methanation of CO_2 requires $\text{H}_2:\text{CO}$ ratio of 4:1, we adjusted the feed gas to this ratio to further study the stability of the catalyst and the results are shown in figure 2. When the conversion level is 42%, the catalyst did not deactivate after 24hrs, then the flow rate was decreased to achieve a conversion of about 55%; the catalyst started to deactivate slowly but leveled off at about 40% CO_2 conversion. It can be concluded that during CO_2 hydrogenation, deactivation is slower than for CO hydrogenation even at high conversion levels.

After 504 hours of using CO_2 as a feed gas, CO hydrogenation was studied with a $\text{H}_2:\text{CO}$ ratio of 2:1 and space velocity of 5SL/hr/gcatalyst. Figure 3 shows the results of CO conversion as a function of time on stream, and figure 4 is CO and CO_2 conversion as a function of time on stream when CO was used as the feed gas first. It can be concluded that CO_2 hydrogenation did cause deactivation of the catalyst for subsequent CO hydrogenation since, after 504 hours of time on stream, CO conversion decreased from 52.5% to 28.7%. However, it can be seen from figure 3 that the deactivation rate of CO hydrogenation is much faster than CO_2 hydrogenation at 30% CO conversion. If the feed gas is CO and the conversion is 60%, the

deactivation rate could have been much higher and after 504 hours of time on stream, CO conversion rate would have been much lower than 28.7%. From figure 3, it seems that the CO conversion stayed at about 20% and it agrees with our CSTR data that the deactivation rate is a function of CO conversion level; the lower the CO conversion, the lower the deactivation rate.

Figure 1. CO₂ hydrogenation over Co-Pt/Al₂O₃, 210°C, 350psig, H₂:CO=2:1, GHSV=5.0SL/hr/gcatalyst.

Figure 2. CO₂ hydrogenation over Co-Pt/Al₂O₃ at 210°C, 350psig, H₂:CO=4:1, GHSV=9.0 and 5.0SL/hr/gcatalyst.

Figure 3. CO hydrogenation over Co-Pt/Al₂O₃ at 210°C, 350psig, H₂:CO=2:1, GHSV=5.0SL/hr/gcatalyst.

Figure 4. CO or CO₂ conversion as a function of time on stream

D. The CSTR studies of Co(10)/B(x)/TiO₂ Fischer-Tropsch catalysts

1. Reaction system

A 1-liter autoclaver, operated as a continuous stirred tank reactor (CSTR), was used for the slurry FTS reactions. Analysis of the gaseous, liquid, and solid (at room temperature) products was conducted both on and off line using a variety of gas chromatographs.

2. Procedure

The catalysts used were 10 wt% Co/TiO₂ and 10 wt% Co/ 0.05% B/TiO₂, prepared by incipient wetness impregnation. Catalyst (about 15 g) was reduced *ex-situ* with hydrogen at 300°C for 16 h and transferred under the protection of helium to CSTR to mix with 300 g of melted P.W. 3000. The catalyst was then reduced *in-situ* in the CSTR; the hydrogen was introduced to reactor at atmospheric pressure with a flow rate of 30 NLh⁻¹gcat.⁻¹ (25°C, 0.1 mPa). The reactor temperature was increased to 280°C at a rate 120°C h⁻¹ and maintained at this activation condition for 24 h. After the activation period, the reactor temperature was decreased to 210°C and synthesis gas was then introduced. During the entire run the reactor temperature was 230°C, the pressure was 350 psig, and the stirring speed was maintained at 750 rpm.

The space velocity of the synthesis gas was varied from 1 to 5 NL h⁻¹ gcat.⁻¹ at a constant H₂/CO ratio of 2. Afterwards, the H₂/CO ratio synthesis gas was varied from 2 to 5 at a constant space velocity of 2 NL h⁻¹gcat.⁻¹. The conversion of carbon monoxide and hydrogen and the formation of products were measured during a period of 24 h at each condition.

3. Results

The attached figures show that synthesis gas conversion, methane selectivity and hydrocarbon production rate varied with space velocity and the H₂/CO ratio for two catalysts.

Synthesis gas conversion for two catalysts is shown in Figure 1. The synthesis gas conversion was found to increase with decreasing space velocity. At the higher space velocity

(SV>4), the two catalysts showed very similar synthesis gas conversion; at low space velocity (SV<4), the catalyst with 0.05 % B showed a slightly higher conversion.

Figure 2 shows the hydrocarbon production rate as a function of reciprocal flow rate. For the catalyst with 0.05% B, the hydrocarbon rate increased almost linearly with increasing space velocity. For B-free catalyst, the hydrocarbon rate increased first and then kept a constant of 2.0 g/gcat./h with increasing space velocity; however, the difference between the two runs is small.

From Figure 3, we find the methane fraction of the hydrocarbons increased with increasing space velocity. For all space velocities, the catalyst with 0.05% B showed higher methane selectivity.

For two catalysts, the effects of H₂/CO ratio on conversion and methane selectivity are very similar (Figures 4 and 5). Increasing the ratio of H₂/CO resulted in: (i) synthesis gas conversion increased first and then decreased and reached a maximum at the H₂/CO of 4; (ii) methane selectivity increased almost linearly.

In summary, the presence of boron produced only minor changes on the properties of the cobalt catalyst. In earlier studies, it was shown that the presence of boron made the catalyst less susceptible to poisoning by sulfur.

Figure 1. Synthesis gas conversion as a function of reciprocal flow rate

Figure 2. Hydrocarbon production rate as a function of reciprocal flow rate

Figure 3. Methane selectivity vs reciprocal flow rate

**Figure 4. Synthesis gas conversion vs ratio of H₂ to CO
(at SV=2 NL/gcat./h)**

**Figure 5. Methane selectivity vs ratio of H₂ to CO
(at SV=2 NL/gcat./h)**

E. Study of supercritical phase Fischer-Tropsch synthesis

1. Introduction:

Fischer-Tropsch synthesis has been studied extensively in both gas and liquid phase reaction media, in which fixed-bed and CSTR or bubble column slurry phase reactors were used respectively. Gas phase reactions may exhibit higher initial reaction rates but also is inevitably accompanied by local overheating of the catalyst surfaces as well as by the deposition of heavy wax in catalyst pores. Local overheating of the catalyst and the plugging of the pores of the catalyst may lead to deactivation of the catalyst and also to an increase in methane selectivity. Liquid phase reactions have superior heat removal capabilities when compared to gas phase reactions and are, therefore, able to maintain a relatively constant reaction temperature throughout the whole reactor. Another advantage of liquid phase synthesis is that the high molecular weight products are more soluble in the liquid media compared to gas phase reaction media. However, the diffusion of synthesis gas into the pores of the catalysts may be slower in the slurry phase so that the overall reaction rate may therefore be lower. In addition, problems may arise as the accumulation of high molecular weight products in the reactor during the operation, and the *in situ* separation of fine catalyst particles from the heavy products remain to be solved for liquid phase reaction. The ideal FT synthesis medium would therefore be one with gas-like transport properties and liquid like heat capacity and solubility characteristics. Such a desired combination of fluid properties can possibly be obtained by conducting the Fischer-Tropsch synthesis in a supercritical reaction media.

The critical temperature of a fluid is the highest temperature at which liquid and vapor can exist together. The pressure at which condensation of vapor to liquid occurs when the temperature is equal to the critical temperature is the critical pressure. At temperatures above the critical temperature a fluid cannot undergo a transition to a liquid phase, regardless of the

pressure applied. A fluid is said to be supercritical when its temperature and pressure exceed the temperature and pressure at the critical point. Supercritical fluid (SCF) are attractive media for chemical reactions because of their unique properties such as viscosity, diffusivity, density and solubility. Many of the physical and transport properties of an SCF are intermediate between those of a liquid or a gas. Changing the pressure near the critical region can tune the density and transport properties of a fluid to obtain unique fluid properties (e.g., gas-like transport properties or liquid-like solvent power), which offer certain advantages in heterogeneous catalysis reactions. Specific to the Fischer-Tropsch synthesis reaction, it seems SCF can possibly in situ extract the heavy hydrocarbons from the catalyst pores, thereby extending catalyst lifetime. The diffusion of reactant, hydrogen and carbon monoxide, as well as both primary and secondary hydrocarbon products could also be effected by SCF and favorably affect reaction rate and selectivity.

Studies on Fischer-Tropsch synthesis in supercritical media have, to date, been done primarily by three groups of scientists. Fujimoto's group is a pioneer in the area, an excellent job was done by applying the idea to Fischer-Tropsch synthesis; however, the lack of steady-state data made the results less convincing than desired. Bukur's group did steady state work; nevertheless, by using propane as the supercritical media, the density of the solvent is not high enough to attain the optimum solubility properties. Subramaniam's group did the pressure tuning work using hexane as the solvent; still, different syngas partial pressures and residence times were used to compare the activity and selectivity. Therefore, too many variables were introduced to draw solid conclusions.

Steady-state supercritical Fischer-Tropsch synthesis was studied in our work using a fixed-bed reactor and an unpromoted Co/SiO₂ catalyst. This serves as the baseline for promoted catalyst studies. A pentane-hexane mixture was used as the supercritical solvent. Overall reactor pressure, syngas partial pressure and contact time were kept constant to obtain a valid

comparison of the impact of solvent density in the catalytic activity and selectivity. Three different partial pressures of the mixture were chosen based on the density-pressure curve in order to investigate the pressure tuning effect to Fischer-Tropsch synthesis near critical region.

2. Experimental

Catalyst preparation: A 2kg batch of 15% Co/SiO₂ catalyst was prepared by incipient wetness impregnation method using Davisil 644 Silica gel as support (surface area 300m²/g, pore volume: 1.15cm³/g, particle size 100-200mesh) and an aqueous cobalt nitrate solution for impregnation. The catalyst was dried by being suspended in air at 80°C in a fluidized vessel and then calcined at 400°C for 4 hrs.

Reactor diagram: A schematic of the reactor Figure 1 is the diagram used to do supercritical Fisher-Tropsch study is shown in Figure 1. Basically, it is a plug-flow reactor with a pump for adding the supercritical solvent. A characteristic of the unit is the capability of being able to be repressurize quickly after taking a liquid product for each mass balance period. Since we pump in a significant amount of solvent during the period, its removal as a liquid cause a remarkable pressure drop. The other difference between the reactor and a traditional plug-flow reactor is that we use a three heating zone furnace and the first zone filled with micro-glass beads to vaporize the solvent. We also set up two parallel sets of hot and cold traps to use for mass balance period and period between mass balance to improve the operation.

Pretreatment condition: The catalyst was reduced with mixture of hydrogen and argon. The temperature was increased to 100°C during 30min and held at 100°C for 30min, and after that the temperature was increased to 350°C with at a rate of 1°C/min, then held at 350°C for 15hrs.

Reaction conditions:

Conditions	P _{overall} (MPa)	P _{syngas} (Mpa) H ₂ :CO =2.0	P _{solvent} +P _{He} (MPa)	T(°C)	Total Flow Rate (ml/min)	Syngas Flow Rate (ml/min)	He Flow Rate (ml/min)	Solvent Fow Rate★ (ml/min)
1	8.0	2.0	6.0	220	200	50	150	0
2	8.0	2.0	6.0	220	200	50	100	50
3	8.0	2.0	6.0	220	200	50	62.5	87.5
4	8.0	2.0	6.0	220	200	50	0	150
★gas phase flow rate								

3. Results and discussion:

Physical and transport properties of certain fluids change dramatically with pressure in a range around the critical pressure and at temperatures slightly higher than the critical temperature. They can be made either more gas-like or liquid-like by tuning the pressure. As to Fischer-Tropsch synthesis, the ideal situation is to find a condition where the maximum extraction of hydrocarbon products from catalyst pores can be reached to increase catalyst lifetime. However, diffusivity and viscosity of the fluid can have an impact on the degree of secondary reactions that take place on the surface of catalyst and therefore lead to changes in selectivity. Thus, different solvent and pressure tuning effects of the solvent are important to supercritical Fischer-Tropsch synthesis study.

A near optimal temperature for the cobalt catalyst being used in this study is about 220°C; therefore, the critical temperature of the solvent chosen should be below 220°C. Since the critical temperature for n-pentane is 197°C and for n-hexane is 232°C, a mixture of these two solvent can be used to obtain the maximum density. Figure 2 shows a curve of the critical temperature of pentane and hexane mixtures versus the hexane volume percentage. From Figure

2, it is calculated that 55%(V) of hexane/45%(V) of pentane mixture has the highest density whose critical temperature is under 220°C.

In order to obtain good representative pressure points to study the tuning effect, it is necessary to have an idea of how density changes with pressure near the critical region. Figure 3 is the density of 55%(V) n-hexane and 45%(V) n-pentane mixture versus pressure curve between 1-15MPa at 220°C (a Hysys 2.1 process simulator was used to calculate the density data). Partial pressures of 2.0MPa, 3.5MPa and 6.0MPa of the mixture were chosen to represent the gas-like, supercritical and liquid like conditions, respectively. Helium was used as a balancing gas to keep the overall pressure and residence time constant. Altogether, four conditions were studied; this included no added solvent and three different solvent partial pressures. After taking a liquid sample, helium was charged to the cold trap to make up the pressure drop. Hot and cold traps temperatures were controlled at 160°C and 0°C respectively. Mass balance time of each sample was around 2 hrs.

Exit flow rate and molar percentage of the components of the gas was used to calculate CO conversion. Normalized exit flow rate was obtained by converting for the increase of flow rate caused by condensation of solvent in the cold trap and the amount of solvent in the exit gas phase. The rate of volume decrease of the reactor-collector may increase rapidly enough for this correction to make a large change in the measured conversion.

CO conversion versus time on stream data are shown in Figure 4. It can be concluded from Figure 4 that the supercritical phase Fischer-Tropsch synthesis significantly alters the total conversion and inhibit the deactivation of the catalyst. As a matter of fact, introducing only 2.0MPa of the pentane-hexane mixture to the reactor increased the CO conversion from 27% to 46%. The mixture at this pressure is not at its supercritical state; however, the density of the reaction media is much higher than condition 1 in which only helium was the balancing gas.

Therefore, the solubility of the hydrocarbon in reaction media was increased, and it is concluded that the catalyst pores contained less liquid and more active sites were available which leads to the increase of the CO conversion. After 3.5MPa of pentane-hexane mixture was fed into the reactor (condition 3), the reaction media should be in the supercritical phase. The density is much higher than that in condition 2, causing the solubility to increase significantly, while, the diffusivity of reactant and the product is reasonably fast; therefore, the highest CO conversion was obtained. When the partial pressure of pentane-hexane mixture reached 6.0MPa (condition 4), the density of the mixture is more liquid-like and the maximum extraction of the heavy wax product occurs; however, the diffusivity of the media is also more liquid like. This may have limited the Fischer-Tropsch reaction and hence slightly lower CO conversion was observed. Several steady-state data were obtained for each condition and the reproducibility is good as shown by the data in Figure 4 for repeating the measurements at each condition. Throughout the period that solvent was introduced into the reactor, the deactivation is rather negligible. After switching back to the condition 1 in which no solvent was introduced, the CO conversion decreased to 40% from 49% at condition 2. The deactivation was rapid at this condition and conversion decreased to 16.0% in only 33 hrs.

Since the analysis of the liquid product is not complete, the α value of the reaction has not been defined. Nevertheless, the selectivities of methane and CO₂ were calculated and the results are interesting. Figures 5 and 6 show the selectivity of methane and carbon dioxide with time on stream, respectively. It can be seen that methane selectivity decreased dramatically with the introduction of solvent into the reactor system. The higher the partial pressure of the pentane-hexane mixture, the lower the methane selectivity. The formation of CO₂, while small, and parallel that of methane.

4. Conclusion

Steady-state supercritical Fischer-Tropsch synthesis was studied using a fixed-bed reactor and a Co/SiO₂ catalyst. A pentane-hexane mixture was used as the supercritical solvent. Overall reactor pressure, syngas partial pressure and contact time were kept constant to obtain valid comparisons.

Three different partial pressure points of the mixture were chosen based on the density-pressure curve to investigate the pressure tuning effect for Fischer-Tropsch synthesis near critical region. It was found that supercritical phase Fischer-Tropsch synthesis can significantly inhibit the deactivation of catalyst, presumably due to the extraction of heavy hydrocarbon products from catalyst pores and possibly improving the heat transfer in plug-flow reactor. The highest CO conversion was obtained when the solvent partial pressure is just above its critical pressure compared to its more gas-like or liquid-like state. Reproducible data were obtained by repeating the measurements.

Methane and carbon dioxide selectivity decreased dramatically with an increase of pentane-hexane partial pressure. The selectivity of reaction and α value of different conditions will be defined in future work.

Figure 1. Supercritical FT Reactor-Flow Diagram

Figure 2. Critical temperature of pentane and hexane mixture with hexane percentage.

Figure 3. Density vs. pressure mixture of 55%(V) pentane and 45%(V) hexane.

Figure 4. Run YQZ 304. CO conversion vs. TOS ($T = 220^{\circ}\text{C}$, $P_{\text{total}} = 8.0 \text{ mpa}$, $P_{\text{syngas}} = 2.0 \text{ mpa}$, $\text{H}_2:\text{CO} = 2:1$; 1 = $P_{\text{He}} = 6.0$, $P_{\text{C5+C6}} = 0$; 2 = $P_{\text{He}} = 4.0$, $P_{\text{C5+C6}} = 2.0$; 3 = $P_{\text{He}} = 2.5$, $P_{\text{C5+C6}} = 3.5$; 4 = $P_{\text{He}} = 0$, $P_{\text{C5+C6}} = 6.0$).

Figure 5. Run YQZ 304. CH₄ selectivity vs. TOS (T = 220°C, P_{total} = 8.0 mpa, P_{syngas} = 2.0 mpa, H₂:CO = 2:1; 1 = P_{He} = 6.0, P_{C5+C6} = 0; 2 = P_{He} = 4.0, P_{C5+C6} = 2.0; 3 = P_{He} = 2.5, P_{C5+C6} = 3.5; 4 = P_{He} = 0, P_{C5+C6} = 6.0).

Figure 6. Run YQZ 304. CO₂ selectivity vs. TOS (T = 220°C, P_{total} = 8.0 mpa, P_{syngas} = 2.0 mpa, H₂:CO = 2:1; 1 = P_{He} = 6.0, P_{C5+C6} = 0; 2 = P_{He} = 4.0, P_{C5+C6} = 2.0; 3 = P_{He} = 2.5, P_{C5+C6} = 3.5; 4 = P_{He} = 0, P_{C5+C6} = 6.0).

Task 9. Cobalt Catalyst Life Testing

The objective of this task is to obtain life data on baseline cobalt Fischer-Tropsch catalysts.

A. Deactivation Study of Co-Re-Al₂O₃ Catalysts

It becomes more likely that, for the short term, the feed gas for a commercial Fischer-Tropsch synthesis operation will be based on natural gas instead of coal; therefore, cobalt catalysts may be preferred. Due to the high cost of cobalt catalysts, a stable catalyst is required to ensure extended runs. Thus, the cobalt catalyst must either be amenable to frequent regenerations over a long catalyst life or it must have a stable catalytic activity over a long (year or longer) period of time. A fundamental understanding of the deactivation mechanisms of cobalt catalysts is thus required to develop understanding that leads to the preparation of more stable catalysts and also to select the operating conditions to extend catalyst lifetime.

Supported cobalt catalysts deactivate during extended periods of time and commonly accepted reasons include: oxidation, carbon deposition, sintering, and sulfur poisoning. Sulfur poisoning can be avoided by deep desulfurization of the feed gas (at the expense of increases in the cost of synthesis gas). Carbon deposition may be minimized by careful control of the temperature protocol. The deactivation caused by sintering and oxidation will therefore be the major concerns. Investigations of the mechanism become very important.

Thermodynamically, bulk oxidation of cobalt to cobalt oxide by water is not favored under the reaction conditions (220°C, 275 psig, H₂:CO=2:1, 50-70% CO conversion). However, there are numerous literature citations to support the view that oxidation of supported catalysts occurs under the reaction conditions. A common belief is that the smaller the cobalt crystal size, the easier the oxidation. Thus, there may be a “magic” dispersion limit where, if the cobalt dispersion is higher than the “magic” number, oxidation takes place very rapidly, resulting in

rapid catalyst deactivation. Another hypothesis is that although bulk oxidation is unlikely, surface oxidation of the cobalt could occur during Fischer-Tropsch synthesis and this would also cause rapid catalytic activity decline.

The objective of the current study is to define the deactivation rate of the Co-Re-Al₂O₃ catalysts at different space velocities, to study the deactivation mechanism, to learn whether the deactivation is caused by sintering of the cobalt crystals, the oxidation of cobalt to cobalt oxide or the formation of cobalt aluminate.

Experimental

Catalysts. Three catalysts with a cobalt loading of 15 wt.% and rhenium loading of 0.2, 0.5 and 1.0 wt.%, respectively, were utilized.

Activation. The catalysts were reduced using 30 % H₂/70% He (V/V) in a fixed bed reactor at a space velocity of 10,000 GHSV at 350°C. The temperature was ramped to 350°C at 1°C per minute and held at 350°C for 4 hours. This was accomplished by overpressuring the reduction tube that contains the reduced catalyst and then opening the appropriate valves to force the entire catalyst volume into the autoclave containing the startup solvent. The reduction reactor was weighed prior to and after catalyst transfer to ensure that a quantitative transfer of the catalyst had been accomplished. The catalyst was then treated in hydrogen flow in the slurry phase reactor at 280°C for 4 hours.

Reaction Conditions. About 20 grams (actual catalyst weight for each run was accurately known) of catalyst was transferred into a 1L stirred autoclave which had been charged with 300g of C₃₀ oil (decene trimer obtained from Ethyl Corp.). Following catalyst reduction at 280°C in situ, the temperature was lowered to 150°C and synthesis gas was fed into the reactor. After the pressure reached 275 psig, the temperature was slowly increased to 220°C during 4 hours. A feed gas with H₂:CO ratio of 2:1 was used.

Results and Discussion

The activity and rate of loss of activity data are shown in figures 1 through 3. The activity measurements for the first two runs (using the two lower Re loaded catalysts) were started at 2.0 SL/g. cat./hr. Considering the scatter of the initial data for the run with the catalyst containing 0.5 wt.% Re (figure 2), the initial conversions for the 0.2 and 0.5 wt.% Re catalysts were essentially the same (70-75% CO conversion). These two catalysts exhibited a rapid and similar deactivation rate of the range 12-14% CO conversion/week. The catalyst containing 1.0 wt.% Re was started up at a higher flow rate so that the initial CO conversion was lower (37% compared to 70-75%) and the activity decline rate was lower (4.35 %CO conversion/week). Extrapolating the linear relation of the space velocity versus conversion data, described later, for these three catalysts, the initial conversion of CO with the 1% Re catalyst at a GHSV of 2.0 SL/g. cat/hr, as was used with the 0.2 and 0.5 wt.% Re catalysts, indicate an initial conversion of 95%. Considering the uncertainty associated with this extrapolation, a tentative conclusion is that the three catalysts with different Re content would have had a similar initial conversion for identical reaction conditions.. However, additional runs are required to better define this, and these will be done during the next quarter.

To establish a deactivation rate to cover a wide range of conversion levels will be a challenge. First, consider the data for the 0.2% Re catalyst. During the initial portion of the run at a space velocity of 2.0 SL/g. cat./hr, the rate of decline is high at 14.1% CO/week during about the first 200 hours of synthesis time. Returning to the same space velocity at about 700 hours of operation yielded a rate of decline that was much lower (figure 1); the rate of decline after returning to this same space velocity at about 1700 hours of synthesis is only 1.64% CO conversion/week. Compare the rate of decline of 4.61 %CO conversion/week when operating at 5 SL/g. cat./hr (during about 200-700 hours) with a conversion range of about 12-25% CO to the

rate at 2.0 SL/g. cat./hr of 1.64 %CO conversion/week at about 1700 to 2300 hours with a range of about 27-33% CO conversion. If the rate of decline was determined only by the conversion level, the rate at 2.0 L/g. cat./hr (1.64) should have been greater than the one at 5.0 L/g. cat./hr (4.61), and this was not the case. It therefore appears that time on stream may be as important, or even more important, than the conversion level. This has been observed with our Co-SiO₂ catalyst and has been reported by Sasol workers [1]. The Sasol workers, operating for a long period of time at the same operating conditions, have shown a rapid rate of decline in conversion during the initial synthesis period that is followed by a much longer period with a much smaller rate of decline (figure 4). The data for the 1% Re catalyst also appear to be consistent with this concept. These data are summarized in Table 1.

After more than 1800 hours of synthesis, regeneration (rejuvenation) was attempted with the catalyst containing 1% Re. The first rejuvenation was at reaction temperature with a H₂ flow rate of 7.5 SL/g. cat./hr and resulted in regaining 49% of the initial activity (figure 5) but this was followed by a rapid decline in CO conversion. The second rejuvenation was conducted at reaction temperature and pressure but at double the total flow (15 SL/g. cat./hr; H₂:Ar = 1:1) and for 4 hours. The second rejuvenation returned the CO conversion to 66% of the initial activity. However, during less than two days of operation, the CO conversion declined to about 40% of the initial activity. Following this rapid decline, there was a slower, but still high, rate of decline of about 17 %CO conversion/week.

Similar studies are continuing.

References

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Table 1				
Deactivation Rate, % CO conversion/week				
Promoter Level, wt. %	Rate	%CO conversion range	Rate	%CO conversion range
0.2	4.61	12-25	14.1	55-75
0.5	---	---	12.3	18-70
4.35	4.35	11-38	---	---

Fig 1 CO Conversion as a function of time on stream on 15%Co-0.2%Re/Al₂O₃

Fig 2 CO conversion as a function of time on stream for 15%Co-0.5%Re/Al₂O₃ catalyst, regenerate at 220⁰C, just stop the CO flow for 24hrs(too long) has no recovery, regenerate at 280⁰C, activity goes up close to the initial activity, but the product was mainly methane

Fig 3 CO conversion as a function of time on stream for 15%Co-1%Re/Al₂O₃ catalyst

FIGURE 4. STABILITY RUN ON THE COBALT CATALYST

Fig 5 Rejuvenation of catalyst 15%Co-1%Re/Al₂O
 1: rejuvenate by H₂(7.5SL/hr/g), 2: rejuvenate
 by H₂ and Ar mixture(H₂:Ar)=1:1, 15SL/g/hr)

B. Effect of Water on the Fischer-Tropsch Catalytic Properties of Ruthenium Promoted Co/TiO₂ Catalyst

Introduction

Fischer-Tropsch synthesis produces hydrocarbons and water. The amount of water produced depends on the synthesis gas conversion, reactor system and catalyst used. The effect of water on the iron Fischer-Tropsch catalysts has widely been investigated. It is well known that water may reoxidize iron during synthesis [1]. Less information is available for the effect of water on the cobalt catalysts. Hilmen et al. [2] recently studied the effect of water on Co/Al₂O₃ and CoRe/Al₂O₃ catalysts by adding water to the synthesis gas feed and by model studies exposing the catalysts to various H₂O/H₂ ratios. It was found that the catalysts deactivated when water was added during Fischer-Tropsch synthesis and the catalysts oxidized in H₂O/H₂ mixtures with a ratio much lower than expected for oxidation of bulk cobalt. For silica supported cobalt catalysts, the addition of water to synthesis gas feed has been shown to decrease the CO conversion [3]. Schulz et al [4] found no deactivation of a CO/Ru/ZrO₂/Aerosil and Co/MgO/ThO₂/Aerosil catalysts when water was added to the feed. Schulz et al. [5] has even reported increased activity. Kim et al. [6, 7] also reported increased activity for Re promoted, non-promoted Co/TiO₂ and unsupported cobalt catalysts as a result of addition of water during the Fischer-Tropsch synthesis. It has been explained that water possibly destroys the strong metal-support interaction (SMSI) effect in titania supported catalysts. In this study, the effect of water addition on the Fischer-Tropsch catalytic properties of a ruthenium promoted Co/TiO₂ catalyst was investigated. The incipient wetness technique was applied to prepare the catalyst and catalytic properties were evaluated in a continuous stirred tank reactor (CSTR) by using varying space velocities.

Experimental

The catalyst used was Ru(0.2 wt%)/Co(10wt%)/TiO₂ prepared in our laboratory, and was found to have good Fischer-Tropsch activity and stability. The catalyst activation was conducted first *ex-situ* and then *in-situ*, according to the following procedure. The catalyst (about 15 g) was put in a fixed bed reactor and pure hydrogen was introduced at a flow rate of 60 NLh⁻¹ (298 K, 0.1 MPa); the reactor temperature was increased from room temperature to 373 K at a rate of 120 Kh⁻¹, then increased to 573 K at a rate of 60 Kh⁻¹ and kept 573 K for 16 h. The catalyst was transferred under the protection of helium to the CSTR where it was mixed with 300 g of melted poly-wax (P.W. 3000). The catalyst was then reduced *in-situ* in the CSTR; the hydrogen was introduced to reactor at atmospheric pressure with a flow rate of 30 NLh⁻¹ (298 K, 0.1 MPa). The reactor temperature was increased to 553 K at a rate 120 K h⁻¹ and maintained at this activation condition for 24 h.

After the activation period, the reactor temperature was decreased to 483 K and synthesis gas (2H₂/CO) was introduced to increase the reactor pressure to 2.35 MPa. The reactor temperature was then increased to 503 K at a rate of 10 Kh⁻¹. During the entire run the reactor temperature was 503 K, the pressure was 2.35 MPa, and the stirring speed was maintained at 750 rpm.

The space velocity of the synthesis gas varied from 1 to 8 NL g⁻¹cat.h⁻¹. Argon was added to the feed gas and the composition was set to 2H₂/1CO/0.5Ar. In order to investigate the effect of water on the catalytic properties of the catalyst, argon was substituted by same amount of water at different space velocity. The conversion of carbon monoxide and hydrogen and the formation of products were measured after a period of 24 h at each condition.

Results and Discussion

Four runs have been done for the effect of water on the catalytic properties of the RuCo/TiO₂ Fischer-Tropsch catalyst using different space velocity procedures. The results for synthesis gas conversion are exhibited in Figures 1 and 2. For the first run, we started run with a space velocity of 2 NLg⁻¹cat.h⁻¹, then gradually increased the space velocity to 5, 7 and 8 NLg⁻¹cat.h⁻¹, respectively, to obtain the activity and selectivity data at different space velocities. After running at 8 NLg⁻¹cat.h⁻¹, the catalyst was treated with pure CO for 24 hours. It was found that CO treatment resulted in a decreased Fischer-Tropsch activity. The catalyst was regenerated by pure H₂ and the space velocity was then changed back to 1 NLgcat.⁻¹h⁻¹. The synthesis gas conversion was found to be almost the same as that obtained at space velocity of 2 NLg⁻¹cat.h⁻¹ before CO treatment. This indicates that the activity of the catalyst was not be recovered by the H₂ regeneration at 230°C. For the second run, we started the run with a low space velocity and obtained almost 100% CO conversion. However, when we changed space velocity to 2 NLg⁻¹cat.h⁻¹, the synthesis gas conversion decreased to about 50%, indicating that the reaction at high conversion level resulted in a deactivation of the catalyst. The results for the third run are strange, synthesis gas conversion decreased with decreasing space velocity, indicating that the catalyst deactivated very quickly. This appears to be due to a problem in the catalyst reduction procedure for that particular run. For the fourth run (Figure 2), we started the run with a space velocity of 7 NLg⁻¹cat.h⁻¹, then decreased the space velocity to 4, 2 and 1 NLg⁻¹cat.h⁻¹, respectively. The results were very similar to those obtained for first run except the data at space velocity of 1 NLg⁻¹cat.h⁻¹, which is much high than that of first and lower than second run.

During the fourth run, the water deactivation tests were made at synthesis gas space velocity of 2 NLgcat.⁻¹h⁻¹ by changing water flow back to same argon flow after feeding water for an extended period. The synthesis gas conversion was found to remain the same as that

obtained before the water addition. This indicated that the water addition did not cause a permanent deactivation of the catalyst.

From Figure 2, we can find that at low conversion levels (high space velocities; greater than $4 \text{ NLg}^{-1}\text{cat.h}^{-1}$), the addition of water to the feed did not have a significant effect on synthesis gas conversion. However, at high conversion levels (low space velocities), the addition of water resulted in a decrease in synthesis gas conversion. The higher the conversion, the more severe the water effect is. This indicates that the Fischer-Tropsch reaction rate is dependent on the partial pressure of water for the ruthenium promoted Co/TiO₂ catalyst and a P_{H_2O} term existed in the kinetic equation. The Fischer-Tropsch synthesis kinetics of cobalt catalysts have been investigated by some researchers. However, for all the kinetic equations P_{H_2O} term has not been included. A kinetic investigation for cobalt catalyst is being done in our laboratory.

The effect of water on the hydrocarbon production rate of catalyst is shown in Figure 3. The hydrocarbon rate increased with increasing space velocity for no water and adding water reaction systems. At high space velocities, the addition of water did not influence hydrocarbon rate. At low space velocities, the addition of water resulted in a decrease in the hydrocarbon rate.

Figure 4 shows methane selectivity vs space velocity. For no water addition, the methane selectivity increased slightly with increasing space velocity. Methane selectivity did change with the addition of water.

Figure 5 shows CO₂ selectivity as a function of reciprocal flow rate. CO₂ selectivity increased almost linearly with decreasing space velocity (increasing conversion) with and

without water addition. The addition of water increased the CO₂ formation about two times that of no water addition. This indicates that water also increased the water gas shift reaction.

References

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Fig. 1. Effect of water on the synthesis gas conversion of RuCo/TiO₂ F-T catalyst

Fig. 2. Effect of water on synthesis gas conversion (fourth run)

Fig. 3. Effect of water on hydrocarbon production rate

Fig. 4. Effect of water on methane selectivity

Fig. 5. Effect of water on CO₂ selectivity

C. Deactivation Rates for Co Catalysts

Introduction

In comparison with low cost Fe FTS catalysts, cobalt catalysts may work at relatively low reaction temperatures and pressures with higher yields of linear paraffins in the C_{5+} range and do not convert water by water gas shift reaction. The cobalt catalysts are believed to deactivate less than the Fe-based catalyst. The major drawback of cobalt catalyst is its high cost. Therefore, the present studies focused on improving the deactivation rates of these catalysts.

Experimental

Preparation of Cobalt Catalysts

The Co/Al₂O₃ catalyst was prepared by incipient wetness impregnation of Al₂O₃ (Condea Vista B alumina, BET surface area 200 m²/g, pore volume 0.4 cm³/g) with cobalt nitrate solution. The preparation procedure includes three step impregnations of cobalt salt and then followed by impregnation of promoter. Finally, calcined the sample at 400°C in the flow Air and Helium.

Pretreatment of the catalysts

The catalysts were pretreated first ex-situ and then in-situ, according to the following procedure. The catalysts were reduced ex-situ using 30% H₂ and 70% He (V/V) in a fixed bed reactor at a space velocity of 10,000 GHSV at 350°C. The temperature was ramped to 350°C at 1°C/min and held at 350°C for 10 hours. This reduced catalysts were transferred to CSTR in inert atmosphere. This was accomplished by over pressuring the fixed bed reactor that contain the reduced catalyst and then opening the appropriate valves to force the entire catalyst volume into the CSTR containing startup solvent. The reduction reactor was weighed prior to and after catalyst transfer to ensure that a quantitative transfer of catalyst had been accomplished. The catalyst was then reduced in-situ in the CSTR; the hydrogen was introduced to reactor at

atmospheric pressure with the flow rate of 30 SL/hr. The reactor temperature was increased to 230°C at the ramp rate 1°C for 12 hours.

Reaction conditions

Approximately 20 g of catalyst was transfer into a 1 liter stirred autoclave which had been charged with 300 g of C₃₀ oil(decene trimer obtained from Ethyl Corp.). The catalyst was reduced at 230°C in-situ in atmospheric pressure for 10 hours in the flow of hydrogen. After reduction, the reactor temperature was lowered to 180°C and synthesis gas was introduced into the reactor. Then the reactor was pressurized to 275 psig and temperature was slowly increased to 220°C during 3 hours. The feed gas used in the reaction was H₂ : CO ratio of 2:1.

Results and Discussion

Unpromoted 15%Co/Al₂O₃ catalysts

The activity and rate of loss of activity of the unpromoted Co/Al₂O₃ catalyst are shown in Fig. 1. The initial CO conversion, at space velocity 5 SL/hr/g catalyst, is 18%. The deactivation rate of unpromoted Co/Al₂O₃ catalyst is low (1.56% CO conversion/week) compared to Re or Ru promoted catalysts.

FT-Kinetic Studies of 15%Co/Al₂O₃ Catalysts

Typically, the activity of the fresh catalyst decreases with time on stream and then levels off in 5-7 days. After this period, the deactivation is slow and linear. The kinetic study was performed during the steady state. Two sets of kinetic studies were carried out with constant CO partial pressure (table 1) and constant H₂ partial pressure (table 2). Four H₂/CO ratios and five space velocities has been used to determine the rates. Argon gas used as the makeup gas to adjust the space velocity. The CO conversion with different space time at different H₂/CO ratio presented in Fig. 2 and Fig. 3. However, the additional calculations are required to determine the reaction rate and that will be done during the next quarter.

To determine the Activation Energy, we have carried out FT runs at four temperatures. The Arrhenius plots are presented in Fig. 4 and Fig. 5. The activation energy, calculated from CO conversion and H₂ conversion from Figs. 4 and 5, respectively, is approximately 17 Kcal/mole in both cases.

Pressure Effect over 0.2%Re-15%Co/Al₂O₃ catalyst

The effect pressure on CO conversion of the 0.2%-Re-15%Co/Al₂O₃ and space velocity 2 SL/hr/ g catalyst is shown in Fig. 6. The CO conversion increases with increasing pressure. The CO conversion increased significantly from 100 psig to 300 psig. The effect of pressure on methane selectivity and CO₂ selectivity is shown in Fig. 7. The methane selectivity decreases slightly with increase in pressure but the CO₂ selectivity remain almost same with increases in pressure.

Activity of 0.5%Ru-15%Co/Al₂O₃ and 0.5%Ru-20%Co/ZrO₂-SiO₂ Catalysts

The objective of this task is to find the stable Co-based Fischer-Tropsch catalysts. In this study, our aim was to determine the effect of support to the deactivation rate of the catalyst in comparison with the unpromoted Co/Al₂O₃ catalyst. The activities of 0.5%Ru-15%Co/Al₂O₃ and 0.5%Ru-20%Co/ZrO₂-SiO₂ Catalysts are shown in Fig. 8 and Fig. 9, respectively. Initial CO conversion of 0.5%Ru-15%Co/Al₂O₃ catalyst is two times greater than the initial activity of unpromoted 15%Co/Al₂O₃ catalyst at a space velocity of 5 SL/hr/g. However, the rate of deactivation is greater for the promoted Ru catalyst. While for the unpromoted catalyst, the CO conversion dropped by 18% of the initial activity after 85 h, and remained stable after that, the CO conversion dropped by 42% of the initial value after 1000 h for the Ru promoted catalyst. The activity of Ru-promoted ZrO₂-SiO₂ catalyst also showed a higher activity than the unpromoted catalyst. However, the deactivation rate is lower (3.53% CO conversion/week) than

for the Ru-promoted Al_2O_3 catalyst (4.2% CO conversion/week) at space velocity of 5 SL/hr/g. Similar studies are continuing .

Activity of 0.5%Pt-15%Co/ Al_2O_3 Catalyst

The activity tests performed in CST and Fixed-bed reactor are presented in Fig. 10 and Fig.11, respectively. The initial activity of Pt-catalyst is about the same as the Ru-promoted catalyst at space velocity 5 SL/hr/g. The CO conversion in the fixed-bed reactor at 210°C is ~30.0% after 500 hrs time on stream (Fig. 11).

Table 1 : Inlet gas composition for the kinetic studies (constant CO partial pressure)

H ₂ /CO ratio	1.0	1.5	2.0	2.4
CO%	25	25	25	25
H ₂ %	25	37.5	50	60
Ar%	50	37.5	25	15

Table 2 : Inlet gas composition for the Kinetic studies (constant H₂ partial pressure)

H ₂ /CO ratio	1.0	1.5	2.0	2.4
CO%	25	16.7	12.5	10.4
H ₂ %	25	25	25	25
Ar%	50	58.3	62.5	64.6

**Fig. 1 : Time on Stream vs CO conversion over
Co/Al₂O₃ at 220°C and 275 psig**

Fig. 2 : Kinetic of 15%Co/Al₂O₃ at 220°C and 275 psig pressure
(constant CO partial press.)

Fig. 3 : Kinetic of CO/ Al_2O_3 catalyst at 220°C and 275 psig pressure (contant H_2 partial Press.)

Fig. 4 : Arhenius plot for Activation energy

Fig. 5 : Arhenius plot for Activation energy

**Fig. 6 : Pressure effect on CO conversion over 0.2%Re-
15%Co/Al₂O₃ at 230°C**

Fig. 7 : Effect of Pressure on CH₄ and CO₂ Selectivity

Fig. 8 : Time on stream vs CO conversion on 0.5%Ru-15%Co/Al₂O₃ at 220°C and 275 psig

**Fig. 9 : Time on stream vs CO conversion over 0.5%Ru-
20%Co/ZrO₂-SiO₂ at 220°C and 275 psig**

**Fig. 10 : Time on stream vs CO conversion on 0.5%Pt-
15%Co/Al₂O₃ at 220°C and 275 psig**

**Fig. 11 : Time on stream vs CO conversion over 0.5% Pt-
15% Co/Al₂O₃ at 210°C, 350 psig, H₂:CO = 2:1, GHSV = 5
SL/hr/g catalysts in Fixed-bed**

D. Fischer-Tropsch Synthesis: Deactivation of Noble Metal Promoted Co/Al₂O₃ Catalysts

Abstract

Fresh and used unpromoted and noble metal promoted 15%Co/Al₂O₃ catalysts were analyzed by XANES and EXAFS to provide insight into catalyst deactivation. XANES analysis of the catalysts gave evidence of oxidation of a fraction of the cobalt clusters by water produced during the reaction. Comparison of XANES derivative spectra to those of reference materials, as well as linear combination fitting with the reference data, suggest that some form of cobalt aluminate species was formed. Because bulk oxidation of cobalt by water is not permitted thermodynamically under normal Fischer Tropsch synthesis conditions, it is concluded that the smaller clusters interacting with the support deviate from bulk-like cobalt metal behavior and these may undergo oxidation in the presence of water. However, in addition to the evidence for reoxidation, EXAFS indicated that significant cobalt cluster growth took place during the initial deactivation period. Promotion with Ru or Pt allowed for the reduction of cobalt species interacting with the support, yielding a greater number of active sites and, therefore, a higher initial catalyst activity on a per gram catalyst basis. However, these additional smaller cobalt clusters that were reduced in the presence of the noble metal promoter, deviated more from bulk-like cobalt, and were therefore, more unstable and susceptible to both sintering and reoxidation processes. The latter process was likely in part due to the higher water partial pressures produced from the enhanced activity. The rate of deactivation was therefore faster for these promoted catalysts.

Keywords: alumina, cobalt, Fischer-Tropsch synthesis, metal-support interaction, XANES, promoters

INTRODUCTION

Decreasing the deactivation rates of Co/Al₂O₃ catalysts for Fischer Tropsch synthesis (FTS) has been one of the important challenges facing the commercial development of these catalysts for the conversion of coal and natural gas to liquid fuels as alternative resources to crude oil. In comparison with low cost iron catalysts, cobalt FTS catalysts produce less water by the water-gas shift reaction. Furthermore, cobalt catalysts are believed to deactivate less rapidly and yield a higher fraction of linear alkanes than their iron counterparts. However, a major drawback of cobalt is its high cost, making catalyst replacement undesirable. Therefore, studies in the literature have focused on decreasing the deactivation rates of these catalysts [1-5]. Cobalt alumina catalysts for FTS have received renewed interest with the development of slurry phase and slurry bubble column reactors (SBCR). A recent article [6] indicated that slurry phase reactor processes employing a highly stable and active cobalt alumina catalyst will likely be employed commercially in the near future, and pilot plants are already in operation.

The aim of the present study is to employ a number of characterization techniques to investigate the causes of cobalt alumina catalyst deactivation. For example, potential causes include sintering of the cobalt, sintering and segregation of the noble metal promoter, and oxidation of the cobalt surface and/or small cobalt clusters. In this investigation, the nature of the deactivation of unpromoted, 0.5% Ru promoted, and 0.5% Pt promoted 15%Co/Al₂O₃ catalysts was studied using a combination of techniques including XANES, EXAFS, and XRD. These methods were particularly amenable to the characterization of used catalysts, because while the paraffinic hydrocarbon products from FTS must be extracted in the case of adsorption studies to characterize used catalysts, a procedure which may alter the state of the cobalt clusters, XAS allows for direct characterization of the used catalysts suspended in the solid wax matrix. These results are compared with reaction testing results obtained from continuously stirred tank reactors

(CSTRs). From the characterization results, it was concluded that important structural changes occurred during reaction which contributed to the initial catalyst deactivation.

EXPERIMENTAL

Catalyst Preparation

Condea Vista Catalox (high purity γ -alumina, 100-200 mesh, 200 m²/g) was used as the support for the cobalt FTS catalysts. To obtain a cobalt loading of 15%, a three-step incipient wetness impregnation method was used with drying at 353 K in a rotary evaporator following each impregnation. Catalysts with different loadings of ruthenium or platinum promoter were prepared by impregnation (see Table 1) using a ruthenium nitrosyl nitrate solution or tetraamineplatinum (II) nitrate, respectively. After promoter addition, the catalysts were dried in a rotary evaporator at 353K again and calcined only one time at 673K for 4hrs.

BET Measurements

BET measurements for the catalysts were conducted to determine the loss of surface area with loading of the metal. These measurements were conducted using a Micromeritics Tri-Star system. Prior to the measurement, samples were slowly ramped to 433K and evacuated for 4hrs to approximately 50mTorr. Results of physisorption measurements are shown in Table 1.

Hydrogen Chemisorption with Pulse Reoxidation

Hydrogen chemisorption measurements were performed using a Zeton Altamira AMI-200 unit, which incorporates a thermal conductivity detector (TCD). The sample weight was always 0.220 g. The catalyst was activated at 623K for 10hrs using a flow of pure hydrogen and then cooled under flowing hydrogen to 373K. The sample was held at 373 K under flowing argon to prevent physisorption of weakly bound species prior to increasing the temperature slowly to 623K. At that temperature, the catalyst was held under flowing argon to desorb the remaining

chemisorbed hydrogen so that the TCD signal returned to the baseline. The TPD spectrum was integrated and the number of moles of desorbed hydrogen determined by comparing to the areas of calibrated hydrogen pulses. Prior to experiments, the sample loop was calibrated with pulses of nitrogen in helium flow and compared against a calibration line produced from gas tight syringe injections of nitrogen under helium flow.

After TPD of hydrogen, the sample was reoxidized at 623K by injecting pulses of pure oxygen in helium referenced to helium gas. After oxidation of the cobalt metal clusters, the number of moles of oxygen consumed was determined, and the percentage reduction calculated assuming that the Co^0 reoxidized to Co_3O_4 . While the uncorrected dispersions are based on the assumption of complete reduction, the corrected dispersions reported in Table 2 include the percentage of reduced cobalt as follows:

$$\%D_{\text{uncorr}} = (\% \text{Co}^0 \text{ atoms on surface} \times 100\%) / (\text{total \#Co atoms})$$

$$\%D_{\text{actual}} = (\# \text{ of } \text{Co}^0 \text{ atoms on surface} \times 100\%) / (\text{total \# } \text{Co}^0 \text{ atoms})$$

$$\%D_{\text{actual}} = (\# \text{ of } \text{Co}^0 \text{ atoms on surface} \times 100\%) / [(\text{total \# Co atoms})(\text{fraction reduced})]$$

Temperature Programmed Reduction

Temperature programmed reduction (TPR) profiles of fresh catalyst samples were obtained using a Zeton Altamira AMI-200 unit. Calcined fresh samples were first heated to 623 K and purged in flowing argon to remove traces of water. TPR was performed using 30 cc/min 10% H_2 /Ar mixture referenced to argon. The ramp was 5K/min from 303K to 623K, and the sample was held at 623K for 30 min.

X-ray Diffraction

X-ray diffraction (XRD) measurements were conducted at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory (BNL), Upton, NY, using beamline X10b. The experimental apparatus consisted of a six circle Huber diffractometer, ion chambers,

and Bicron scintillation detectors. The scanning step was 0.020° and each point was scanned for approximately 13.8 s.

EXAFS/XANES

XAS measurements on reference samples, calcined catalysts, reduced/passivated fresh catalysts, and used catalysts were conducted at NSLS at BNL, using this time beamline X-18b equipped with a Si (111) channel cut monochromator. The crystal was detuned to prevent glitches from the interference of harmonics. The X-ray ring at the NSLS has a flux of 1×10^{10} photons per second at 100 mA and 2.5 GeV, and the energy range capability was 5.8–40 keV. XAFS data were recorded near the *K* edge of cobalt. The XAFS spectra were recorded at liquid nitrogen temperatures in a cell to minimize the contribution from the dynamic Debye Waller factor. Several scans were taken and the average obtained by adding the scans. The pre-edge background was subtracted by using power series curves and then the post-edge background was removed using appropriate splines. The spectra were normalized by dividing by the height of the absorption edge. XANES spectra were compared after normalization, and these were fitted using WinXAS 97 [7]. References used for XANES measurements included a Co foil, Co_3O_4 , CoO, and CoAl_2O_4 . For EXAFS, χ -data were obtained by truncating the normalized spectra 50 eV after the edge jump and background subtracting with appropriate splines based on the Nyquist criteria, to avoid damaging the data. The χ -results in energy space were converted to *k* space and weighted with either k^0 or k^3 weighting for examination of the changes in degree of coordination for the different *Z* scatterers. To obtain qualitative information on the Co-O and Co-Co coordination, the k^0 and k^3 weighted spectra were transformed from *k* space to *r* space to obtain the radial distribution functions. Furthermore, to obtain quantitative information of the degree of cobalt-cobalt coordination for the used catalysts, the first Co-Co coordination shell was isolated and the

inverse Fourier Transform was conducted. Fitting of the spectra in k space was carried out using FEFFIT [8]. The k -range used was from 3 to 17 Å⁻¹. Theoretical EXAFS were generated using FEFF [8] for model cobalt metal crystal parameters generated by Atoms [9]. In order to use coordination number N_1 as a fitting parameter, S_0^2 was first obtained from analysis of the Co foil assuming a fixed coordination number N_1 of 12 for the first shell. The other fitting parameters utilized by FEFFIT included the overall E_0 shift e_0 applied to each path, Δr to account for lattice expansion, and σ^2 , which is based on a correlated Debye model used to approximate the mean square disorder in the path length of each path.

Reaction Testing

Catalyst activation was conducted first ex-situ at 623K for 10 h in a fixed bed reactor and then re-reduced in-situ in a CSTR operating at 750 rpm. Approximately 15 g of catalyst (weight accurately determined) was used in each test. The H₂:CO ratio used for all catalysts was 2. The total pressure of syngas used was 1.8 MPa and the reaction temperature was 493K.

RESULTS AND DISCUSSION

Figure 1 shows TPR of the unpromoted Co/Al₂O₃ catalyst in comparison with TPR spectra for Ru promoted catalysts with increasing loadings of ruthenium, and the 0.5% Pt promoted catalyst. Note that during TPR, the temperature was not ramped high enough to observe the reduction of the small fraction of cobalt aluminate species, which has been demonstrated above 1073 K with up to 30% loading of cobalt [10]. The low temperature peak (500-650K) is typically assigned to reduction of Co₃O₄ to CoO, though a fraction of the peak likely includes the reduction of the larger, bulklike CoO species to Co⁰. This is based on our previous TPR study [11], which showed that increasing the cobalt loading caused a new peak appear in the TPR on the high temperature side of this low temperature peak, which increased

with loading, resembling the second step of CoO to Co^0 in the reduction of bulk Co_3O_4 . Although the precise identity is not clear, the broad peak on the unpromoted catalyst (700 to 1000 K) is attributed to the reduction of cobalt species interacting with the support, and the different shoulders are likely due to varying degrees of interaction that depends on the size. In a previous study [3], XRD was scanned after reduction of the first peak in TPR. The observation was made that the 31.2° and 59.4° peaks for Co_3O_4 disappeared, while the 42.4° and 61.3° peaks for CoO appeared. Therefore, the broad high temperature peak in the TPR may be due to the reduction of small CoO clusters interacting with the support. From this perspective, the smallest species, with the highest degree of interaction with the support, would likely reduce to produce the 950K shoulder in the TPR. A somewhat different viewpoint [12] suggests that the broad peak is the result of the reduction of a surface overlayer of, for the most part, Co^{2+} species containing atoms of the support in their structure. The addition of Ru caused the peaks to shift markedly to lower temperatures, presumably due to spillover of hydrogen from the reduced promoter to reduce the cobalt oxide species, in agreement with an earlier study [13]. Of particular importance, peaks that are attributed to the cobalt species interacting with the support are reduced at lower temperatures with increasing Ru loading, or with addition of Pt. Results of hydrogen chemisorption by TPD (Table 2) indicate that the number of surface sites increases with addition of either Ru or Pt promoter. By performing pulse reoxidation, it is clear that the gain in the number of active sites is mainly due to an enhancement in the percentage reduction, and not to improvements in the actual dispersion (cluster size) [14]. However, addition of Ru or Pt causes a slight contraction in the average cluster size. This is reasonable, because the comparison was conducted on samples treated at the same reduction temperature of 623 K, and the addition of Ru or Pt causes a fraction of the smaller cobalt species interacting with the support to be reduced at this temperature, resulting in a slight decrease in the average cobalt metal cluster size.

XRD patterns for the calcined fresh unpromoted and Ru promoted catalysts are shown in Figure 2. The peaks at 46.1° and 66.5° correspond to the $\gamma\text{-Al}_2\text{O}_3$ support, while other peaks correspond to the different crystal planes of Co_3O_4 [10]. From line broadening analysis using the Winfit program for the peak at 36.8° corresponding to diffraction by the (311) planes, it was determined that the average Co_3O_4 cluster size after calcination was approximately 10.6 nm (unpromoted) and 10.3 nm (0.5% Ru promoted) corresponding to 7.95 nm and 7.73 nm when reduced to the metal, respectively. This agrees reasonably well in comparison to the results of hydrogen chemisorption/pulse reoxidation. XRD on the used catalysts was also performed and the resulting spectra were very complex. The benefit of using synchrotron radiation is that the intensity of X-rays decreases the signal to noise ratio considerably, allowing for the analysis of species which would otherwise be below detectable limits. Interestingly, the series of 16 complex peaks between 30° and 80° were identical for both the promoted and unpromoted used catalysts. Tentative assignments of peaks for cobalt metal were made at 2θ values of 43.9° , 51.1° , 91.4° , and 75° in the spectra, which correlate with the reported literature values of 44.2° , 51.5° , 92.2° , and 75.8° for a cubic cobalt structure. The presence of CoO was also suggested by the peaks located at 42.5° and 36.5° . Also, it appears that a small amount of Co_2C may also have been formed during the synthesis. Clearly, peaks are present at 42.5° , 41.3° , 56.6° , and 71.4° which correlate well with Co_2C . In addition, peaks for Co_2C may be present at 36.8° and 45.7° , but these are likely hidden in the broad peaks. Support peaks were also still observed at 46.1° and 66.5° in the used catalysts. The identification of the remaining peaks is not clear. However, the relative intensities and positions of the sharp peaks located at 29.6° and 35.8° values indicate some form of a spinel structure. Peaks were also observed at 39.3° , 40.0° , 52.4° , and 54.4° , but no assignment for these peaks could readily be ascertained.

XANES analysis was conducted for the reference compounds CoO, Co₃O₄, CoAl₂O₄, and the Co foil and for the calcined, freshly reduced/passivated, and used unpromoted, 0.5% Ru promoted, and 0.5% Pt promoted catalysts. The normalized and derivative spectra are displayed in Figures 3 and 4. The XANES of the *K*-edges of some cobalt compounds contain a pre-edge only a few electron volts below the edge, a feature useful for identifying various species. The pre-edge appears for tetrahedral cobalt environments but is forbidden for octahedral environments [15], and arises from the 1s to 3d absorption transition. The intensity is inversely dependent on the degree of inversion symmetry in the first coordination shell, as well as the extent of occupancy of the 3d shell. Atoms in tetrahedral sites often exhibit pre-edge peaks due to lack of symmetry [16], while the peak is very low for octahedral environments, due to the center of symmetry. Therefore, the intensities follow the order CoAl₂O₄ > Co₃O₄ > CoO, as the cobalt atoms in CoAl₂O₄ are in a tetrahedral environment, the cobalt atoms in the spinel structure of Co₃O₄ are in a mixed environment (one Co atom in a tetrahedral environment, while the other two are in octahedral), and the cobalt atoms in CoO are in an octahedral environment [15].

The XANES analysis of the calcined catalysts, in agreement with XRD, clearly display Co₃O₄ as the major species present on the support. After performing a linear combination (LC) fitting with WinXAS97 of the XANES spectra for the calcined catalysts using reference materials, the result revealed that only Co₃O₄ was present. For the derivative spectra, the calcined catalysts have a pre-edge feature that is similar to Co₃O₄, while the reduced/passivated catalysts have a smaller pre-edge feature similar to that of CoO. Also, for the reduced/passivated catalysts, the XANES spectra are very similar in shape to that of CoO. This is in agreement with the conclusion from TPR. After reduction at 623K, the cobalt species associated with the first peak in the TPR, assigned to reduction of Co₃O₄ and bulk-like CoO, is completely reduced, while the species in interaction with the support are only partially reduced. From pulse reoxidation

measurements, the extent of reduction is 20% and 30% greater for Ru and Pt promoted catalysts, respectively, than for the unpromoted sample. Based on the previous discussion on the nature of the broad peak in the TPR, it is reasonable that the XANES features of the reduced/passivated catalysts will most resemble the reference spectrum of CoO. As expected, after performing a linear combination (LC) fitting of the XANES with WinXAS 97, CoO was found to contribute 93.6%, 99.2%, and 48.2% to the XANES LC fitting for unpromoted, Ru promoted, and Pt promoted catalysts, respectively, as shown in Table 3.

For the used catalysts, the spectra appear to be very similar for both the promoted and unpromoted catalysts. It is clear that the resulting complex spectra for the used catalysts represent a combination of superimposed spectra of different species rather than the case of one dominating contribution. The presence of a large fraction of cobalt metal is clearly indicated, and since the edge energy of bulk metallic cobalt is 7709 eV, the pre-edge features from oxidized phases that are present are obscured. However, the XANES display features which suggest the presence of either Co_3O_4 or CoAl_2O_4 , and these are superimposed over the signal of the metal.

To further strengthen this conclusion, three separate fittings were performed on the data for the used catalysts, and the results are shown in Table 3 for the unpromoted, Ru, and Pt promoted catalysts. In fitting number 1, the XANES spectra were fitted with Co^0 , Co_3O_4 , and CoO, while CoAl_2O_4 was omitted. The resulting residual was calculated to be 2.00, 1.43, and 1.6 for the unpromoted, Ru-promoted, and Pt-promoted catalysts, respectively. In fitting number 2, the spectra were fitted with Co^0 , CoAl_2O_4 , and CoO, and Co_3O_4 was omitted from the fitting. In this case, the residuals for all three spectra were lower, indicating a better fit, with the values of 1.49, 1.29, and 1.54, respectively. In fitting number 3, both Co_3O_4 and CoAl_2O_4 were included in the fitting procedure, and the results for the unpromoted and Ru-promoted catalysts showed no further improvement, indicating that the CoAl_2O_4 was a better fit. The Pt-promoted catalyst

displayed some further improvement with both species present in the fitting; however, the cobalt aluminate percentage was higher than that of Co_3O_4 . Note that samples of the used catalysts were taken after reactor shutdown, where the catalyst was cooled in the solid wax under argon, and the reactors were not shut down at different times on-stream. Therefore, the catalysts exhibited different stages of deactivation. The primary aim of this work was to identify potential reoxidized species responsible for deactivation. Further studies are currently being carried out to obtain better quantitative information on the evolution of cobalt oxide/aluminate formation, as well as information on the sintering of the metal clusters as a function of time on-stream. For example, we are currently implementing a technique to sample catalyst directly from the reactor with time on-stream, suspending the catalyst in the solid wax under inert gas, a method ideal for XAS investigation.

Nevertheless, the results here suggest that H_2O produced from the FTS reaction may have oxidized a fraction of the small cobalt clusters, which do not exhibit the same properties as the bulk metal. Note that very large $P_{\text{H}_2\text{O}} / P_{\text{H}_2}$ ratios (>50) are needed to reoxidize bulk cobalt metal [17], and these ratios are not encountered under normal FTS conditions. It has been suggested [2] that the support interaction promotes the deviation of small clusters from bulk-like behavior. Therefore, the very small clusters may undergo reoxidation during FTS. It is clearly of interest to continue to investigate the effect of increasing the cluster size for Al_2O_3 supported cobalt catalysts to determine the impact of the cluster size on the deactivation rate of the catalyst.

EXAFS was also employed as a qualitative method to analyze the used catalysts, and determine if the catalysts displayed Co-O coordination matching that of either Co_3O_4 or CoAl_2O_4 . Also, it was of interest to determine if shifts in the position of the peak for Co-Co coordination occurred, indicating reoxidation. As shown in Figure 5, both the k^0 and k^3 weighted Fourier

transform magnitude spectra of the used catalysts strongly match the spectrum of the cobalt metal foil. Results of the fitting shown in Table 4 of the first Co-Co shell (k^3 weighted) indicate that the resulting degree of Co-Co coordination N_1 for all three used catalysts is very similar. Also, the low r -factor values (<0.02) suggest good fits with only the Co metal foil. However, there is detected a small contribution for Co-O, which appears in the k^0 -weighted spectra for the used catalysts, which suggests that reoxidation occurred for a small fraction of the cobalt.

To examine the change in the cobalt metal cluster size, EXAFS was conducted on the freshly reduced/passivated and the used catalysts. The k^3 -weighted Fourier Transform magnitudes are displayed in Figure 6 in reference to the Co foil, which displays a coordination of 12. Note that the XANES LC results suggest that the reduced/passivated catalysts may not be representative of the freshly reduced catalyst at the onset of reaction. However, our current investigation, where samples of catalyst are removed with time onstream, should provide more conclusive evidence on the extent of sintering by following the changes in the degree of Co-Co coordination with deactivation time. Interestingly, both reduced/passivated catalysts (promoted and unpromoted) displayed similar Fourier Transform magnitudes for Co-Co metal coordination, indicating a similar cluster size. After reaction testing, the degree of Co-Co coordination was slightly higher for the Ru and Pt promoted catalysts than the unpromoted. Based on the good fits obtained in Table 4 using only Co metal as a standard for the first Co-Co shell, the results strongly suggest sintering of the clusters occurred during the initial deactivation period. However, in light of the XANES spectra for the used catalysts, one cannot rule out the possibility that the smaller clusters reoxidized during reaction, leaving a higher intensity of Co-Co coordination in the k^3 weighted Fourier Transform for the used catalyst.

Reaction testing in the CSTR revealed that higher conversions and, therefore, increasing P_{H_2O} , resulted in a higher catalyst deactivation rate. In a previous investigation for a 0.5% Pt promoted 15%Co/Al₂O₃ catalyst, whereby water was added to the feed, $P_{H_2O} > 28\%$ of the total pressure resulted in drastic irreversible deactivation to the catalyst, while the catalyst recovered activity between 3% and 25% due to the reversible kinetic effect of water [5]. In the present investigation, the unpromoted and Ru promoted catalysts were run at the same space velocity on a per gram catalyst basis, but the number of active sites was higher for the Ru catalyst, resulting in higher initial activity. In agreement with our previous findings, more active catalysts displayed a higher rate of deactivation, as shown in Figure 7. For the unpromoted catalyst, the CO conversion declined by 18% of the initial activity after 85 h, and was stable after that. In contrast, the CO conversion decreased by 42% of the initial value after 1000 h for the Ru-promoted catalyst, and 43% after 620 h for the Pt-promoted catalyst (note lower space velocity). The influence of pressure and temperature on FTS has been well-documented. Studies on Co catalysts have shown that while increasing temperature results in a shift of products to lower carbon numbers, increasing total pressure shifts product selectivities to heavier products. The process conditions used in this work were $T = 493\text{K}$ and 1.8 MPa. Note that while the space velocity was the same (33 SL CO/ hr g cat) for the unpromoted and Ru promoted catalyst, a lower space velocity (5 SL CO/g cat) was employed for the Pt promoted catalyst.

In a previous investigation of unpromoted and Re promoted Co/Al₂O₃ catalysts, Schanke et al. [2] showed by gravimetric analysis and XPS that reoxidation occurs when water is introduced after reduction of the catalyst. The extent of reoxidation was found to be dependent on the partial pressure of water and the composition of the feed mixture. Even at atmospheric pressure and a low water partial pressure of 2 kPa, without hydrogen in the feed, complete surface

reoxidation was found to occur after short exposure times, while only slight indications of reoxidation were seen under hydrogen. However, at high pressure conditions of 2 MPa, which is comparable to the pressure in a FTS reactor, reoxidation occurred to a greater extent. In their investigation, the Re promoted catalyst was found to be more susceptible to reoxidation than the unpromoted catalyst. The authors noted that bulk cobalt metal will not reoxidize in $\text{H}_2\text{O}/\text{H}_2$ mixtures, as predicted by thermodynamic calculations. However, the influence of the support on metal and metal oxide clusters causes deviations from bulk behavior. Re, Pt, and Ru allow the reduction of smaller clusters which will not be reduced on the unpromoted catalyst [11]. It is suggested that these smaller clusters may deviate more strongly from bulk-like behavior and will be more susceptible to reoxidation. Therefore, the faster deactivation rate observed for the Ru and Pt promoted catalysts in this work can be likely attributed to two factors. First, the increased activity, due to more active sites, will yield a higher water partial pressure in the reactor. Also, with a higher fraction of smaller clusters after reduction, the promoted catalyst is more susceptible to reoxidation. Secondly, smaller metal clusters, with a greater fraction of surface atoms, are more unstable than the larger clusters, and therefore more susceptible to sintering processes.

A recent study [3] reported on the effect of water partial pressure on the reducibility of Co for a Ru-promoted cobalt catalyst. Increasing the water partial pressure was found to increase the temperature of the second peak of the TPR, which was assigned to the reduction of well dispersed cobalt species that strongly interact with the support. Furthermore, adding water decreased the overall degree of reduction. This latter result suggests that water promotes interactions between cobalt oxide species and the $\gamma\text{-Al}_2\text{O}_3$ support, so that some type of irreducible cobalt aluminate was formed. Therefore, in the case of catalyst deactivation, one cannot rule out the possibility of cobalt aluminate formation. Although the exact identity of the

cobalt aluminate-like structure cannot yet be determined, it is possible that the structure may be indicated in XRD as the unknown spinel assignment. It is conceivable that, once oxidized by water, the well dispersed clusters, for which there exists a strong interaction with the support, may diffuse as ions into the support in the presence of water produced from reaction, and form some type of irreducible tetrahedral cobalt aluminate species.

CONCLUSIONS

XANES analysis of used unpromoted and Ru or Pt promoted 15% Co/Al₂O₃ catalysts gave evidence of oxidation of a fraction of the catalyst by water produced during the reaction. Analysis of the XANES normalized and derivative spectra indicated that either Co₃O₄ or cobalt aluminate was formed. The two are not easily distinguished by either XRD or XANES but comparison of XANES spectra of used and calcined catalysts and linear combination fitting against reference spectra suggested cobalt aluminate formation. Because bulk oxidation of cobalt by water is not permitted by thermodynamics under FTS conditions, the results suggest that only the small clusters interacting with the support and deviating from bulk-like behavior reoxidize in the presence of water produced during the reaction.

However, EXAFS results strongly suggested that the deactivation was due in large part to sintering, as growth in the Fourier transform magnitudes for Co-Co metal coordination in the used catalysts was observed. Furthermore, both k^0 and k^3 weighted radial distribution functions strongly matched the spectra of the cobalt metal foil.

TPR and hydrogen chemisorption/pulse reoxidation results indicated that promoting the catalyst with Ru or Pt allowed for the reduction of a fraction of cobalt species in interaction with the support which were not reduced for the unpromoted catalyst. Therefore, the resulting smaller cobalt metal clusters deviated even more so from the bulk, making them susceptible to reoxidation and sintering processes. While the noble metal promoted catalyst displayed higher

initial activity due to the presence of a greater number of active sites from enhanced reducibility, the deactivation rates for these catalysts were higher than the unpromoted catalyst.

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Table 1			
BET Measurements			
<i>Catalyst Description</i>	<i>BET Surface Area (m²/g)*</i>	<i>Average Pore Radius (nm)</i>	<i>Pore Volume (cm³/g)</i>
Al ₂ O ₃	200 (211)	4.7	0.500
15%Co/Al ₂ O ₃	158	4.2	0.328
0.5%Pt-15%Co/Al ₂ O ₃	162	4.1	0.328
0.5%Ru-15%Co/Al ₂ O ₃	161	3.9	0.310
0.2%Ru-15%Co/Al ₂ O ₃	154	4.0	0.305
1.0%Ru-15%Co/Al ₂ O ₃	159	3.1	0.293
*Measured value in brackets for Al ₂ O ₃ support.			

Table 2 Hydrogen Chemisorption and Pulse Reoxidation							
Sample Description	$\mu\text{mol H}_2$ desorbed per g cat	Uncorr % <i>D</i>	Uncorr diam. (nm)	$\mu\text{mol O}_2$ pulsed per g catalyst	% Red	Actual % <i>D</i>	Actual diam. (nm)
15%Co/Al ₂ O ₃	66.9	5.3	19.6	509	30	17.5	5.9
0.5%Pt-15%Co/Al ₂ O ₃	140.6	9.3	11.0	1024	60	18.4	5.6
0.5%Ru-15%Co/Al ₂ O ₃	115.5	9.7	11.4	823	50	18.2	5.7

Table 3 XANES LC Fits										
Fitting	Sample Name	Co ⁰	E ₀ shift (eV)	Co ₃ O ₄	E ₀ shift (eV)	CoO	E ₀ shift (eV)	CoAl ₂ O ₄	E ₀ shift (eV)	Res
-	15%Co/Al ₂ O ₃ calcined	ND	ND	100	1.11+/- 0.002	ND	ND	ND	ND	-
-	15%Co/Al ₂ O ₃ reduced/passivated	6.4	-0.672 +/-0.072	ND	ND	93.6	1.189 +/-0.003	ND	ND	2.19
fitting #1	15%Co/Al ₂ O ₃ used	36.8	0.045 +/-0.007	24.5	0.174 +/-0.093	38.7	-0.095 +/-0.054	not included	not included	2.00
fitting #2	15%Co/Al ₂ O ₃ used	38.3	-0.105 +/-0.070	not included	not included	31.9	-0.086 +/-0.058	29.8	0.813 +/-0.055	1.49
fitting #3	15%Co/Al ₂ O ₃ used	38.3	-0.105 +/-0.070	ND	ND	31.9	-0.086 +/-0.058	29.8	0.813 +/-0.055	1.49
-	0.5%Ru-15%Co/Al ₂ O ₃ cal	ND	ND	100	1.03+/- 0.002	ND	ND	ND	ND	-
-	0.5%Ru-15%Co/Al ₂ O ₃ reduced/passivated	0.8	-0.385 +/-0.001	ND	ND	99.2	1.031 +/-0.003	ND	ND	2.60
fitting #1	0.5%Ru-15%Co/Al ₂ O ₃ used	52.1	-0.235 +/-0.087	12.2	0.577 +/-0.298	35.7	-0.128 +/-0.093	not included	not included	1.43
fitting #2	0.5%Ru-15%Co/Al ₂ O ₃ used	53.2	-0.315 +/-0.083	not included	not included	33.2	-0.094 +/-0.011	13.5	1.32 +/-0.189	1.29
fitting #3	0.5%Ru-15%Co/Al ₂ O ₃ used	53.2	-0.315 +/-0.083	ND	ND	33.2	-0.094 +/-0.011	13.5	1.32 +/-0.189	1.29
-	0.5%Pt-15%Co/Al ₂ O ₃ reduced/passivated	32.3	-0.287 +/-0.052	19.5	0.876 +/-0.067	48.2	1.375 +/-0.026	ND	ND	1.81
fitting #1	0.5%Pt-15%Co/Al ₂ O ₃ used	67.2	-0.153 +/-0.007	11.1	1.035 +/-0.034	21.7	-1.45 +/-0.015	not included	not included	1.60
fitting #2	0.5%Pt-15%Co/Al ₂ O ₃ used	69.3	-0.189 +/-0.007	not included	not included	19.9	-1.38 +/-0.016	10.9	1.65 +/-0.026	1.54
fitting #3	0.5%Pt-15%Co/Al ₂ O ₃ used	64.9	-0.238 +/-0.008	6.9	-0.251 +/-0.071	20.8	-1.873 +/-0.017	7.4	3.718 +/-0.043	1.49

Table 4

Best-fit values for average coordination number (N_1) for the first Co-Co shell, shift in E_0 , Debye-Waller factor (σ^2), lattice expansion ($deltar$), and fractional misfit (r). Relative uncertainties are also shown.

<i>Used Catalyst</i>	n	Δn	e_0	Δe_0	σ^2	$\Delta\sigma^2$	$deltar$	$\Delta delt ar$	r -factor
Unpromoted	5.69	0.2913	5.6315	0.5942	0.00422	0.00045	-0.0179	0.0039	0.0187
w/ 0.5%Ru	6.44	0.1568	7.6258	0.2852	0.00371	0.00021	-0.00838	0.0018	0.00441
w/ 0.5%Pt	6.29	0.1952	6.6122	0.3653	0.00382	0.00027	-0.0116	0.0023	0.0071

Figure 1: Comparative TPR spectra of unpromoted (bottom) 15%Co/Al₂O₃ catalyst with those promoted with (moving up, solid) 0.2%, 0.5%, and 1.0% Ru and 0.5%Pt (dotted).

Figure 2: XRD patterns for calcined and spent Ru-promoted and unpromoted 15% loaded Co/Al₂O₃ catalysts.

Figure 3: (left) Normalized XANES and (right) XANES derivative profiles for references, calcined, freshly reduced/passivated catalysts, and used catalysts for a comparison of Ru promoted and unpromoted FTS catalysts [rp, reduced/passivated; calc, calcined; unp, unpromoted].

Figure 4: (left) Normalized XANES and (right) XANES derivative profiles for references, calcined, freshly reduced/passivated catalysts, and used catalysts for a comparison of Pt promoted and unpromoted FTS catalysts [rp, reduced/passivated; calc, calcined; unp, unpromoted].

Figure 5. k^3 and k^0 -weighted Fourier transform magnitudes of Co K -edge EXAFS spectra of the used catalysts (unpromoted, ZYQ000; Pt promoted, ZYQ036; Ru promoted, ZYQ050) after Fischer-Tropsch synthesis in the CSTR reactor versus those of comparative standards, including Co metal foil, Co_3O_4 , CoO, and CoAl_2O_4 .

Figure 6. k^3 weighted Fourier transform magnitudes of Co foil (solid), reduced/passivated catalyst (dotted), and used (dashed) catalyst for (left) unpromoted, (center) 0.5% Ru promoted, and (right) 0.5% Pt promoted catalysts.

Figure 7. Deactivation of Ru and Pt promoted and unpromoted 15%Co/Al₂O₃ catalysts in during FTS in a CSTR (493K, 1.8 MPa).

E. Cobalt Catalyst Life Testing and Deactivation

Preparation of Cobalt Catalysts

The 15%Co/Al₂O₃ and 1.0%Re-15%Co/Al₂O₃ catalysts were prepared by incipient wetness impregnation of Al₂O₃ (Condea Vista B alumina, BET surface area 200 m²/g, pore volume 0.4 cm³/g) with cobalt nitrate solution. The preparation procedure includes three step impregnations of cobalt salt and then followed by impregnation of promoter. 25%Co/Al₂O₃ and 0.5%Pt-15%Co/Al₂O₃ were prepared by slurry impregnation method using Catalox-Sba-150 (Condea Vista) alumina support. The volume of impregnation solution was 2.5 times of the pore volume of the support. The catalysts were dried and calcined immediately at 400°C in the flow Air and Helium.

Pretreatment of the catalysts

The catalysts were pretreated first ex-situ and then in-situ, according to the following procedure. The catalysts were reduced ex-situ using 30% H₂ and 70% He (V/V) in a fixed bed reactor at a space velocity of 10,000 GHSV at 350°C. The temperature was ramped to 350°C at 1°C/min and held at 350°C for 10 hours. This reduced catalysts were transferred to CSTR in inert atmosphere. This was accomplished by over pressuring the fixed bed reactor that contain the reduced catalyst and then opening the appropriate valves to force the entire catalyst volume into the CSTR containing startup solvent. The reduction reactor was weighed prior to and after catalyst transfer to ensure that a quantitative transfer of catalyst had been accomplished. The catalyst was then reduced in-situ in the CSTR; the hydrogen was introduced to reactor at atmospheric pressure with the flow rate of 30 SL/hr. The reactor temperature was increased to 230°C at the ramp rate 1°C for 12 hours.

Reaction conditions

~20 g of catalyst was transferred into a 1 liter stirred autoclave which had been charged with 300 g of Polywax 3000. The catalyst was reduced at 230°C in-situ in atmospheric pressure for 10 hours in the flow of hydrogen. After reduction, the reactor temperature was lowered to 180°C and synthesis gas was introduced into the reactor. Then the reactor was pressurized to 275 psig and temperature was slowly increased to 220°C during 3 hours.

Results and discussion

Unpromoted 25%Co/Al₂O₃ catalyst

The activity and deactivation rate of unpromoted 25%Co/Al₂O₃ catalyst at 220°C and 275 psig pressure are shown in Fig. 1. The initial CO conversion at space velocity 5 SL/h/g catalyst is ~35% as compared to 18% CO conversion of unpromoted 15%Co/Al₂O₃ at same space velocity. This catalyst is very stable catalyst and the deactivation rate is ~0.05% CO conversion/week on 1200 hours time on stream at space velocity 5 SL/h/g catalyst. The deactivation rate increases with decrease in space velocity. The deactivation rate is ~1.4% CO conversion/week at space velocity 3 SL/h/g catalyst. After time on stream ~3200 h, the catalysts were regenerated at 230°C for 4 h in the flow of H₂ and Ar. The activity of the catalysts increases slightly after regeneration but rate activation rate very high as compared to nonregenerated catalysts at same space velocity.

Pt promoted 0.5%Pt-25%Co/Al₂O₃ catalyst

The activity and rate of loss of activity of Pt promoted 0.5%Pt-25%Co/Al₂O₃ catalyst at 220°C and 275 psig pressure are shown in Fig. 2. The initial activity of Pt promoted catalyst is higher than the unpromoted 25%Co/Al₂O₃ catalysts but the deactivation rate is more in case of Pt promoted catalyst as compared to unpromoted 25%Co/Al₂O₃ catalysts. The initial activity of 0.5%Pt-25%Co/Al₂O₃ catalyst is ~38% CO conversion at space velocity 8 SL/h/g catalyst. The deactivation rate at space velocity 8 SL/h/g catalyst is found to be ~3.2% CO conversion/week.

The catalyst was regenerated at 280°C for 24 h in flow of H₂ and Ar. After regeneration the CO conversion did not increase at all.

1.0%Re-15%Co/Al₂O₃ catalyst

This catalyst run was performed to know the effect of start up solvent. It was found that polywax 3000 is the better start up solvent than the C-30 oil. The partial pressure of C-30 oil is much higher than the polywax 3000, apparently the C-30 oil evaporated more when the space velocity is relatively high which caused the liquid level drop in the autoclave. Therefore the catalyst particles stuck on the wall of the reactor and did not make the contribution to the Fischer Tropsch reaction. The activity and deactivation rate of 1.0%Re-15%Co/Al₂O₃ catalyst are shown in Fig. 3. This catalyst is very stable when the polywax 3000 is used as start up solvent at the CO conversion level ~50% and space velocity 2 SL/h/g catalyst and the deactivation rate is ~0.98% CO conversion/week. The regeneration of catalyst was performed at 280°C for 24 h in the flow of H₂ and Ar. The CO conversion increases slightly after regeneration but the deactivation rate is more as compared to unregenerated catalysts.

Effect of Reduction temperature of unpromoted 15%Co/Al₂O₃ catalyst

15%Co/Al₂O₃ catalyst was reduced at 350°C and 500°C, respectively to study the effect of reduction temperature. The results are shown in Figs. 4 and 6. It seems that the increase in reduction temperature increases the CO conversion from 16% to 26%. The results of the degree of reduction and chemisorption indicated that 57% of cobalt oxide has been reduced to metallic cobalt at 500°C and only 30% was reduced at 350°C. The average particle size of cobalt changed from 5.9 nm to 6.2 nm. But the overall metal dispersion is almost same at 350°C and 500°C reduction. As the percentage reduction of cobalt oxide is more at 500°C reduction, the overall availability of surface cobalt sites increased therefore leads to higher activity. Similarly, 25%Co/Al₂O₃ catalyst was reduced at 350°C and 450°C, respectively and the activity was tested.

The activity and the deactivation rates are shown in Figs. 1 and 5. The deactivation rate for 500°C reduction is more (~4.33% CO conversion/week) than 350°C reduction (0.05% CO conversion/week). The smaller clusters are reduced high temperature and those smaller clusters could be oxidized easily during the Fischer Tropsch synthesis therefore caused deactivation.

Fig. 1 : Activity of 25%Co/Al₂O₃ catalyst at 220°C and 275 psig (Reduced at 350°C)

Fig. 2 : Activity of 0.5%Pt-25%Co/Al₂O₃ catalyst at 220^oC and 275 psig

Fig. 3 : Activity of 1.0%Re-15%Co/Al₂O₃ catalyst at 220°C and 275 psig

**Fig. 4 : Activity of 15%Co/Al₂O₃ catalyst reduced at 500°C
(Temp. 220°C and Pressure 275 psig)**

**Fig. 5 : Activity of 25%Co/Al₂O₃ catalyst reduced at 450°C
(Reaction Temp. = 220°C, Press. = 275 psig)**

Fig. 6 : Activity of 15%Co/Al₂O₃ catalyst at 220°C and 275 psig(Reduced at 350°C)

F. Fischer-Tropsch Synthesis: Effect of water on the catalytic properties of a Co/SiO₂ catalyst

Abstract

The effect of water on the catalytic properties of a Co/SiO₂ catalyst (12.4 wt%) during Fischer-Tropsch (FT) synthesis was investigated in a continuously stirred tank reactor (CSTR) using two approaches: (1) changing the space velocity to change the CO conversion and therefore the water partial pressure and (2) by adding varying amounts of water into the feed gas. Even at a space velocity of 1 SL/gcat./h at a CO conversion of about 75%, the catalyst displayed very high stability. The addition of water in the range of 5 to 25% (vol.%) increased the CO conversion. Continuous addition of small amounts of water (5 vol.%) over a period of days caused an increase of CO conversion and did not have a significant effect on the catalyst deactivation; however, for larger amounts of water, continuous addition resulted in a severe catalyst deactivation.

Keywords: silica, cobalt, Fischer-Tropsch synthesis, synthesis gas conversion, deactivation, water effect

Introduction

Supported cobalt catalysts are important for the Fischer-Tropsch (FT) synthesis of long chain hydrocarbons from synthesis gas. The effect of water on iron-based Fischer-Tropsch catalysts has been investigated widely and it is well known that water may reoxidize iron catalysts during synthesis [1]. The effect of water on cobalt catalysts is less well understood. In a previous study [2], we have investigated the effect of water on the catalytic properties of a Pt promoted Co/Al₂O₃ catalyst during Fischer-Tropsch synthesis in a continuous stirred tank reactor (CSTR) by (1) varying the conversion through changes of the space velocity and (2) by including additional water in the feed gas. At higher space velocities (> 2 SL/gcat./h), the catalyst was exposed to low water partial pressures and exhibited stable activity. The runs with lower space

velocities with the alumina supported catalyst resulted in higher water partial pressures and higher catalyst deactivation rates. The addition of small amounts of water slightly decreased CO conversion and the effect was reversible. Increasing the amount of added water to provide $P_{H_2O}/P_{CO} \sim 1$ in the feed resulted in permanent deactivation of the catalyst. Hilmen et al. [3,4] studied the effect of water on Co/Al₂O₃ and CoRe/Al₂O₃ catalysts by adding water to the synthesis gas feed and by model studies exposing the catalysts to H₂O/H₂. It was found that the catalysts deactivated when water was added during Fischer-Tropsch synthesis and the catalysts oxidized in H₂O/H₂ mixtures with a ratio much lower than expected for oxidation of bulk cobalt. On silica supported cobalt catalysts, the addition of water to the synthesis gas feed has been shown to slightly decrease the CO conversion [5]. Schulz et al. [6] investigated the effect of water addition on Co/Ru/ZrO₂/Aerosil and Co/MgO/ThO₂/Aerosil catalysts and found that CO conversion was not influenced significantly and, remarkably, the product selectivity was improved when water was added to the feed. Schulz et al. [7] even found increased activity. Kim et al. [8,9] also reported increased activity for a Re promoted and an unpromoted Co/TiO₂ catalysts and for an unsupported cobalt catalyst as a result of addition of water during the Fischer-Tropsch synthesis. In contrast, Li et al. [10] found that water decreased CO conversion of a Co/TiO₂ catalyst. An explanation that has been offered is that water possibly destroys the strong metal-support interaction (SMSI) effect for titania supported catalysts. In this study, the effect of water on the catalytic properties of Co/SiO₂ Fischer-Tropsch catalyst was investigated and, since the procedures used were similar with those used in our earlier studies with Pt promoted Co/Al₂O₃ and CoTiO₂ catalysts, the results allow a comparison of the support effect as it impacts the influence of water [2] on CO conversion and product selectivity.

Experimental

Catalyst preparation and characterization

A 12.4 wt% Co/SiO₂ catalyst was prepared by two incipient wetness impregnations of a SiO₂ support (PQ Co. CS-2133, BET surface area: 352 m²/g; pore volume: 2.36 cm³/g; average pore size: 12.9 nm) with cobalt nitrate solution. The sample was dried at 333 K for 3 hours, 353 K for 2 hours and 373 K for 5 hours under vacuum. Calcination was not utilized between impregnations.

The catalyst was characterized by BET, TPR, H₂ chemisorption and pulse reoxidation; the methods have been described earlier [11]. BET measurements were conducted for calcined and uncalcined catalysts using a Micromeritics Tri-Star system. Prior to the measurement, the sample was slowly ramped to 433 K and evacuated for 4 hrs to approximately 50 mTorr. Temperature programmed reduction (TPR) profiles of catalysts were recorded using a Zeton Altamira AMI-200 unit. The sample was first purged in flowing argon to remove traces of water. TPR was performed using a 10% H₂/Ar mixture referenced to argon at a flow rate of 30 cm³. The sample was then heated from 323 K to 1073 K using a heating ramp of 10 K/min. The hydrogen chemisorption and reducibility by reoxidation were measured using the Zeton Altamira AMI-200 unit, which incorporates a thermal conductivity detector (TCD). The sample weight was always 0.220 g. The catalyst was reduced using hydrogen at 623 K for 10 hours and cooled under flowing hydrogen to 373 K. The sample was held at 373 K under flowing argon to eliminate physisorbed and weakly bound species prior to increasing the temperature slowly to the reduction temperature. At that temperature, the catalyst was held under flowing argon to desorb the remaining chemisorbed hydrogen until the TCD signal returned to the baseline. The TPD spectrum was integrated and the number of moles of desorbed hydrogen determined by comparing to the areas of calibration pulses of hydrogen in argon. Prior to experiments, the

sample loop was calibrated with pulses of nitrogen in a helium flow and compared against a calibration line produced from data generated using gas tight syringe injections of known amounts of nitrogen into a helium flow.

After TPD of hydrogen, the sample was reoxidized at the activation temperature by injecting pulses of pure oxygen in helium carrier referenced to helium gas. After oxidation of the cobalt metal clusters (when the entire oxygen pulse was observed by the TCD), the number of moles of oxygen consumed was determined, and the percentage reducibility was calculated assuming that Co^0 oxidized to Co_3O_4 .

Reactor system and procedure

An uncalcined catalyst was used for activity testing. The catalyst activation was conducted first *ex-situ* and then *in-situ*, according to the following procedure. The uncalcined catalyst (about 15 g; actual weight accurately known) was placed in a fixed bed reactor and pure hydrogen was introduced at a flow rate of 60 NLh^{-1} (298 K, 0.1 MPa); the reactor temperature was increased from room temperature to 373 K at a rate of 120 Kh^{-1} , then increased to 623 K at a rate of 60 Kh^{-1} and kept at 623 K in a hydrogen flow for 16 h. The catalyst was transferred under the protection of helium to the CSTR to mix with 300 g of melted poly-wax (P.W.) 3000. The catalyst was then reduced *in-situ*. Hydrogen was introduced to the reactor at atmospheric pressure with a flow rate of 30 NLh^{-1} (298 K, 0.1 MPa). The reactor temperature was increased to 553 K at a rate 120 K h^{-1} and maintained at this activation condition for 24 h.

The FTS reactor system has been described earlier [12]. Separate mass flow controllers were used to add hydrogen, carbon monoxide and inert gas at the desired rate to a mixing vessel that was preceded by a lead oxide-alumina containing vessel to remove iron carbonyls. The mixed gases entered the CSTR below the stirrer operated at 750 rpm. Products were continuously removed from the vapor and passed through two traps, one maintained at 373 K and the other at

273 K. The uncondensed vapor stream was reduced to atmospheric pressure through a pressure letdown valve. The gas flow was measured with a bubble-meter and composition quantified using an on-line GC. The accumulated reactor liquid products were removed every 24 hrs by passing through a 2 μm sintered meter filter located below the liquid level in the CSTR. The contents of the 273 K and 373 K traps were combined, the hydrocarbons and water fractions separated, and then each was analyzed by GC. The reactor wax sample was analyzed by a high-temperature GC to obtain a carbon number distribution for C_{20} - C_{80} products.

After the activation period, the reactor temperature was decreased to 453 K and the synthesis gas mixture (46.67% H_2 /23.33% CO /30% Ar) was introduced to increase the reactor pressure to 20 atm (2.02 MPa). The reactor temperature was then increased to 483 K at a rate of 10 K h^{-1} . During the entire run, the reactor temperature was 483 K, the pressure was 20 atm (2.02 MPa), and the stirring speed was maintained at 750 rpm. The ratio of H_2 to CO was 2.0. The conversion of carbon monoxide and hydrogen and the formation of products were measured after a period of 24 h at each condition. Conversion was varied using a range of space velocities.

A series of measurements were conducted so that the pressure of carbon monoxide and hydrogen in the feed remained constant and was 70% of the total pressure, with the remainder being argon. A high precision, high pressure ISCO syringe pump was used to add water to the reactor. When water was added, a fraction of the argon was replaced by water. Thus, the sum of water added plus argon partial pressure was always 6 atm (0.606 MPa). The added water, along with the water produced by the reactor, was collected in two traps (a hot and a cold trap) and results were quantified and combined to ensure that the water balance was accurate. The added water is expressed in one of two ways; in the first the water added to the feed is expressed as the percentage of the total feed and in the second it is expressed as the partial pressure in the reactor. The text indicates which is being used.

Results and Discussion

Characterization

Figure 1 shows the TPR profiles for the uncalcined and calcined catalysts. Two peaks are apparent and these are attributed to the reduction of Co_3O_4 to CoO , which then reduces at higher temperatures to metallic Co^0 . The calcination shifted the position of the high temperature peak to a lower temperature, indicating a larger cluster size and therefore a decreased interaction of the cluster with the support [11,13]

Table 1 shows the hydrogen chemisorption data, where dispersion calculations are based on the assumption that the H:Co stoichiometric ratio is 1:1. Without taking into account the amount of oxidized Co remaining after reduction, estimates of dispersion are much lower than the true value, leading to considerable overestimates of the cluster size. For the calcined catalyst, twice the amount of Co was reduced in comparison to the uncalcined sample. After correcting for the percentage reduction, the two catalysts displayed large differences in dispersion and cluster size. The cluster size for the calcined catalyst was 38.2 nm, twice that of the uncalcined catalyst. This was consistent with the results of TPR.

Effect of Space Velocity/Conversion on Deactivation

The effects of space velocity on catalytic properties were investigated by changing the synthesis gas flow rate. Firstly, the catalyst was used at a space velocity of 8 SL/gcat/h, and the catalytic activity was quite stable at this space velocity. The catalyst deactivation rate, based on CO conversion, was only 1.8% per week (0.26% per day). Thus, a space velocity of 8 SL/gcat/h, with a deactivation rate of 0.26% per day, was used as a reference condition. After each period at some other space velocity, the space velocity was again adjusted to 8 SL/gcat/h to compare the conversion change. After several days at the reference flow, 5 vol.% water was added to the feed for 5 days. The water effect will be discussed in the next section. After the water addition was

terminated, the run was continued at a space velocity of 8 SL/gcat./h for a week to re-establish the earlier rate. The catalyst was then utilized with different space velocities (5, 3, 2 and 1 SL/gcat./h). The results are shown in Figures 2 and 3 and Table 2. At higher space velocities (8, 5 SL/gcat./h), the CO conversion increased linearly with increasing space time but deviated from linearity as the space velocity was decreased to lower values (Figure 3). At higher space velocities (SV= 5 and 3 SL/gcat/h), the catalyst did not show an apparent deactivation. Even when the space velocity was decreased to 1 SL/gcat/h, the catalyst showed stability; during a 2 week period at 1 SL/gcat/h, the catalyst did not show a measurable deactivation. This result is completely different from the performance of Pt promoted Co/Al₂O₃ catalyst, which displayed higher deactivation rate at the lower space velocity, and higher water partial pressure [2]. The cobalt metal crystallite size may explain the different effects for these two catalysts. It was found that the average cobalt crystallite size of the alumina supported catalyst was 5.6 nm [2], much smaller than the silica supported catalyst (13.2 nm). The cobalt metal with smaller crystallite size appears to be more easily oxidized by higher partial pressure water to form cobalt oxide and the catalyst deactivates more rapidly [11,13].

Figure 4 shows the effect of space velocity on methane and carbon dioxide selectivities. With decreasing space velocity, methane selectivity decreased slightly while CO₂ selectivity increased slightly.

Effect of Water Addition on the Catalytic Properties

To determine the effect of water on Fischer-Tropsch synthesis with the Co/SiO₂, different amounts of water (5.0 to 25 vol.%) were added into the feed gas at a total space velocity of 8 SL/gcat./h. The partial pressures of the inlet hydrogen and carbon monoxide were kept constant during all periods by use of an inert gas (argon). When water was added it replaced some or all of the argon. After every run with added water, the reaction conditions were changed back to the

standard conditions, but without added water, in order to compare the effect of different amounts of water on the FTS rate. The results are shown in Figure 5 and Table 3. In the range from 5 to 25 vol.% water added ($P_{H_2O}/P_{H_2} = 0.12$ to 0.8 , $P_{H_2O}/P_{CO} = 0.24$ to 1.6), the additional water increased the CO conversion. In order to determine the effect of water addition time on the catalyst activity, a smaller or a larger amount of water (5 or 25 vol.%, respectively) was added continuously into the feed for 96 h. It was found that the continuous addition of the smaller amount of water maintained the higher CO conversion in comparison to that without water addition, and did not show a significant effect on the catalyst deactivation rate (Figure 2). The deactivation rate with water addition was 0.36% per day, slightly higher than the value of 0.26%/day without water addition during the initial period (0 to 120 hrs). The deactivation rate, based on the values at the standard condition following the addition of water (150 to 475 hrs. on stream) is 0.37%/day (Figure 5). Thus, the deactivation during the intermittent water addition is about the same as obtained during the constant addition of 5 vol%/water (Figure 2). For the addition of the larger amount of water (25%), CO conversion increased the first day, but the continuous addition of this level of water resulted in rapid deactivation of the catalyst at a rate of 1.5 % per day. More importantly, the catalyst activity was not recovered to the expected value after the addition of water was terminated, indicating that the catalyst had deactivated permanently. It is likely that the cobalt was partially oxidized during the long time exposure to the higher water partial pressure. Furthermore, the activity declined about as rapidly following termination of the addition of 25% water as it did during water addition (Figure 5).

The effects of water partial pressure in the reactor on the catalytic properties are shown in Figures 6, 7, 8 and 9. The CO conversion first increased, then remained nearly constant as P_{H_2O}/P_{CO} was increased to ~ 1 at a constant space velocity (Figure 6). Methane selectivity

decreased while CO₂ selectivities increased slightly with increasing water partial pressure (Figure 7). The C₂⁼ fraction was not effected, and remained essentially zero over the entire P_{H_2O}/P_{CO} range; the C₃⁼ and C₄⁼ fractions increased slightly with increasing water partial pressures (figure 8).

The effect of water on the silica supported cobalt catalyst is in marked contrast to the alumina supported cobalt catalyst. In our previous studies for Pt-Co/Al₂O₃ catalyst, it was found that water decreased the CO conversion in the range of the water added (3 to 25 vol.%). Increasing the amount of added water to 28 vol.% resulted in a permanent deactivation of the alumina supported catalyst [2]. Water also exhibited a deactivating effect on CO conversion while it was added with the feed for a CoRu/TiO₂ catalyst. However, in this study, water had a positive effect on the CO conversion for the Co/SiO₂ catalyst. Iglesia et. al [14] as well as some early workers [7-9] also found similar results, with water having an accelerating effect on the Fischer-Tropsch reaction for a silica-supported cobalt catalyst. At current, we do not have a reasonable explanation for the support effect. A series of cobalt catalysts prepared with different pore size supports are being tested in our laboratory. There was a slight increase in the C₅+ yield as P_{H_2O}/P_{H_2} increased to about 0.4 and then remained constant (Figure 9).

The impact of water partial pressure on catalyst deactivation is puzzling. The conditions during the period at a space velocity of 1 SL/gcat./hr. (Figure 2) that produces nearly 80% CO conversion provides $P_{H_2O} = 4.99$ atm (0.502 MPa) and $P_{H_2O}/P_{H_2} = 1.6$; under these conditions the catalyst did not lose measurable catalytic activity during a period of about 260 hours. On the other hand, adding water (25%) when operating at a space velocity of 8 SL/gcat./hr. with a CO conversion in the 20-27% CO conversion range to give P_{H_2O}/P_{H_2} of 0.84 and P_{H_2O} of 6.6 atm

(0.667 MPa) caused a rapid loss in catalytic activity during a period approaching 100 hours on stream (Figure 5). These data indicate that it is not P_{H_2O}/P_{H_2} or P_{H_2O}/P_{CO} , that determines whether the catalyst will lose its catalytic activity. The water partial pressure was slightly higher (6.6 atm vs. 5.0 atm) when the catalyst underwent deactivation. Significantly, the catalytic activity continued to decline after the addition of 25% water had been terminated even though the P_{H_2O}/P_{H_2} ratio was now only about 0.08

One could devise a number of possible reasons for the different impact of water on the loss of catalytic activity. The situation is complex and requires much more study. However, it appears that the presence of a reasonably high P_{CO} is necessary if catalyst deactivation is to occur. This suggests that some complex that involves both P_{H_2O} and P_{CO} is involved in the loss of catalytic activity. The formation of a cobalt formate like species is a potential explanation although this is very speculative with the data available.

Another possibility is the formation of cobalt silicates. In a previous TPR study [15], it was shown that hydrothermal treatment of a reduced Co/SiO₂ catalyst with H₂O (and subsequent calcination) led to the formation of both nonreducible and reducible mixed species of Co that interact with the support silica. These species have been referred to as Co-silicates, although their precise identify is not clear. Higher H₂O pressures and extended exposure times led to greater fractions of the cobalt-silica species. Since it is not known what effect the calcination step has on their formation, direct correlation of the results of that study with the results of a catalyst under reaction conditions is speculative. This is supported by a comparison of the differences observed at a H₂O partialpressure of about 5 atm. between the high conversion condition (Figure 2) and the water co-feed experiments (Figure 5). In the latter case, the H₂ partial pressure is higher, and may

result in a greater fraction of reduced Co, which could be more susceptible to interactions with the support in the presence of water. Also, examination of the used catalyst by XANES may provide conclusive evidence in the future. XANES has already been employed to demonstrate the presence of cobalt aluminate species in used Co/Al₂O₃ catalyst samples taken from the reactor and stored in solidified wax [16].

Conclusions

The space velocity and water addition were found to have a significant effect on the properties of a silica supported cobalt catalyst during Fischer-Tropsch synthesis. The short time addition of water in the range of 5 to 25% (vol.%) was found to have a positive effect on the CO conversion. The long time addition of small amounts of water (5 vol.%) increased CO conversion and did not have a significant effect on the catalyst deactivation; however, for larger amounts of water, long time addition resulted in a severe catalyst deactivation.

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Table 1							
H ₂ chemisorption and pulse reoxidation results for Co/SiO ₂ catalysts							
Catalyst	Calcination	μmol H ₂ per g	Uncorr %D	Uncorr. Diam (nm)	% Red .	Corr %D	Corr. Diam (nm)
12.4%Co/SiO ₂	None	25.6	3.04	33.9	39	7.79	13.2
12.4%Co/SiO ₂	623K in air	18.2	1.73	59.7	64	2.70	38.2

Table 2			
Effect of space velocity on CO conversion and water partial pressure ^a for Co/SiO ₂			
1/Space Velocity (h gcat/SL)	CO Conversion (%)	Water partial Pressure (atm) ^b	P_{H_2O}/P_{H_2} ^b
0.125	22.1	0.801	0.091
0.200	31.6	1.45	0.194
0.333	45.0	2.60	0.414
0.500	56.9	3.47	0.657
1.000	77.7	4.99	1.589
a. Reaction condition: 483 K, 20 atm, $P_{H_2} + P_{CO} = 14$ atm, H ₂ /CO=2.0.			
b. Based on reactor partial pressure.			

Table 3			
Effect of water addition on CO conversion ^a for Co/SiO ₂			
Water Amount Added (volume%)	CO Conversion(%)	Water Partial Pressure atm ^b (MPa)	P_{H_2O}/P_{H_2} ^b
0	22.5	0.967	0.120
5	28.1	2.27	0.290
8	29.2	3.02	0.389
12	28.1	3.96	0.510
15	28.9	4.82	0.627
20	28.6	5.78	0.743
25	27.4 ^c	6.64	0.835
a. Reaction condition: 483 K, 20 atm (2.02 MPa), H ₂ /CO=2.0, $P_{H_2} + P_{CO}$ =14 atm (1.41 Mpa). b. Based on reactor partial pressure. c. Based on conversion after first day at this condition.			

Figure 1. TPR profiles of uncalcined and calcined Co/SiO₂ catalysts.

Figure 2. CO conversion as a function of time on stream and space velocity for a Co/SiO₂ catalyst (T = 483 K; P = 20 atm (2.02 MPa); H₂/CO = 2.0).

Figure 3. CO conversion as a function of space time for a Co/SiO₂ catalyst [T = 483 K, P = 20 atm (2.02 MPa), H₂/CO = 2.0].

Figure 4. CO₂ and CH₄ selectivity as a function of space time for the Co/SiO₂ catalyst [T = 483 K, P = 20 atm (2.02 MPa), H₂/CO = 2.0].

Figure 5. Effect of water on CO conversion for Co/SiO₂ catalyst (T=483K, P=20 atm (2.02 MPa), P_{H₂}+P_{CO}=14 atm (1.41 MPa), H₂/CO=2.0, S.V.=8 SL/gcat.h; % is volume % of total feed).

Figure 6. CO conversion as a function of P_{H_2O}/P_{H_2} for Co/SiO₂ catalyst (T = 483K, P = 20 atm (2.02 MPa), $P_{H_2} + P_{CO} = 14$ atm (1.41 MPa), $H_2/CO = 2.0$, partial pressure is based on reactor exit).

Figure 7. $\text{CH}_4(\text{CO}_2)$ selectivity as a function of $\text{P}_{\text{H}_2\text{O}}/\text{P}_{\text{H}_2}$ for the Co/SiO_2 catalyst

Figure 8. Olefin ratio as a function of P_{H_2O}/P_{H_2} for the Co/SiO₂ catalyst

Figure 9. C5+ selectivity as a function of P_{H_2O}/P_{H_2} for the Co/SiO₂ catalyst [T=483 K, P=20 atm. H₂/CO=2, SV=8 SL/gcat./h]

Task 10. Cobalt Catalyst Mechanism Study

The objective of this task is to determine the impact of secondary reactions on the relationship of cobalt Fischer-Tropsch catalysts under conditions appropriate to slurry bubble column reactors.

A. The Formation of Branched Hydrocarbons in the Fe and Co Catalyzed FT Reactions

Introduction

To fully understand the mechanism for the FT reactions, it is important to understand how branched alkanes and alkenes being formed. If they are the products of the secondary reactions, the question to be answered is how and under what conditions that they are produced. On the other hand, if they are the primary products of the FT reactions, then it is necessary for any mechanistic scheme proposed for FT reactions to include the formation of branched alkenes and alkanes. In this study, we want to know how much branched hydrocarbon is formed under different conditions and different catalysts and try to understand which factor or factors plays the more important role in the formation of the branched products.

In order to understand how branched alkenes and alkanes being formed, it is necessary to quantitatively measure each isomers of each carbon number. Since some GC peaks of branched alkanes were buried in the branched alkene peaks and the vice versa, it is necessary to use indirect means to measure the amount of each isomer. In this study, the FT products were hydrogenated or brominated and an accurate amount of each branched alkane was obtained.

Experimental

1. Hydrogenation of FT Products

Six grams of FT products (oil and wax) and 0.5 g of Pt/C were placed in a jar. The reaction mixture was reduced under hydrogen pressure (30 psig) at room temperature with

excellent stirring until no alkenes were found in the reaction mixture. Then the reaction mixture was filtered prior to GC and GC/MS analysis. The FT products hydrogenated are the following: for Fe catalyzed FT products: Bao20, Bao22, Bao26, Bao28 and Bao29; for Co catalyzed FT products: L366, L367 and L368 (Table 1).

2. Bromination of FT Products

To the FT oil (for some samples, oil and wax), 22.3% bromine in acetic acid was added drop by drop with vigorously stirring until the solution gave a permanent yellow to orange color. The oils brominated are: for Fe catalyzed FT products: Bao20, Bao22, Bao26, Bao28 and Bao29; for Co catalyzed FT products: L366, L367 and L368.

3. Analysis of FT Products

The FT oil and the samples after hydrogenation and bromination were analyzed by GC and GC/MS. The branched alkanes in each carbon number were identified by GC/MS, and quantitatively determined by GC/FID.

Results and Discussion

Five oil samples from Fe catalyzed FT reactions and 3 oil samples from Co catalyzed FT reactions were hydrogenated and brominated. The FT reaction conditions and the catalyst compositions were given in Tables 1 and 2.

All of the FT products in the runs reported in this report contain 1-alkene, alkane, 2-alkenes, alcohols as well as branched hydrocarbons. After hydrogenation, the alkenes were converted to corresponding alkanes; after bromination, the alkenes were converted to corresponding dibromides.

Figure 1 is a partial chromatogram of the sample from Fe catalyzed FT reaction (Bao20). The top curve in this figure is for the FT products; the bottom figure is the sample after bromination and the middle chromatogram is for the sample after hydrogenation.

Figures 2 through 6 are the chromatograms of carbon 7, 8, 9, 10 and 11 of run Bao20, respectively. Again, the top in each figure is the FT products; the middle, after hydrogenation; and the bottom, after bromination (for the other 4 Fe catalyzed FT samples, the figures are similar and are not reprinted). After hydrogenation, the branched alkenes were converted to the corresponding branched alkanes and normal alkenes were converted to normal the alkane. The mole percent of branched alkanes of each carbon number is defined as:

$$\% \text{ branched} = \frac{\text{branched alkanes}}{\text{branched alkanes} + \text{normal alkane}} \times 100 \quad (1)$$

In the case of hydrogenated sample, the % branched alkanes represent the total branched hydrocarbons (branched alkenes plus branched alkanes). Since it is difficult to quantitatively measure the amount of branched alkanes in the original FT oil due to peak overlap, bromination of the FT oil is useful. The bromination of FT oil enable us to quantitatively measure the % branched alkanes from C₇ to C₁₁ since the dibromide formed from these olefins elute following C₁₁. In this case, the % branched alkanes represents the total branched alkanes in the reaction product. The results are given in Tables 3-7 for Fe catalyzed FT reactions produced in runs Bao20, Bao22, Bao26, Bao28 and Bao29, respectively.

Figure 7 is the partial chromatogram of a sample from the Co catalyzed FT reaction (L366), and Figures 8 through 12 are the chromatograms of carbon numbers 7, 8, 9, 10 and 11 formed during run L366, respectively. The chromatograms of the other two Co catalyzed FT runs (L367 and L368) are similar to Figures 7 through 12. As Figures 1 through 6, the top is the FT products; the middle, after hydrogenation; bottom, after bromination. The mole percent of branched alkanes are compiled in Table 8.

As can be seen from Tables 3 and 4, Runs Bao20 and Bao22 were conducted using the same catalyst and same reaction conditions except temperature. Bao20 was run at 230°C and

Bao22 was run at 270°C. As the reaction temperature was increased, the amount of branched alkanes in most of the carbon numbers increased by more than 5%.

Runs Bao22 and Bao26 (data in Table 4 and Table 5) were conducted using the same catalyst at the same temperature but at different H₂:CO ratios and WHSV. When the H₂:CO ratio increased from 0.67 to 1.70 and the WHSV increased from 10 to 40, the amount of branched alkanes (Bao26) decreased by 5-10% for all of the carbon numbers, with few exceptions.

In all of the five Fe catalyzed FT runs, it appears that the catalyst composition has a more significant impact on the formation of branched hydrocarbons than the reaction conditions, such as temperature, flow rate and H₂:CO ratio. The only difference between runs Bao26 (data in Table 5) and Bao28 (data in Table 6) is that the catalyst used in the run Bao28 differs slightly from that of Bao26 (1.4% and 4% K, respectively), and yet the amount of the branched alkanes increased more than 10% for most carbon numbers for the higher potassium containing catalyst.

Run Bao29 was conducted using pure Fe catalyst (100% Fe). The amount of branched alkanes (data in Table 7) is lower than runs Bao22 and Bao28. Since this run was also conducted at a higher H₂:CO ratio, lower temperature and lower WHSV, it is difficult to tell which factor played the major role.

The major difference between Fe catalyzed FT reactions and Co catalyzed FT reactions is the production of larger amounts of branched hydrocarbons with the catalyzed FT reaction. As can be seen from Tables 3 through 8, the Fe catalyzed FT reaction produced 10 to 25% of branched hydrocarbon (data after hydrogenation), whereas the Co catalyzed FT reaction produced only 1-4% of branched hydrocarbons (Table 8).

The reaction conditions of the three Co catalyzed FT reactions are different (see Table 2) and the catalyst compositions are also slightly different. Therefore, it is hard to tell which factor

is more responsible for the formation of the branched hydrocarbons. Run L367 produced highest percentage of branched hydrocarbons (about 4%) among these three runs and this is probably due to the low WHSV.

The mole percent of branched alkanes after hydrogenation is the percentage of total branched hydrocarbons (branched alkenes and branched alkanes) in the total hydrocarbons. Designating the P_B as branched alkanes; O_B , branched alkenes; P_n , normal alkane; O_n , normal alkenes, then after hydrogenation, we have:

$$\text{Mol\% (branched alkanes after hydrogenation)} = \frac{P_B + O_B}{P_B + O_B + P_n + O_n} \times 100 \quad (2)$$

The mole percent of branched alkanes after FT reaction can be represented by the mole percent of branched alkanes after bromination as shown in eq. 3:

$$\text{Mol\% (branched alkanes after bromination)} = \frac{P_B}{P_B + P_n} \times 100 \quad (3)$$

If $O_n/P_n = O_B/P_B$, it can be proven that

$$\text{Mol\% (branched alkanes after [H])} = \text{Mol\% (branched alkanes after [Br])} \quad (4)$$

However, if $O_n/P_n < O_B/P_B$, then

$$\text{Mol\% (branched alkanes after [H])} > \text{Mol\% (branched alkanes after [Br])} \quad (5)$$

And if $O_n/P_n > O_B/P_B$, then

$$\text{Mol\% (branched alkanes after [H])} < \text{Mol\% (branched alkanes after [Br])} \quad (6)$$

As seen in Figures 13 through 17 for in Fe catalyzed FT reactions, the mole percent of branched alkane after hydrogenation in all of these five runs is either higher than or close to that of the branched alkanes after bromination. This indicated that the ratio of O_n/P_n is less than or

close to the ratio of O_B/P_B . These results suggest that during the formation of these FT products, the rate of hydrogenation of n-alkenes is close to or only slightly larger than that of branched alkenes. Similar results were obtained for Co catalyzed FT reactions (Figures 18 through 20).

The relative ratio of n-alkenes/n-alkane (O_n/P_n) can be measured accurately based on the GC. Because of the GC peak overlap, it is very difficult to measure accurately the ratio of branched-alkenes/branched alkanes (O_B/P_B). However, the ratio of O_B/P_B can be calculated based on the mole percent of the branched alkanes (after hydrogenation and after bromination) and the ratio of O_n/P_n .

Let

$$(P_B + O_B)/(P_B + O_B + P_n + O_n) = \alpha \quad (7)$$

where α is the mole percent of branched alkanes after hydrogenation, and

$$P_B/(P_B + P_n) = \beta \quad (8)$$

where β is the mole percent of branched alkanes after bromination. The ratio of n-alkenes/n-alkane is represented in eq. 9:

$$O_n/P_n = \gamma \quad (9)$$

Solving the eq. 7, 8 and 9, we have

$$O_B/P_B = \frac{\alpha(1 - \beta)(1 + \gamma) - \beta(1 - \alpha)}{\beta(1 - \alpha)} \quad (10)$$

Based on eq. 10, the ratio of O_B/P_B can be calculated. Also based on the eq. 10, it can be proven that if $\alpha = \beta$, then $O_B/P_B = O_n/P_n = \gamma$; if $\alpha > \beta$, then $O_B/P_B > O_n/P_n$; if $\alpha < \beta$, then $O_B/P_B < O_n/P_n$.

The representative results were given in Table 9 (for Fe catalyzed FT reactions) and Table 10 (for Co catalyzed FT reactions).

The mole percent of branched alkanes in Fe catalyzed FT products (Figure 21) varies from run to run. However, for any run, the different carbon number compounds have about same mole percent of branched alkanes. This is also true for Co catalyzed FT reactions (Figure 22). The major difference between Fe and Co catalyzed FT reaction in term of mole percent of branched alkanes is that Co catalyzed FT reactions only produce 1-4% of branched alkanes, whereas the Fe catalyzed FT reactions can produce as high as 20% (probably more) of branched alkanes.

Table 1					
The Reaction Conditions and the Catalyst in the Fe Catalyzed FT Reactions					
Run ID	Bao20	Bao22	Bao26	Bao28	Bao29
Catalyst	4.6% Si, 64.6% Fe, 2.0% Cu, 1.4% K	4.6% Si, 64.6% Fe, 2.0% Cu, 1.4% K	4.6% Si, 64.6% Fe, 2.0% Cu, 1.4% K	4.6% Si, 62.2% Fe, 2.0% Cu, 5% K	100% Fe
Temp. (°C)	230	270	270	270	255
H ₂ : CO	0.67	0.67	1.70	1.70	1.91
WHSV	10	10	40	40	3.0

Table 2			
The Reaction Conditions and the Catalyst in the Co Catalyzed FT Reactions			
Run ID	L366	L367	L368
Catalyst	10% Co/0.2% Ru/ TiO ₂	15% Co/ 0.5% Ru/ SiO ₂	15% Co/ 0.53% Pt/ Al ₂ O ₃
temp. (°C)	230	220	220
Pressure (psig)	350	300	275
H ₂ : CO	2	2	2
WHSV	18.29	6.73	13.40

Table 3						
The Mole Percent of Branched Alkanes in Fe Catalyzed FT Products (Run ID: Bao20)						
	FT Products		After Hydrogenation		After Bromination	
Carbon #	# of isomers	Mol %	# of isomers	Mol %	# of isomers	Mol %
7	-	-	2	15.12	2	11.03
8	2	26.1	3	14.50	3	14.43
9	3	18.12	3	11.51	3	11.31
10	2	12.06	6	12.59	4	11.15
11	4	12.23	4	8.93	4	9.68
12	3	4.58	5	7.16		
13	3	7.43	5	11.61		

Table 4						
The Mole Percent of Branched Alkanes in Fe Catalyzed Ft Products (Run ID: Bao22)						
	FT Products		After Hydrogenation		After Bromination	
Carbon #	# of isomers	Mol %	# of isomers	Mol %	# of isomers	Mol %
7	2	8.82	2	16.05	2	5.10
8	3	17.67	3	19.71	3	15.92
9	3	16.60	5	19.01	3	15.32
10	4	12.69	5	19.06	4	17.27
11	4	11.89	5	20.00	4	17.27
12	4	18.94	5	15.47		
13	5	21.71	5	20.43		

Table 5						
The Mole Percent of Branched Alkanes in Fe Catalyzed FT Products (Run ID: Bao26)						
	FT Products		After Hydrogenation		After Bromination	
Carbon #	# of isomers	Mol %	# of isomers	Mol %	# of isomers	Mol %
7	2	9.81	2	9.03	2	10.44
8	3	15.67	3	8.89	3	11.25
9	3	9.62	3	10.05	3	9.42
10	4	9.44	5	10.39	4	9.02
11	4	9.57	4	9.37	4	5.72
12	3	6.14	4	8.35		
13	4	5.89	5	9.15		

Table 6						
The Mole percent of Branched Alkanes in Fe Catalyzed FT Products (Run ID: Bao28)						
	FT Products		After Hydrogenation		After Bromination	
Carbon #	# of isomers	Mol%	# of isomers	Mol%	# of isomers	Mol%
7	-	-	2	14.82	2	19.21
8	2	19.68	2	25.74	3	18.04
9	3	18.50	7	20.73	3	18.04
10	3	20.86	7	19.99	3	16.41
11	4	24.77	6	19.42	4	11.71

Table 7						
The Mole Percent of Branched Alkanes in Fe Catalyzed FT Products (Run ID: Bao29)						
	FT Products		After Hydrogenation		After Bromination	
Carbon #	# of isomers	Mol%	# of isomers	Mol%	# of isomers	Mol%
7	-	-	2	10.05	2	13.48
8	2	15.18	3	14.50	3	14.58
9	3	13.86	3	10.89	3	11.90
10	3	12.88	6	12.27	4	11.55
11	4	11.83	5	10.37	5	11.43
12	-	-	-	-	-	-
13	-	-	-	-	-	-

Table 8 The Mole percent of Branched Alkanes in Co Catalyzed FT Products							
		FT Products		After Hydrogenation		After Bromination	
Carbon #	Run #	# of isomers	Mol%	# of isomers	Mol%	# of isomers	Mol%
7	L366	2	1.85	2	1.99	2	1.40
	L367	2	7.52	2	6.00	2	3.71
	L368	2	2.28	2	1.55	2	1.18
8	L366	2	2.33	2	2.45	3	1.67
	L367	3	4.69	3	4.15	3	4.05
	L368	3	2.26	3	1.57	3	1.35
9	L366	3	2.81	3	2.17	3	2.06
	L367	3	4.80	3	3.78	3	4.10
	L368	3	1.53	3	1.62	3	1.34
10	L366	3	2.19	3	2.39	3	2.08
	L367	4	4.34	4	4.05	4	4.29
	L368	3	1.51	3	1.61	3	1.37
11	L366	4	2.62	4	2.79	4	2.00
	L367	4	4.47	4	4.26	4	4.35
	L368	4	1.69	4	1.84	4	1.84
12	L366	4	1.87	5	3.02		
	L367	5	4.31	5	4.26		
	L368	4	1.60	4	1.73		
13	L366	5	3.10	5	3.34		
	L367	5	4.70	5	4.59		
	L368	5	1.84	5	1.96		
14	L366	5	3.45	5	3.72		
	L367	5	4.88	5	4.86		
	L368	-	-	-	-		

Table 9				
The Relative Ratio of the Products in Fe Catalyzed FT reactions (Run ID: Bao22)				
Carbon Number	branched- hydrocarbons/ total- hydrocarbons	branched-alkanes/ total alkanes	n-alkenes/ n-alkane	branched-alkenes/ branched alkanes
7	0.1605	0.051	2.3329	1.8574
8	0.1971	0.1592	2.0029	1.9647
9	0.1901	0.1532	1.6416	1.6063
10	0.1906	0.1727	1.4831	1.4688
11	0.2000	0.1727	1.2705	1.2516

Table 10				
The Relative Ratio of the Products in Co Catalyzed FT reactions (Run ID: L367)				
Carbon Number	branched- hydrocarbons/ total- hydrocarbons	branched- alkanes/ total alkanes	n-alkenes/ n-alkane	branched-alkenes/ branched alkanes
7	0.0600	0.0371	0.371	0.2018
8	0.0415	0.0405	0.2973	0.2871
9	0.0378	0.041	0.2390	0.2738
10	0.0405	0.0429	0.1973	0.2193
11	0.0426	0.0435	0.1645	0.1719

Figure 1. The Partial Chromatogram of the Oil Sample from Fe Catalyzed FT reaction (Run ID: Bao20) (Top: FT products; Middle: after hydrogenation; Bottom: after bromination).

Figure 2. The Chromatogram of the Carbon-7 of the Run Bao20 (Top: FT products; Middle: after hydrogenation; Bottom: after bromination).

Figure 3. The Chromatogram of the Carbon-8 of the Run Bao20 (Top: FT products; Middle: after hydrogenation; Bottom: after bromination).

Figure 4. The Chromatogram of the Carbon-9 of the Run Bao20 (Top: FT products; Middle: after hydrogenation; Bottom: after bromination).

Figure 5. The Chromatogram of the Carbon-10 of the Run Bao20 (Top: FT products; Middle: after hydrogenation; Bottom: after bromination).

Figure 6. The Chromatogram of the Carbon-11 of the Run Bao20 (Top: FT products; Middle: after hydrogenation; Bottom: after bromination).

Figure 7. The Partial Chromatogram of the Oil Sample from Co Catalyzed FT reaction (Run ID: L366) (Top: FT products; Middle: after hydrogenation; Bottom: after bromination).

Figure 8. The Chromatogram of the Carbon-7 of the Run Bao20 (Top: FT products; Middle: after hydrogenation; Bottom: after bromination).

Figure 9. The Chromatogram of the Carbon-8 of the Run Bao20 (Top: FT products; Middle: after hydrogenation; Bottom: after bromination).

Figure 10. The Chromatogram of the Carbon-9 of the Run Bao20 (Top: FT products; Middle: after hydrogenation; Bottom: after bromination).

Figure 11. The Chromatogram of the Carbon-10 of the Run Bao20 (Top: FT products; Middle: after hydrogenation; Bottom: after bromination).

Figure 12. The Chromatogram of the Carbon-11 of the Run Bao20 (Top: FT products; Middle: after hydrogenation; Bottom: after bromination).

Figure 13. The Mole Percent of Branched Alkanes in Fe Catalyzed FT Products (Run ID: Bao20).

Figure 14. The Mole Percent of Branched Alkanes in Fe Catalyzed FT Products (Run ID: Bao22).

Figure 15. The Mole Percent of Branched Alkanes in Fe Catalyzed FT Products (Run ID: Bao26).

Figure 16. The Mole Percent of Branched Alkanes in Fe Catalyzed FT Products (Run ID: Bao28).

Figure 17. The Mole Percent of Branched Alkanes in Fe Catalyzed FT Products (Run ID: Bao29).

Figure 18. The Mole Percent of Branched Alkanes in Co Catalyzed FT Products (Run ID: L366).

Figure 19. The Mole Percent of Branched Alkanes in Co Catalyzed FT Products (Run ID: L367).

Figure 20. The Mole Percent of Branched Alkanes in Co Catalyzed FT Products (Run ID: L368).

Figure 21. The Mole Percent of Branched Alkanes in Fe Catalyzed FT Products (after bromination).

Figure 22. The Mole Percent of Branched Alkanes in Co Catalyzed FT Products (after bromination).

B. D₂O Tracer Studies in Co Catalyzed Fischer-Tropsch Reaction

Abstract

The data show that the deuterium added in water together with synthesis gas provides hydrogen for the Fischer-Tropsch synthesis. In fact, the deuterium initially present in water nearly equilibrates with the hydrogen present in synthesis gas. Thus, water, once formed, is not inert but adsorbs competitively on the cobalt-titania catalyst to activate hydrogen. The data do not permit a definition of whether the exchange occurs on cobalt or the alumina support. The H/D ratio in the paraffin products is 4.4 and is very close to the H/D ratio in the feed of D₂O/H₂ (4.1).

Keywords: Cobalt-alumina; isotopic tracer; Fischer-Tropsch Synthesis; deuterium, deuterium oxide; water, deuterated.

Introduction

The Fischer-Tropsch (FT) reaction can be summarized by Equation 1.

Under FT reaction conditions, with some catalysts and/or reaction conditions, the water-gas shift (WGS) reaction also can occur as a side reaction (eq. 2).

The amount of water converted to hydrogen by the WGS reaction depends on the reaction conditions and the catalyst used. It has been reported that water can affect the FT reaction rate and the selectivity [1].

According to eq. 2, water can be converted to hydrogen, which can be used by FT reaction to produce hydrocarbons. The question how effective a hydrogen source the H₂O can be in the FT synthesis with a cobalt catalyst is still not answered. In this study, D₂O was used as a probe to study the deuterium distribution of FT products. The H/D ratio of the products give

some clue about H/D ratio of the surface H-D pool and quantitative measure of the effectiveness of H₂O as the hydrogen source.

Experimental

The FT reaction (LGX372) was carried out in a 1-L continuously stirred autoclave reactor (CSTR) as described previously [2]. Fourteen grams of catalyst (Co (10 wt.%)/ Ru (0.2 wt.%)/TiO₂) was activated using H₂ at 300°C in a plug flow reactor and transferred to the CSTR without exposure to air. Synthesis was conducted at 2.40 MPa (350 psig) and 230°C using 300 g of PW 3000 as the startup oil (a polyethylene fraction with average MW = 3000). Three traps follow the reactor and are held at 200°, 130° and 0°C. For the D₂O tracer run, D₂O was co-fed with syngas (D₂O, 4.19 SLPH; H₂, 17.09 SLPH; CO, 8.50 SLPH) for 7 hours. Immediately prior to addition of the tracer, the three product traps were emptied. At the end of the addition of D₂O, the product traps were again drained and the contents were analyzed using the normal GC procedures as well as GC/MS analysis. During the tracer run, a gas sample was taken every 1.5 hours for analysis.

The relative amounts of the isotopomers of the hydrocarbons were determined by GC/MS. The data were corrected for the ¹³C content of the products. Because of the inverse isotope effect of the deuterated compounds with gas chromatography, the relative amount of the total area of the molecular ion of each isotopomer was used to calculate the molar ratio [3].

The relative amount of H₂, HD and D₂ were measured by GC using a 90-meter molecular sieve column and He carrier. H₂, HD and D₂ were separated at 80°C. The thermal conductivity differences of hydrogen and the carrier causes a negative peak to be obtained for H₂.

The relative amount of H₂O, HDO and D₂O was analyzed using GC/MS. The ratio of H/D obtained using this method has a standard deviation of ± 0.12 .

Results and Discussion

Table 1 contains the deuterium distribution of alkane products collected following the 7-hour D₂O tracer run of a Co catalyzed FT reaction. The relative amounts of the isotopomers of each carbon number from C₅ to C₁₆ were determined using the GC/MS method. As can be seen from the data in Table 1, the relative amount of d₀ isomer of each carbon number is unusual higher than expected if we assume a binomial distribution of H and D atoms in a compound. Also, the relative amount of the d₀ isotopomer of alkanes increases as the carbon number increases. These results indicate the presence of accumulated products (Δ) [4,5].

Products accumulation (Δ) is a phenomena that must always be considered for an isotope tracer study in FT reactions. In most tracer studies of the FT synthesis, the unlabeled syngas conversion is conducted until the catalytic activity has stabilized and then the labeled compound is added for some time period. Usually the products are collected during the period of labeled compound addition. The products thus collected will consist of three fractions: (1) the products derived from the labeled compounds, which will contain at least one labeled atom; (2) the products from the normal FT synthesis that are derived from the unlabeled syngas, and (3) any products formed from unlabeled synthesis gas during the period of activity stabilization, that is, the period before the labeled compound is added.

It has been reported [6] that the relative value of Δ of a carbon number increases as the carbon number increases. It also has been reported that product accumulation (Δ) can affect the data interpretation of all of isotope tracer studies in FT reaction run at both small flow and large CSTR reactors [4]. Failing to include this factor in the data analysis could lead to conclusions that are consistent with the data but are not representative of the reaction mechanism [4,7,8].

Since the presence of product accumulation is the nature of the isotope tracer experiment in FT reaction, this factor cannot be eliminated completely. However, the effect of the

accumulated products can be minimized by applying some experimental techniques. For example, by collecting the gas sample of a tracer experiment after the experiment has run for a period of time (3 hours under the present conditions, for instance) and using the data derived from only the gas sample, the accumulation factor can be minimized. In ^{13}C and deuterium labeled tracer experiments, this factor can be removed by utilizing only the products that contain ^{13}C or deuterium for all carbon numbers. This method has been used to reinterpret ^{13}C labeled tracer data [4]. In this study, this method is used to interpret the data that has been obtained for the D_2O tracer experimental data shown in Table 1.

The d_0 isomers of each carbon number in Table 1 come from two sources: the product accumulation (Δ) and the products from normal FT synthesis that are derived from the unlabeled syngas. In the D_2O tracer experiment, the amount of d_0 isomer of each carbon number from normal FT synthesis during the tracer experiment is determined by the H/D ratio of the surface pool as well as the carbon number. As can be seen from the data in Table 2, by assuming the H/D ratio of 4, based upon the total H and D in the feed, as the surface H-D pool, the amount of d_0 isotopomer of C_7 alkane that could be produced during the tracer experiment is 2.8%. As the carbon number increases, the amount of d_0 isotopomer decreases, with the amount of d_0 isomer of C_{16} alkane decreasing to 0.05%. These values are smaller than the experimental error of GC/MS analysis [3]. Therefore, if we eliminate the d_0 isomers in considering the data in Table 1 and recalculate the deuterium distribution of the remaining isotopomers of each alkane, the products present in the reactor before the tracer experiment are eliminated from consideration since all of the Δ s are d_0 isomers. Also, based on the above analysis and the data in Table 2, removing all of the d_0 isomer in each carbon number introduces very small errors.

Table 3 lists the deuterium distribution of the isotopomers of each carbon number calculated after eliminating the d_0 isotopomers. As can be seen from the data in this table, the

deuterium distribution of each compounds is close to a binomial distribution with a H/D ratio of about 4.4. For example, a plot is shown in Figure 1 for the deuterium distribution of octane (d_0 isomer was eliminated) that was obtained experimentally and one that is calculated for the binomial distribution and the agreement of the two is excellent. Based on the mol% of each isotopomer, the H/D ratio of octane (Table 3) was calculated to be 4.4. Assuming a binomial distribution of the deuterium with a H/D ratio of 4.4 in the surface H-D pool, the calculated mol% of each isotopomer fit the experimental value nicely.

Figure 2 shows the H/D ratio of alkanes measured for carbon numbers C_5 to C_{16} . When the d_0 isomer is included for each carbon number, the H/D ratio increases as the carbon number increases, consistent with the impact of accumulated products. When the d_0 isomers are not included for each carbon number, the H/D ratio is essentially constant (in this case, 4.4), indicating that all of the deuterium and hydrogen in the compounds comes from a common H-D source: the surface H-D pool with a ratio of 4.4.

Table 4 is the summary of the samples analyzed. The ratio of H/D in the feed is based on accurately measured rates of addition of D_2O , H_2 and CO. The H/D ratio of the hydrocarbons was obtained from GC/MS data as described above. The H/D ratio of water was measured using GC/MS. Known mixtures of H_2O and D_2O were prepared by accurate weight and the calibration curve was nearly linear (Figure 3). The H_2 , HD and D_2 were separated by GC as shown in Figure 4 with H_2 as a negative peak. The r^2 for the standard calibration data for H_2 , HD and D_2 are 0.994, 0.997 and 0.999, respectively.

There is an inverse kinetic isotope effect (kie) for the hydrogenation of carbon monoxide (9). Thus, it is not unusual for the D/H ratio in the hydrocarbons to be higher than was present in the feed if the syngas contained an equimolar mixture of H_2 and D_2 . Introducing the isotopes as H_2 and D_2O complicates the situation so that the inverse kie cannot be used to predict the results.

Based upon the average H/D in the hydrocarbons, the kie is not as great as when H₂ or D₂ are used alone.

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Table 1												
The Deuterium Distribution of the Alkane Products of the FT Reaction (while adding D ₂ O)												
# of C ^a	C ₅ ^c	C ₆	C ₇	C ₈	C ₉	C ₁₀	C ₁₁	C ₁₂	C ₁₃	C ₁₄	C ₁₅	C ₁₆
# of D ^b												
0	41.7	45.9	49.4	61.0	70.2	73.5	78.0	80.7	84.2	87.7	91.0	94.1
1	16.1	9.8	7.3	6.2	4.4	4.1	3.4	2.9	2.5	1.9	1.6	0.7
2	17.6	12.7	10.6	7.4	4.9	3.3	2.3	2.0	1.4	1.2	0.8	0.5
3	13.9	13.1	12.3	8.4	5.8	4.3	3.1	2.4	1.8	1.2	0.8	0.5
4	7.5	9.8	9.9	7.7	5.9	4.9	3.9	3.0	2.2	1.6	0.9	0.7
5	2.4	5.5	6.1	5.1	4.4	4.3	3.6	3.2	2.5	1.7	1.2	0.8
6	0.8	2.3	3.0	2.8	2.7	3.0	2.7	2.6	2.2	1.7	1.3	0.8
7	0.12	0.8	1.0	1.1	1.2	1.6	1.7	1.7	1.6	1.4	1.0	0.8
8		0.2	0.3	0.4	0.5	0.7	0.9	1.0	1.1	0.9	0.8	0.7
9				0.1	0.1	0.3	0.4	0.5	0.6	0.6	0.5	0.4
10							0.1	0.2	0.2	0.2	0.3	0.3
11									0.1	0.2	0.1	
H/D	7.6	7.7	8.8	12.8	17.8	20.5	25.5	29.9	37.3	49.5	69.2	104
a. Carbon number. b. Number of deuterium. c. The values for all isotopomers of all the alkanes are mol%.												

Table 2	
The Mol% of d ₀ Isomers Calculated for C ₅ -C ₁₆ Hydrocarbons that are Produced for a Binomial Distribution from a Syngas with a H/D Ratio of 4	
Carbon Number	d ₀ isomer (mol%)
C5	6.9
C6	4.4
C7	2.8
C8	1.8
C9	1.2
C10	0.7
C11	0.5
C12	0.3
C13	0.2
C14	0.1
C15	0.08
C16	0.05

Table 3												
The Deuterium Distribution of the Alkane Products of the FT Reaction (Tracer: D ₂ O; after eliminated d ₀ isomers of each carbon number of the data in Table 1												
# of C ^a	C ₅ ^c	C ₆	C ₇	C ₈	C ₉	C ₁₀	C ₁₁	C ₁₂	C ₁₃	C ₁₄	C ₁₅	C ₁₆
# of D ^b												
1	27.5	18.1	14.5	15.9	15.0	16.0	16.2	16.5	17.5	18.0	20.5	15.1
2	30.2	23.5	21.1	19.2	16.6	13.0	11.1	11.1	10.0	11.3	10.7	9.9
3	23.8	24.3	24.5	21.9	19.9	17.0	15.2	13.7	12.5	10.9	10.7	11.2
4	12.9	18.2	19.8	19.9	20.2	19.3	18.8	17.0	15.8	14.8	12.0	13.4
5	4.1	10.2	12.1	13.2	14.9	16.7	17.4	17.8	17.5	16.0	16.1	16.8
6	1.3	4.3	6.1	7.2	9.3	11.9	13.0	14.6	15.7	15.8	16.9	16.2
7	0.2	1.4	2.0	2.9	4.2	6.2	8.4	9.4	11.2	13.3	13.2	17.5
8		0.3	0.6	0.9	1.7	2.9	4.2	5.9	7.6	8.3	10.6	14.0
9			0.1	0.1	0.3	1.1	2.1	2.9	4.1	6.0	6.6	8.3
10						0.2	0.4	0.9	1.7	2.1	3.2	5.6
11								0.2	0.5	1.4	1.8	0.8
H/D	4.0	3.7	3.9	4.4	4.6	4.7	4.8	5.0	5.2	5.4	5.6	5.5
a. Carbon number. b. Number of deuterium. c. The values in all the alkanes are mol%.												

Table 4		
The H/D Ratio of Starting Reagents, Products and Unreacted Gas		
Category	Compounds Analyzed	H/D
Starting Reagents	D ₂ O; H ₂	4.1
Products	Alkanes	4.4
Products	H ₂ O; HDO; D ₂ O	2.5
Unconverted Gas	H ₂ ; HD; D ₂	5.8

Figure 1. The deuterium distribution of the isotopomers of octane.

Figure 2. The ratio of H/D of alkanes in Co catalyzed FT reactions (Tracer: D_2O ($H_2:D_2O = 4:1$)).

Figure 3. Plot of H/D ratio in standard H₂O/D₂O samples prepared by weight versus the H/D ratio from GC water peak.

Figure 4. GC trace of signal from thermal conductivity cell (First peak H₂; middle peak, HD and last peak D₂).

C. Fischer-Tropsch Synthesis: Supercritical Conversion Using a Co/Al₂O₃ Catalyst in a Fixed Bed Reactor

Abstract

A cobalt catalyst (25%Co/ γ -Al₂O₃) was used in a fixed bed reactor under a pressure/density tuned supercritical fluid mixture of n-pentane/n-hexane. By using inert gas as a balancing gas to maintain a constant pressure, the density of the supercritical fluid could be tuned near the supercritical point while maintaining constant space velocity within the reactor. The benefits of the mixture allowed for optimization of transport and solubility properties at an optimum reaction temperature for Fischer Tropsch synthesis with a cobalt catalyst. There was an important increase in conversion due to greater accessibility to active sites after extraction of heavy wax from the catalyst, and additional benefits included decreased methane and carbon dioxide selectivities. Decreased paraffin/(olefin + paraffin) selectivities with increasing carbon number were also observed, in line with extraction of the hydrocarbon from the pore. Faster diffusion rates of wax products resulted in lower residence times in the catalyst pores, and therefore, decreased probability for readsorption and reaction to the hydrogenated product. Even so, there was not an increase in the alpha value over that obtained with just the inert gas.

1. INTRODUCTION

In the near future, increasing dependence on stranded natural gas reserves for fuel production is expected. This combined with increasing political pressure on oil companies to limit flaring of gas has renewed focus on Gas-to-Liquids (GTL) technology. Most GTL plants considered for commercialization consist of three process steps: (1) synthesis gas production from natural gas; (2) Fischer-Tropsch synthesis (FTS) to convert syngas to a crude hydrocarbon mixture (syncrude); and (3) hydroprocessing of syncrude to transportation fuels. Due to the

perception of high activity and stability, the catalyst of choice for FTS is typically a supported cobalt catalyst.

There are positive features as well as drawbacks to conducting Fischer-Tropsch by the traditional gas phase route or even by the more advanced liquid phase methods. For example, gas phase FTS, which is typically carried out in a fixed or fluid bed reactor, produces high product yields, due to the superior catalyst concentration per reactor volume. However, these higher initial rates, coupled with the potential for poor heat removal capacities of fixed-bed gas phase processing, typically lead to localized overheating of the catalyst, due to the exothermicity of the reaction, resulting in sintering of cobalt clusters, as well as the deposition of heavy waxes within catalyst pores, both contributing adversely to catalyst deactivation.

Better heat control throughout the reactor can be gained by conducting FTS in the liquid phase, due to the better heat removal capacities of the liquid. Liquid phase FTS is typically conducted in the laboratory in a continuously stirred tank reactor (CSTR) or commercially in the slurry bubble column reactor (SBCR). Deactivation rates are lower because the liquid media facilitates dissolving wax products, both internal and external to the catalyst pores. However, the liquid itself provides a resistance to the diffusional transport of gas phase reactants to active sites, resulting in a possible decrease of the reaction rate in comparison to gas phase FTS. Also, separation of the attrited catalyst fines from the waxy product remains a demanding task for liquid phase FTS in comparison to the typical fixed bed gas phase reactor, whereby the wax products typically trickle down the catalyst bed.

By conducting FT in a supercritical media [1], where the supercritical fluid is usually a relatively low molecular weight solvent, one may take advantage of both the gas-like transport properties as well as the liquid-like heat capacity and solubility characteristics of a liquid, and utilize the fixed bed reactor. Implementing a fixed bed supercritical reactor process may achieve

two important goals of improving the economics of GTL operations: (1) catalyst lifetimes can be extended by suppressing deactivation by pore plugging via heavy molecular weight wax products and (2) the requirement of filtration to effect the removal of the wax product, as is needed for CSTR and SBCR operations, is avoided.

A 25%Co/ γ -Al₂O₃ catalyst, prepared using a slurry phase impregnation method, was found to exhibit high activity and stability in a CSTR ($H_2/CO = 2$, $T = 220^\circ\text{C}$, $P = 1.9\text{ MPa}$). Considerable effort was made to stabilize the catalyst against deactivation by reoxidation and other instabilities, which occur when the cluster size of cobalt is below about 10 nm [2,3].

Choice of supercritical fluid, in our case a mixture, was based on, with some modification, the following criteria set forth by Fujimoto et al. [4]:

- A. The critical temperature and pressure should be slightly lower than the typical reaction temperature and pressure. In this case, reaction temperature was similar to normal FTS, but the reactor total pressure (8.24 MPa) was considerably higher than used for either a gas-phase or liquid phase FTS reactor (approximately 2.00 MPa). Although much less sensitive to total pressure than temperature, FTS is reported to shift to produce heavier products with an increase in the total pressure of syngas [5]. This pressure dependence is more pronounced for cobalt than for an iron catalyst [6].
- B. The solvent should be one which does not poison the catalyst and should be stable under the reaction conditions. The low molecular weight paraffins chosen for this study are unreactive and stable. Also, the paraffins are not coke precursors under the mild temperatures of FTS.
- C. The solvent should have a high affinity for aliphatic hydrocarbons to extract the wax from the catalyst surface and reactor.

Because the upper optimum temperature for FTS for cobalt catalysts is approximately 220°C, the critical temperature of the solvent was selected to be below this temperature. In a previous study [7] by our group, and reproduced here in Figures 1 and 2, it was determined using the Hysys 2.1 process simulator that a 55% hexane/45% pentane mixture should give favorable liquid-like densities, while still maintaining gas-like transport properties at a pressure of approximately 8.24 MPa. Using these conditions with the 25%Co/Al₂O₃ catalyst, supercritical studies were conducted by varying the partial pressure of the supercritical fluid, maintaining constant space velocity by using argon as a balancing gas, to determine if the increased solubility of the wax products in the supercritical fluid improved the activity and deactivation profile during reaction testing.

2. EXPERIMENTAL

2.1 Catalyst Preparation

Condea Vista Catalox (high purity γ -alumina, 100-200 mesh, 175 m²/g) was used as the support material for the cobalt FTS catalyst. The catalyst was prepared by a slurry impregnation method, and cobalt nitrate was used as the precursor. In this method, which follows a Sasol patent [8], the ratio of the volume of solution used to the weight of alumina was 1:1, such that approximately 2.5 times the pore volume of solution was used to prepare the cobalt solution. Two impregnation steps were used, each to load 12.5% of Co by weight. Between each step the catalyst was dried at 333 K under vacuum in a rotary evaporator and the temperature was slowly increased to 373 K. After the second impregnation/drying step, the catalyst was calcined under an air flow at 673K.

2.2 BET Measurements

The surface areas of the support and catalyst were measured by BET using a Micromeritics Tri-Star system. Prior to the measurement, the sample was slowly ramped to 433 K and evacuated for 4 hrs to approximately 6.7 Pa. Results of physisorption measurements are shown in Table 1.

2.3 Hydrogen Chemisorption with Pulse Reoxidation

Hydrogen chemisorption measurements were performed using a Zeton Altamira AMI-200 unit, which incorporates a thermal conductivity detector (TCD). The sample weight was 0.220 g. The catalyst was activated at 623 K for 10 hrs using a flow of pure hydrogen at atmospheric pressure and then cooled under flowing hydrogen to 373 K. The sample was held at 373 K under flowing Ar to prevent physisorption of weakly bound species prior to increasing the temperature slowly to 623 K. At that temperature, the catalyst was held under flowing Ar to desorb the remaining chemisorbed hydrogen so that the TCD signal returned to the baseline. The TPD spectrum was integrated and the number of moles of desorbed hydrogen determined by comparing to the areas of calibrated hydrogen pulses. Prior to experiments, the sample loop was calibrated with pulses of N₂ in helium flow and compared against a calibration line produced from gas tight syringe injections of N₂ under helium flow.

After TPD of H₂, the sample was reoxidized at 623 K by injecting pulses of pure O₂ in helium referenced to helium gas. After oxidation of the cobalt metal clusters, the number of moles of O₂ consumed was determined, and the percent reducibility calculated assuming that the Co⁰ reoxidized to Co₃O₄.

2.4 Temperature Programmed Reduction

The temperature programmed reduction (TPR) profile of the fresh catalyst was obtained using a Zeton Altamira AMI-200 unit (Figure 3). The calcined fresh sample was first heated and purged at 473 K in flowing Ar to remove traces of water. TPR was performed using 30 cc/min

10% H_2 /Ar mixture referenced to Ar. The ramp was 5 K/min from 303 K to 623 K, and the sample was held at 623 K for 30 min.

2.5 *X-ray Diffraction*

The powder diffractogram of the calcined catalyst was recorded using a Philips X'Pert diffractometer. First, short-time scans were taken over the range from 2θ of 20° to 70° to verify the formation of Co_3O_4 after calcination. A long-time scan was then made over the intense peak at 36.8° corresponding to (311) so that estimates of Co_3O_4 cluster size could be assessed from Scherrer line broadening analysis. The scanning step was 0.01, the scan speed was 0.0025 sec^{-1} , and the scan time was 4 sec.

2.6 *Reaction Testing*

The plug flow reactor configuration illustrated in Figure 4 was used and operated at a total pressure of 8.24 MPa. The catalyst (3 g) was diluted in 15 g of glass beads (80-100 mesh). Temperature control was achieved using a three heating-zone furnace. Reactant feed gases (H_2 and CO; H_2 :CO of 2:1), as well as argon balancing gas and nitrogen calibration gas, were introduced into the reactor by Brooks 5850 mass flow controllers, which were calibrated over a wide range of pressure for each of the gases. The solvent, a mixture of 55% hexane and 45% pentane (by volume), was introduced to the reactor using an Altex Model 110A liquid feed pump.

The configuration, with dual hot and cold traps, allowed for switching of the product stream in order to maintain the reactor under normal operation and system total pressure during sample collection. The traps were maintained at 423 K and 273 K, respectively. In addition, a dry ice/acetone trap was brought online as necessary. Since collection of the oil, liquid, and supercritical fluid caused a substantial drop in the pressure of the traps, they were repressurized

to system pressure using argon as the inert gas prior to restoring the traps online. This complicated the gas analysis, since the gas stream from the traps was diluted by the argon used to bring the traps back to operating pressure. To solve this problem and assess CO conversion, inert N₂ gas was used for calibration, as follows:

For the reactor:

$$X_{CO} = (N_{CO, in} - N_{CO, out}) / (N_{CO, in})$$

$$X_{CO} = [(V_{in})(y_{CO, in}) - (V_{out})(y_{CO, out})] / [(V_{in})(y_{CO, in})]$$

In the calculation, N_{CO, out} refers to the moles of CO exiting the reactor, not the traps, which contain diluted gases. Nitrogen is unreactive and, therefore, the molar flow of nitrogen will be the same entering and exiting the reactor. To correct for the argon dilution of the traps, nitrogen is used to calibrate as follows.

For the traps:

$$\text{calibration factor} = C_F = \text{molar flow}_{N_2, in} / \text{molar flow}_{N_2, out}$$

$$C_F = [(V_{in})(y_{N_2, in})] / [(V_{out})(y_{N_2, out})]$$

$$X_{CO} = [(V_{in})(y_{CO, in}) - (V_{out})(y_{CO, out})(C_F)] / [(V_{in})(y_{CO, in})]$$

Note that the molar flow of nitrogen entering the trap is the same as the molar flow of nitrogen exiting the reactor, which is the same as the molar flow of nitrogen entering the reactor. Therefore, all quantities are easily measured. Trap outlet gas flows were measured using a wet test meter. This procedure was implemented to address problems encountered in our earlier work [7].

As another means to calculate the conversion, the CO:N₂ ratio was analyzed both before entering and after reaction, as follows.

$$X_{\text{CO}} = 1 - (\text{N}_2/\text{CO})_{\text{in}}/(\text{N}_2/\text{CO})_{\text{out}}$$

Organic phase condensed liquid products of Fischer-Tropsch synthesis were analyzed by gas chromatography. The analyses of C_5 - C_{30} hydrocarbons were performed on a Hewlett Packard (HP 5890) Gas Chromatograph equipped with a capillary column DB-5 (length: 60m, i.d.: 0.32 mm and film thickness: 0.25 micrometer), He as a carrier gas and FID, and operated with temperature programming from 308-598 K at 4 K/min. The analyses of reactor wax were performed on a Hewlett Packard (HP 5890) Gas Chromatograph equipped with a capillary column (length: 25 m, i.d.: 0.53 mm and film thickness: 0.15 micrometer), He as a carrier gas and FID with temperature programming from 323-663 K at 10 K/min. The product data were handled using Hewlett-Packard Chemstation data analysis software.

3. RESULTS AND DISCUSSION

3.1 *Characterization*

To obtain an estimate of the Co^0 cluster size by adsorption methods, it is necessary to first determine the fraction of the cobalt that is reduced during activation of the catalyst. It is not unusual to use the weight of the catalyst and the percentage of metal to determine the number of metal atoms in the sample, and place this in the denominator for the dispersion calculation. However, the TPR profile in Figure 3 indicates that not all of the cobalt is reduced during activation at 623 K; thus, a pulse reoxidation method was used to quantify the percentage reduction, a method that has been used extensively in characterizing cobalt catalysts for Fischer-Tropsch synthesis [9]. To estimate the cluster size, the following equations are used, and the results for hydrogen TPD/pulse reoxidation are shown in Table 2.

$$\%D = (\text{Number of } \text{Co}^0 \text{ atoms on surface} \times 100)/(\text{total } \text{Co}^0 \text{ atoms})$$

$$\%D = (\text{Number of } \text{Co}^0 \text{ atoms on surface} \times 100)/[(\text{total Co atoms in sample})(\text{fraction reduced})]$$

After calcination of the catalyst, the spinel phase of Co_3O_4 was detected by XRD. To provide another estimate of the cobalt cluster size, the calcined catalyst was scanned by X-ray diffraction. Scherrer line broadening analysis by determination of the full width at half the maximum (FWHM) of the peak at 36.8° was used to estimate the average size of the Co_3O_4 clusters. After reduction, the metal cluster size should be approximately 75% of this size. Therefore, as displayed in Table 2, there is very good agreement between the results based on calculations using chemisorption with reoxidation data and the results from calculations using XRD data.

3.2 *Reaction Testing*

There has been great interest in utilizing the unique physical and transport properties of fluids near their critical pressures and temperatures, as they can be made either more gas-like or liquid-like by pressure tuning. With pressure tuning of the supercritical fluid, solubilities can be enhanced to facilitate the dissolution and removal of wax products from the catalyst, while maintaining gas-like diffusional properties of the reactants CO and H_2 through the elimination of interphase transport limitations on the reaction rate [10]. Figure 2 reveals that the density change from gas-like to liquid-like occurs between 1 and 6 MPa. Most previous studies of Fischer-Tropsch synthesis in the literature have focused on using pure solvents as supercritical fluids [10-12]; therefore, the solvents in these studies were not at the optimum conditions for FTS. For example, n-hexane has been used [11,12], with critical properties $T_C = 506.7 \text{ K}$ and $P_C = 2.97 \text{ MPa}$, but the temperature of the reactor must be operated at approximately 513 K, a temperature which is too high for cobalt-based FTS catalysts and favors production of light products. n-Pentane, with critical properties $T_C = 469.6 \text{ K}$ and $P_C = 3.33 \text{ MPa}$, was also used in previous work, but the density is not high enough to attain optimum solubility properties at the FTS conditions. Propane was also used [13], with the same problem.

Among, if not the first, group to study the pressure tuning affect of the solvent pressure on the transport and solubility properties was Subramaniam [12]. In that work, the pressure of the reactor was changed, while the CO/H₂ ratio of the gas feed and supercritical liquid feeds were kept constant. The partial pressures and the residence times were altered with each change of condition and this makes it difficult to draw solid conclusions.

As an extension to this previous work, efforts were made to overcome the above problems. In this work, a constant overall reactor pressure and constant partial pressures of the feed CO and H₂ gases were maintained. [We refer to nonsupercritical conditions although the inert gases are present at supercritical conditions but at very low density conditions.] Only the partial pressure of the supercritical fluid mixture is changed to tune the transport and solubility properties, while a balancing inert gas (argon) is fed to maintain constant space velocity. Nitrogen is also fed, but it is used as a calibration gas, so that CO conversion can be accurately assessed.

The data in Figure 5 show that when no or inadequate partial pressures of supercritical fluid are present, the catalyst undergoes deactivation, probably by heavy wax buildup. However, when the partial pressure of the supercritical fluid was 5.45 MPa, a higher CO conversion was observed due to the increased solubility of wax products in the supercritical media. The amount of wax products sampled from the collection traps increased dramatically when the partial pressure of the supercritical fluid was increased to 5.45 MPa and then declined to approach the predicted value consistent with wax extraction, as shown in Figure 6.

In practice, the chain growth probability α is used to define the distribution of products, based on Anderson-Schulz-Flory (ASF) polymerization kinetics, as follows:

$$\alpha = R_p / (R_p + R_t)$$

where R_p and R_t are the rates of chain propagation and termination. Therefore, except for deviations from this ideal model, with methane showing much higher termination probabilities yielding higher than predicted values, and C_2 products giving lower than predicted values [14], these kinetics define the distribution of products based on carbon number, n . In contrast with Fe-based FTS catalysts, the distribution of components for cobalt catalysts strongly favors paraffins, although measurable quantities of olefins and traces of oxygenated products are also present, primarily in lower carbon number components. In this study, the products were lumped into the parameter m_n , representing the sum of the components for each carbon number, where:

$$m_n = (1 - \alpha)\alpha^{n-1}$$

Therefore, the slope of the natural log of the mole fraction versus the carbon number yields α as follows:

$$\alpha = \exp[\Delta \ln m_n / \Delta n]$$

Table 3 and Figure 7 show that the resulting α value was very close to the value obtained during CSTR testing, and remained constant during the course of reaction testing with or without supercritical fluid, with values ranging between 0.87 and 0.90%.

Product selectivities were determined in two ways, as commonly reported in the literature. Methane selectivity was defined on a carbon molar basis, not on a product molar basis, and CO_2 from the water-gas-shift reaction was not included. C_5+ selectivity was defined in a similar manner. In contrast, the CO_2 selectivity was based on the rate of water-gas-shift divided by the rate of water-gas-shift plus the FTS rate, again on a carbon molar basis, as follows:

$$S_{CH_4} = r_{CH_4} / r_{FTS} = r_{CH_4} / (r_{CO} - r_{CO_2})$$

$$S_{C_{5+}} = r_{C_{5+}} / r_{FTS} = r_{C_{5+}} / (r_{CO} - r_{CO_2})$$

$$S_{CO_2} = r_{CO_2} / (r_{CO_2} + r_{FTS}) = r_{CO_2} / r_{CO}$$

The C₂+ total olefin selectivity was defined on a carbon molar basis. First, the olefin selectivity for each carbon number was calculated, as follows:

$$S_{O,n} = O/(O+P)_n$$

Then, the C₂+ total olefin selectivity “C₂⁼⁺” was determined by integrating over the distribution up to C₂₀.

$$C_2^{=+} = \sum S_{O,n} \alpha^n n / \sum \alpha^n n$$

Initially, there are not important differences between the catalyst run with or without supercritical fluid because early in the run, the catalyst is relatively free of wax products as it is in the initial stage of deactivation. However, as shown in Table 3 and Figure 8, after the deactivation period and especially under the condition of no supercritical hydrocarbon addition during days 15 - 20, the CO₂ selectivity is approximately 10% and the methane selectivity is greater than 15%. This is the most important time to observe the differences between supercritical and non-supercritical conditions, at the point where the catalyst has deactivated by wax buildup. Clearly, after switching to the supercritical fluid partial pressure of 5.45 MPa, important benefits in product selectivity occurred, with notable decreases in the selectivities of both CO₂ and methane.

CO₂ is produced by the water-gas-shift reaction: H₂O + CO ⇌ CO₂ + H₂. Yokota et al. [15] attributed the decrease in CO₂ production over an iron-based catalyst to the improved extraction and transport of water by the supercritical fluid. This implies that the residence time

of the H_2O relative to the reactants H_2 and CO in the reactor was shortened and this leads to a lower production rate of CO_2 . Our results are consistent with this explanation.

The methane selectivity is sensitive to changes in the process parameters. Increasing temperature, decreasing the pressure, increasing the $\text{H}_2:\text{CO}$, and changing conversion all may result in an increase in methane fraction for cobalt catalysts [14,16,17]. In this work, we attempted to maintain constant all parameters in our control in order to make comparisons under supercritical and nonsupercritical conditions. After deactivation of the catalyst by wax buildup, during days 15-20 under nonsupercritical conditions, the methane selectivity is high (greater than 15%). However, when the 5.45 MPa of the SCF is added, the methane selectivity decreases while the conversion increases. Therefore, one could assume that the increased availability of active sites after extraction of long chain wax from the pores resulting in increased conversion could decrease the methane selectivity. Another explanation is that the observed decreased methane selectivity is the result of better heat distribution in the reactor. That is, under supercritical conditions, localized hotspots in the reactor are avoided [18] due to the better heat capacities of the SCF, resulting in lower methane selectivities. In that case, one would also expect an increase of the chain growth parameter α . However, in Table 3, very little, if any, change in α is observed with or without addition of supercritical fluid. Another explanation is that mass transfer limitations are decreased with addition of the SCF due to the improved extraction of the FTS products from the catalyst. The slow transport of heavy wax products from the catalyst contribute to the deactivation of the catalyst and may increase the mass-transfer limitations when no SCF is present. Therefore, this could also explain the increase of methane selectivity with time onstream, since it is well known that mass transport limitations can result in an increase in the hydrogen partial pressure with increasing distance into the particle and this

leads to enhanced production of the thermodynamically favored product methane [19]. When a high enough density of SCF is achieved (5.45 MPa) and solubilization of the wax occurs, resulting in its extraction, it is possible that the mass transfer barrier is decreased, resulting in the decreased methane selectivity.

That wax extraction occurred is also evident when one considers the selectivity of olefins to paraffins with increasing carbon number. These are reported in Table 4 for both conditions - with or without SCF, and with changes in the SCF partial pressure. There is currently a debate in the literature as to the cause of the decrease in olefin content with higher carbon number for FTS. One is the higher solubility of higher carbon number product α -olefins in the liquid phase, resulting in increased residence times which lead to their increased conversion to paraffins. Henry's law constants, which indicate the fugacity (in many cases, partial pressure) of a component in the gas phase divided by the concentration of the solute gas in the liquid phase, have been observed for paraffins to decrease exponentially with carbon number, indicating higher solubility with carbon number [14]. Therefore, several authors [e.g., 14] have advanced the view that the greater solubility of larger hydrocarbons result in increased residence times and therefore, higher rates of readsorption.

However, a different explanation has been offered [20-24]. The decrease in olefin content with carbon number in this view is due to the decrease in the diffusivities of longer chain hydrocarbons, which would lengthen their time in the catalyst pores. This has been coined "diffusion enhanced α -olefin readsorption."

The results presented here show that with the addition of SCF, the paraffin content is much lower with increasing carbon number than without SCF. Therefore, the diffusivities of hydrocarbons may be much higher in the presence of the supercritical fluid. This could result in

lower residence times in the pores, and therefore, decreased probability for readsorption.

Certainly, this is a possible explanation for the results. However, a more likely explanation is based on a VLE study [25]. Based on a reaction scheme which took into account reversibility of both olefin hydrogenation and adsorption and derived from material balances, it was demonstrated that the residence time of each carbon number was inversely related to the saturated vapor pressure. Moreover, the olefin to paraffin ratio was inversely related to the residence time. Therefore, the results here may be explained in terms of this model. When no SCF is present, $O/(O+P)$ decreases with carbon number due to the higher residence times of the higher carbon number intermediates resulting from their lower saturation vapor pressures. With addition of SCF, extraction results in removal of the bulk liquid filling the catalyst pores, which results in a decrease of the residence time of intermediates and an increase in $O/(O+P)$ as a function of carbon number relative to the nonsupercritical condition, as shown in Figures 8 and 9, and Table 4.

The research may also lead to other developments. For example, reaction intermediates could potentially be added to the supercritical fluid in order to achieve incorporation into the wax products. For example, Fujimoto's group [26] has extended the idea to explore the addition of middle α -olefins to promote wax selectivities. Also, our group has added ^{14}C labeled α -olefin compounds to the supercritical fluid in order to test the merits of α -olefin reincorporation [27].

D. CONCLUSIONS

The anticipated benefits of running FTS in a supercritical fixed bed reactor are clear. In comparison with gas phase fixed bed processes, using pressure tuned supercritical media, in this case a C_5/C_6 mixture, the condensation of high molecular weight hydrocarbons leading to catalyst deactivation was avoided. In contrast to conventional slurry phase processes, which

suffer from catalyst attrition, whereby the catalyst fines eventually breakdown to the point at which they can channel through the filter, running FTS under the supercritical media avoids this problem. With the increase in conversion due to greater accessibility to active sites after wax extraction, additional benefits included decreased methane and carbon dioxide selectivities. The decreased paraffin/(olefin + paraffin) selectivities with increasing carbon number was in line with extraction of the hydrocarbon from the pore. Two possibilities are considered. Faster diffusion rates of wax products may result in lower residence times in the pores, and therefore, decreased probability for readsorption and reaction to the hydrogenated product. A more probable explanation is that the residence times of intermediate olefins, which are inversely related to their saturation vapor pressures, are decreased due to removal of the liquid phase during extraction.

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Table 1			
Results of BET Surface Area Measurements			
Catalyst Description	Calcination T (K)	Measured BET SA (m ₂ /g)	Measured Ave. Pore Rad (nm)
Condea Vista γ -Al ₂ O ₃ Catalox SBa-150	623K	149	5.4
25% Co/ γ -al ₂ O ₃ Catalox Sba-150 Slurry	623K	89	4.8

Table 2										
Results of H ₂ Chemisorption by TPD of H ₂ and Pulse Reoxidation for Co/Al ₂ O ₃ Catalysts Compared with Results from XRD by Scherrer Line Broadening Analysis										
H ₂ TPD/Pulse Reoxidation										
Catalyst Description	BET SA m ₂ /g	Red T (K)	μmol H ₂ Desorbed per g	Uncorr % Disp	Uncorr Diam (nm)	μmol O ₂ Uptake per g	% Red	Corr % Disp	Corr Co ^o Diam (nm)	Co ₃ O ₄ Diam (nm) XRD
25%Co/Al ₂ O ₃	89	623	77.7	3.7	28.2	1174	42	8.7	11.8	13.7

Table 3						
Product Selectivities at Different Conditions						
			Average Selectivities			
TOS (days)	Condition	Final CO Conv	CO ₂	CH ₄	C ₅ +	Final α
0 - 3	No SCF	45.3%	2.1%	8.3%	89.7%	0.88
3 - 5	2.34 MPa SCF	41.9%	4.1%	9.7%	89.3%	0.90
5 - 7	3.90 MPa SCF	37.9%	5.5%	11.3%	87.4%	0.90
7 - 9	5.45 MPa SCF	41.7%	4.7%	10.7%	88.4%	0.87
9 - 11	3.90 MPa SCF	35.9%	5.7%	12.1%	87.1%	0.89
11 - 12	5.45 MPa SCF	41.8%	5.8%	12.1%	86.8%	0.90
12 - 15	2.34 MPa SCF	35.9%	7.2%	13.7%	85.0%	0.88
15 - 20	No SCF	18.9%	10.3%	16.2%	78.9%	0.88
20 - 22	5.45 MPa SCF	40.6%	4.7%	10.4%	88.9%	0.86
23 - 24	5.45 MPa SCF	42.0%	4.2%	10.5%	88.8%	0.88
24 - 25	5.45 MPa SCF	40.8%	4.3%	10.4%	89.0%	0.87
26 - 27	5.45 MPa SCF	41.6%	3.7%	9.9%	89.6%	0.88
28 - 29	5.45 MPa SCF	41.2%	4.3%	10.4%	89.0%	0.87
42 - 26	No SCF	21.3%	4.8%	18.3%	76.0%	---
46 - 53	5.45 MPa SCF	27.9%	2.2%	11.9%	87.2%	—

Table 4									
Olefin Selectivities as a Function of Supercritical Fluid Partial Pressure									
	O/O + P								
P _{SCF} (MPa)	No SCF	2.34	3.90	5.45	3.90	5.45	2.34	No SCF	5.45
TOS (days)	0-3	3-5	5-7	7-9	9-11	11-12	12-15	15-20	20-29
Carbon No.									
2	0.20	0.20	0.16	0.14	0.18	0.13	0.20	0.20	0.11
3	0.70	0.72	0.73	0.71	0.71	0.70	0.73	0.70	0.71
4	---	0.65	0.64	0.67	0.60	0.69	0.61	0.60	0.61
5	---	---	---	---	---	---	---	---	---
6	0.54	---	---	---	---	---	---	---	---
7	0.51	0.49	0.49	0.44	0.44	0.41	0.46	0.55	0.45
8	0.46	0.55	0.59	0.58	0.58	0.58	0.55	0.53	0.58
9	0.40	0.56	0.63	0.62	0.61	0.62	0.61	0.49	0.60
10	0.40	0.47	0.55	0.55	0.60	0.56	0.50	0.44	0.55
11	0.34	0.42	0.50	0.54	0.48	0.53	0.41	0.38	0.54
12	0.29	0.36	0.46	0.52	0.44	0.51	0.36	0.32	0.52
13	0.24	0.30	0.43	0.50	0.40	0.53	0.31	0.25	0.51
14	0.20	0.25	0.38	0.48	0.35	0.56	0.26	0.20	0.48
15	0.17	0.21	0.34	0.45	0.30	0.59	0.21	0.16	0.46
16	0.14	0.16	0.28	0.43	0.26	0.41	0.17	0.13	0.43
17	0.12	0.15	0.25	0.41	0.21	0.39	0.14	0.12	0.42
18	0.10	0.08	0.23	0.37	0.18	0.36	0.13	0.10	0.39
19	0.09	0.07	0.21	0.36	0.15	0.33	0.10	0.09	0.36
20	0.07	0.05	0.16	0.31	0.12	0.32	0.06	0.08	0.35

Figure 1. Critical temperature of pentane and hexane mixture with increasing hexane percentage.

Figure 2: Density versus pressure of the mixture of 55% hexane and 45% pentane.

Figure 3: TPR profile of the 25%Co/Al₂O₃ catalyst prepared by the slurry phase impregnation method.

Figure 4: Flow diagram of the supercritical FT reactor system.

Figure 5: CO conversion vs time-on-stream on a 25%Co/γ-Al₂O₃ slurry phase impregnation catalyst in a fixed-bed reactor with varying partial pressure of SCF.

Figure 6: (top) Wax collection during each sampling period. Note that wax collected is on a wet basis and contained solvent. (bottom) Predicted C₁₁+ based on the extent of CO conversion.

Figure 7: Wax product distribution under nonsupercritical conditions.

Figure 8: Product selectivities versus time-on-stream.

Figure 9: Olefin selectivity as a function of carbon number for supercritical and gas phase FTS.

D. Assessment of Internal Diffusion Limitation on Fischer-Tropsch Product

Distribution

Abstract

A reactor is modeled for ideal vapor-liquid equilibrium conditions and is operated with a single- α catalyst. Under steady-state conditions, the relative concentration of hydrocarbon product in the catalyst pores decreases with increasing carbon number until about C_{20} . It is deduced that the two- α product distribution in Fischer-Tropsch reactions is not due to the effect of product diffusion limitations of the heavier products.

Introduction

It has been generally agreed that a simple polymerization mechanism can be used to describe the distribution of Fischer-Tropsch (FT) synthesis product. On a catalyst surface, a FT chain growth intermediate can either propagate to form another intermediate of one higher carbon number or terminate to produce an oxygenate, paraffin, or olefin of the same carbon number. The path of termination to olefin is reversible due to the well documented feature of olefin adsorption/desorption and hydrogenation/dehydrogenation (1). The propagation probability (α value) of each surface intermediate has been assumed to be a constant that is independent of carbon number (single α distribution), and this produces the so-called Anderson-Schulz-Flory distribution (ASF). The experimental observation of a two, or more, α distributions, or more precisely an α value that is an increasing function of carbon number, results in different models being proposed to explain this phenomenon. One of the prevailing ones is the diffusion enhanced olefin readsorption model which describes the effect of diffusion limited removal of olefins from catalyst pores (2-4). According to this model, since olefin termination is reversible and its diffusivity decreases rapidly with increasing carbon number, the higher olefins should have longer residence times and higher fugacities in the pores of the

catalyst pellet. As a result, accumulation of these heavy hydrocarbons in the catalyst pores leads to olefin diffusion limitation, which enhances olefin readsorption and leads to the observation of a two α product observation.

In other words, this model relies on increased hydrocarbon concentration with carbon number in catalyst pores which might result from internal diffusion limitation. The pore concentration of a hydrocarbon component relative to its surface concentration (relative concentration) must increase with carbon number to contribute to the two α distribution. It is obvious that in the presence of internal diffusion limitation of hydrocarbon products, the concentration of a hydrocarbon component in the catalyst pores must be significantly higher than that at the catalyst surface. However, the hydrocarbon concentration profile in the catalyst pores was not demonstrated and the existence of internal diffusion limitation of hydrocarbons was not verified by a theoretical approach, by simulation or by experimental data. Also, this model does not consider the existence of vapor-liquid equilibrium of hydrocarbon products in a typical low temperature Fischer-Tropsch reactor.

It is therefore of interest to examine the conditions under which product diffusion limitation might exist in catalyst pores and how reaction conditions affect this diffusion limitation. The FT reaction is simulated in a CSTR slurry reactor whose modeling and simulation has been reported previously (5).

Fischer-Tropsch Reaction

The products of the Fischer-Tropsch reaction consist primarily of a spectrum of paraffins and olefins. Paraffins and olefins of the same carbon number have essentially the same physical properties, such as vapor pressure and diffusivity. Therefore, for simplicity of discussion, it can be assumed that CO and H₂ react stoichiometrically to produce exclusively paraffins (non-reactive) and water following a single α ASF distribution. This assumption is reasonable and the

result is sufficiently informative since the objective of this work is simply to examine the possible existence of internal diffusion limitation of hydrocarbon products. Nonetheless, the olefin reactivity has also been considered and will be discussed later in this manuscript as it applies to the above assumption. Thus, for all non-reactive paraffin products, the FT reaction can be written as

($\bar{n}$ is average carbon number) and the hydrogen reaction rate is assumed to follow

$$(-r_H) = k_H C_H \quad 2)$$

Again, this simple rate expression is for ease of discussion. Adoption of a more complicated or simpler rate expressions does not change the general conclusions of this work. In addition, Equation (1) is for reactions typical of cobalt catalyst where CO₂ production is negligible. For reactions typical of iron catalysts, the water gas shift reaction should be considered and the total reaction equation has to be rewritten. The importance of addressing this difference is due to the formation of hydrogen in the latter case, whose concentration is required in this analysis for the liquid phase. However, the analysis method will be the same as described in this manuscript and we have shown that the general conclusion of this work will not change for the iron catalyst.

The only assumption that is required to develop the following equations is that the FTS products follow a single alpha distribution and that vapor-liquid equilibria is established. Since 1 mole of hydrocarbon is formed for each (2n + 1) moles of hydrogen converted, the hydrocarbon generation can be described as:

$$r_{HC} = 1 / (2n + 1) r_H = (1 - \alpha) / (3 - \alpha) \quad 3)$$

Since the product hydrocarbons follow a single alpha distribution, the molar fraction of a product of carbon number i present in the product mixture is $(1 - \alpha) \alpha^{i-1}$. The rate, r_i , of formation of the product with carbon number i is:

$$r_i = (1 - \alpha) \alpha^{i-1} r_{HC} = \frac{(1 - \alpha)^2}{(3 - \alpha)} \alpha^{i-1} k_H C_H = k_i C_H \quad 4)$$

where

$$k_i = \frac{(1 - \alpha)^2}{(3 - \alpha)} \alpha^{i-1} k_H \quad 5)$$

is the production rate constant of hydrocarbon component i and is a function of α .

Mass Transfer in Catalyst Pores

Assuming that the catalyst pellet is spherical, the steady state material balance of hydrogen and of a hydrocarbon component i in catalyst pores can be described by equations 6 and 7, respectively:

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dC_H}{dr} \right) = \frac{k_H}{D_H} C_H \quad 6)$$

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dC_i}{dr} \right) = - \frac{k_i}{D_i} C_H \quad 7)$$

and boundary conditions are:

$$r = R_p, \quad C_H = C_{H,s} \quad \text{and} \quad C_i = C_{i,s}$$

$$r = 0, \quad \frac{dC_H}{dr} = 0 \quad \text{and} \quad \frac{dC_i}{dr} = 0$$

where C_H, C_i : concentrations of hydrogen and hydrocarbon i in the catalyst pores, respectively;
 $C_{H,s}, C_{i,s}$: concentrations of hydrogen and hydrocarbon i at the catalyst surface, respectively; $D_H,$
 D_i : effective diffusivities of hydrogen and hydrocarbon i, respectively; k_H, k_i : rate constants of
hydrogen consumption and hydrocarbon i production, respectively; and, R_p : radius of the
catalyst particle.

The concentration profiles of hydrogen and a hydrocarbon component i in the catalyst
pores thus can be obtained by solving the above equations analytically, as shown in Equations
(8) and (9). [Note that readsorption need not be considered here since this is only a material
balance equation].

$$\frac{C_H}{C_{H,s}} = \left(\frac{R_p}{r} \right) \frac{\sinh(\phi_H r / R_p)}{\sinh(\phi_H)} \quad 8)$$

$$\frac{C_i}{C_{i,s}} = 1 + \left(\frac{\phi_i}{\phi_H} \right)^2 \left(1 - \frac{C_H}{C_{H,s}} \right) \quad 9)$$

where

$$\phi_H = R_p \sqrt{\frac{k_H}{D_H}} \quad 10)$$

$$\phi_i = R_p \sqrt{\frac{k_i C_{H,s}}{D_i C_{i,s}}} \quad 11)$$

ϕ_H and ϕ_i are Thiele moduli characterizing reaction-diffusion process of hydrogen and generation-diffusion process of hydrocarbon component i in the catalyst pores, respectively; and, ϕ_i is a measure of the relative scale of reaction and diffusion rates in the catalyst pores. For large ϕ_i , the diffusion rate is smaller than the reaction rate and hence the effect of internal diffusion on the total observed rate is significant, or even controlling. For the same catalyst pellet, the effective diffusivity D_i is calculated using two correlations:

$$D_n = D_0 e^{-0.3n} \quad 12)$$

and

$$D_n = D_0 n^{-0.6} \quad 13)$$

where D_0 is a constant and n is the carbon number. Equation (12), which predicts a strong dependence of diffusivity on carbon number was used in reference 2 . However, it has been argued that the dependence is actually much weaker than required by Equation (12) and that the formula shown in Equation (13) should be used (6).

It can be seen from Equation (9) that the relative concentration of component i depends on its Thiele modulus and hydrogen concentration distribution in the catalyst pores. Clearly, the higher the value of ϕ_i , the higher the relative concentration $C_i/C_{i,s}$, and therefore the higher the reversible rate when it is considered. Also it is seen that the surface concentration is important in determining the Thiele modulus and thus pore concentration. When vapor-liquid separation is considered, the surface concentration of each component at the catalyst particle boundary is the

same as its bulk liquid concentration in a CSTR, ignoring external diffusion. The latter can be obtained with model simulation (5).

Reactor Modeling and Simulation

The CSTR modeling and simulation for FT synthesis has been reported in detail elsewhere (5). Briefly, the CSTR is assumed to operate at constant temperature and pressure without catalyst deactivation. Reaction product is separated into liquid and vapor, which are assumed to be in thermodynamic equilibrium following Raoult's law under the reaction conditions. For simplicity of simulation, it is further assumed that hydrocarbon products are linear paraffins from C_1 to C_{100} and that they follow single α ASF distribution. The vapor pressure of each paraffin is calculated using Equation (14), obtained from the literature (7). In this equation, the unit for vapor pressure is atm and the unit for temperature is Kelvin.

$$P_i^s = 176.0452 \exp \left(- 427.218 \left(\frac{1}{T} - 1.029807 \times 10^{-3} \right) (i - 1) \right) \quad 14)$$

For this section, CO and H_2O are assumed to be insoluble in the reactor liquid. For a cobalt catalyst, the ratio of H_2/CO in the feed is about 2:1, about the utilization ratio, and this will be the ratio in the reactor. Therefore, we can select either CO or H_2 as dependent variable in the kinetic expression. For the iron catalyst, the water-gas-shift activity provides a source of hydrogen. However, equation (2) is known to be applicable for kinetic description for the iron catalyst. Thus, in this manuscript, hydrogen is selected for the iron catalyst as well. H_2 is considered soluble in hydrocarbon liquid since it is critical in evaluating the product Thiele modulus as reflected in Equation (9). The hydrogen solubility in the reactor liquid is calculated based on the following formula for Henry's law constant (8)

$$H = 2.291 \times 10^7 \exp(-1.2326 + 583 / T) \quad 15)$$

in which H is in kPa cm³/mol and T in Kelvin.

Three conditions are selected to illustrate the hydrocarbon product distribution in catalyst pores. A pressure of 20 atm and CO conversion of 60% are common for the three conditions considered while condition A consists of temperature 230 °C and an α value 0.85, condition B consists of temperature 270 °C and an α value 0.65, and condition C consists of temperature 310 °C and an α value 0.85.

Results And Discussion

Diffusion Limitation. In any heterogeneous catalytic reaction, the so-called rate determining step is the one whose mass transfer capability is the smallest one of the series steps and thus represents the rate of the overall reaction process. When a step becomes the determining step, it means that its mass transfer capability cannot meet the demand of its upstream steps or that required by its downstream steps. This concept applies to a process consisting of a series of steps since the mass transfer reflux is the same for each step under steady state. For Fischer-Tropsch synthesis products, it is true that the heavier the hydrocarbon, the more difficulty its diffusion in catalyst pores because the diffusivity decreases significantly with carbon number. This fact has been extended and is considered to be the major assumption that leads to the conclusion that the higher hydrocarbon product causes severer transport limitation (2-4). The above argument implies that the mass transfer reflux is the same for each hydrocarbon product. This is not the case in FT reactions in which the higher the carbon number, the lower its production rate, and therefore it imposes less demand on the mass transfer capability by diffusion in catalyst pores. According to the correlation in Equation (11), the hydrocarbon diffusivity decreases with carbon number at the rate of $D_{n+1}/D_n = 0.74$. The

magnitude of this rate is comparable with a typical single α value in FT synthesis in which the hydrocarbon production rate decreases by the factor of $r_{n+1}/r_n = \alpha$. Therefore, it is not necessarily more difficult for a heavier component, compared to a lighter one, to be transported out of the catalyst pores. It is true that the rate of diffusion of heavier material is smaller than for lighter material. But in terms of diffusion limitation, it is not necessarily more difficult. For example, while the heavier material has a lower diffusion rate, it also has lower diffusion duty since smaller amounts are generated. More importantly, the heavier material has a higher solubility in the liquid phase, and this contributes to developing a more uniform concentration distribution in the catalyst pores (Figure 4). Therefore, the diffusion limitation of the heavier material may be lower than for the lighter one. It should be recognized that the concentration profile in the catalyst pores, rather than diffusivity, is being used to judge the impact of diffusion limitation. For instance, when the α value is less than 0.74, the concentration gradient required to transfer a hydrocarbon product out of catalyst pores actually decreases with increasing carbon number. In general, the presence of diffusion limitation should be judged using the Thiele modulus, or more precisely, the concentration profile in the catalyst pores, rather than simply looking at the diffusivity even though it is an important component in the definition of Thiele modulus.

Single Phase Product. As shown in Equation (11), the Thiele modulus of a hydrocarbon product depends on its concentration at the catalyst surface, in addition to its generation rate constant and its diffusivity. Due to the complexity of the Fischer-Tropsch reaction, many researchers assume that the products are in a single phase, either vapor or liquid phase, when developing their models. With this assumption, the product concentration at the catalyst surface should also follow a single α distribution under steady state, if the FT reaction follows single α chemistry. Thus, the Thiele modulus of a hydrocarbon product is inversely proportional to the square root of its effective diffusivity and must increase with carbon number. As a result,

internal diffusion limitations always have to occur and, starting from some carbon number, then increase with increasing carbon number, as shown in Figure 1. This appears to be why the two α product distribution was attributed exclusively to the effect of internal diffusion limitation of hydrocarbon products (2).

The assumption of single phase product distribution is an oversimplification of the problem since this ignores the effect of vapor-liquid equilibrium in a typical FT reactor. It has been argued that, in the presence of vapor-liquid equilibrium, the chemical potential of a given species is identical in both liquid and vapor phases and thus the rate of a chemical reaction cannot depend on the identity of the phase and the hydrocarbon solubility in the liquid phase (2, 9). The scope of thermodynamics and kinetics needs to be considered. As a thermodynamic intensive property, chemical potential defines the processing direction and the processing limit, but does not define the processing rate. According to the standard definition, the chemical potential of a species in a phase is the sum of its standard free energy and the contribution of such species in its current mixture, and the later is a function of its composition. The fundamental difference between a vapor only and a vapor/liquid system lies in the fact that the standard free energy of a species in the liquid phase is different from that in the vapor phase; the difference can be quantified as a function of its vapor pressure. For an idea vapor/liquid system in equilibrium, the relationship between vapor and liquid can be described using Raoult's law. The concentration of a species in the liquid phase depends not only on its vapor composition but also its vapor pressure under the process conditions. For two species whose chemical potentials are identical in both vapor and liquid phases, the component having a lower concentration in the vapor phase may have a higher concentration in the liquid phase, simply because it has lower vapor pressure. In a Fischer-Tropsch reactor, due to the effect of vapor liquid separation (when it exists), the hydrocarbon concentration in the liquid phase increases with increasing carbon

number, and is in contrast to the opposite trend in vapor phase (5). As a result, the product concentration profile in the catalyst pores and the trend of its diffusion limitation are totally different in the vapor and vapor/liquid systems.

On the other hand, reaction kinetics, or simply reaction rate, has to be used to evaluate catalyst performance. Without question, the catalyst performance depends on the phase in which the catalyst resides because the reactant concentration varies in the different phases, even though these phases are in equilibrium and the chemical potential of the reactant is identical in each phase. Any impact resulting from the others phases has to go through the phase the catalyst is in contact with and can therefore affect the catalysts performance indirectly. Although an active site on the catalyst surface does not depend on whether the reactant molecule comes from the liquid or vapor phase, it does depend on how many molecules surround it. According to collision theory, the nature of chemical reactions is a measure of effective collisions between reactant molecules. A higher population of reactant molecules will lead to a higher probability for effective collisions and thus higher reaction rates. Very often, the assumption of a vapor phase operation gives rise to incorrect conclusions when there is vapor-liquid separation and the catalyst is in the liquid phase, especially when the reaction rate is of concern.

Light Hydrocarbon Products (C_{20}). It is a general observation that for light hydrocarbons (C_{20}), most of the products are removed from the reactor through the vapor phase. This observation has been supported by VLE simulation for a CSTR slurry reactor in which the hydrocarbon product follows a single α distribution in vapor phase (5). Within this range, the ratio of the Thiele moduli of two successive hydrocarbons becomes the competition between their relative volatility and their diffusivity, as shown in the following equation:

$$\left(\frac{\phi_{i+1}}{\phi_i} \right)^2 = \frac{P_{i+1}^s}{P_i^s} \bigg/ \frac{D_{i+1}}{D_i} \quad 16)$$

A magnitude of ϕ_{i+1}/ϕ_i greater than unity indicates that the diffusion limitation increases with increasing carbon number, while a value less than unity points to the opposite direction.

Although disagreement remains about the relationship between hydrocarbon diffusivity and carbon number, Equation (12) is used in this work since it shows the strongest dependency on carbon number. Substituting Equations (12) and (14) into Equation (16) shows that ϕ_{i+1}/ϕ_i is greater than unity only when the temperature is higher than 304 °C, which approaches the typical high temperature Fischer-Tropsch synthesis with its gas phase operation. At lower temperatures or if diffusivity follows Equation (13), there is no opportunity for ϕ_{i+1}/ϕ_i to be greater than unity.

VLE Effect. In the presence of vapor-liquid separation, the product concentration at the catalyst surface, $C_{i,s}$ as in Equation (11), is the same as the bulk liquid concentration, and can be obtained by VLE simulation since the impact of vapor-liquid separation has to be considered. Figure 2 shows the liquid composition in a CSTR slurry reactor under conditions simulated in this work. Conditions A and C chosen for example calculation represent normal operating conditions under steady state when both vapor and liquid are generated and Condition B represents an unsteady state condition. Under these conditions, the hydrocarbon concentration increases with carbon number to a maximum and then decreases. Condition B is an unsteady state operation in which the liquid product does not accumulate because of the low alpha value. This type of operation will lead to drying out of a CSTR reactor over time due to excessive evaporation of the starting solvent and the inability of the low alpha catalyst to generate the liquid products faster than they are removed in the vapor phase.

Applying the liquid concentration shown in Figure 2 to Equation (11), the Thiele modulus of each hydrocarbon component can be calculated. Figure 3 shows the Thiele modulus of each hydrocarbon component relative to that of C_2 which is selected as reference because it is the lowest boiling molecule of interest. Under Condition C, when the reaction temperature is 310 °C, ϕ_i/ϕ_2 increases with increasing carbon number indicating the direction of severer diffusion limitation. Although this temperature is typical of a low α and vapor phase operation, its impact on two α product distribution should not be ruled out, no matter how slowly ϕ_i/ϕ_2 changes with carbon number. When the operating temperature is lower than 300 °C, ϕ_i/ϕ_2 decreases with increasing carbon number up to about C_{20} , and then increases. This value becomes higher than unity only when the carbon number is higher than 30. This phenomenon indicates that the hydrocarbon diffusion in catalyst pores does not become more and more difficult as expected with the assumption of a single phase product. In fact, it is just the opposite; it becomes relatively easier with increasing carbon number for the lower carbon number components. When there is no diffusion limitation for C_2 , there is also no diffusion limitation for higher hydrocarbons until at least carbon number C_{30} . Even if the removal of C_2 is diffusion limited, it is not necessary for higher hydrocarbons to have diffusion limitation because the effect of internal diffusion become less and less significant with increasing carbon number up to about C_{30} . This eliminates the cornerstone assumption of any model that requires stronger product diffusion limitation with increasing carbon number.

Of course, for carbon numbers higher than 30, there might be diffusion limitation starting with some hydrocarbon component. These heavy hydrocarbons tend to accumulate in catalyst pores until they have enough driving force to transfer the products out of the pores. However, this issue should not affect the total FT product distribution since olefins of these high carbon numbers typically are not produced from the catalyst surface. The accumulation of heavy

hydrocarbons in catalyst pores may lead to internal diffusion limitation of reactants and catalyst deactivation, but does not produce a two α distribution. It therefore can be concluded that, in the presence of VLE, the internal diffusion limitation of products does not necessarily exist and, even if it does exist, should not be responsible for the two alpha product distribution in FT synthesis.

Figure 4 shows the relative concentration profile of several hydrocarbon components in the catalyst pores under Condition A and $\phi_H=1.0$ (catalyst efficiency 94%). For carbon numbers lower than 20, the higher the carbon number, the lower its relative concentration in the catalyst pores, indicating that the effect of internal diffusion is less significant with increasing carbon number. This is, in fact, the same result as has been discussed above when the analysis is made in terms of the Thiele modulus.

Figure 5, plotted with the volumetrically average concentration of C_2 vs. the hydrogen Thiele modulus, shows that the effect of internal diffusion of C_2 increases with ϕ_H . When there is no internal diffusion limitation of hydrogen, e.g., $\phi_H < 0.2$, there is also no internal diffusion limitation of C_2 . Of course there is also no diffusion limitation for other hydrocarbons up to about C_{35} as has been discussed previously (Figures 3 and 4). The same conclusion can be drawn simply by examining Equation (9) directly. It also can be seen from Figure 5 that, with the same catalyst efficiency (same ϕ_H), the significance of product diffusion is affected by reaction conditions. When the catalyst efficiency is only 80% ($\phi_H = 2.0$), the average concentration of C_2 in the catalyst pores can be less than 1% higher than its surface concentration under Condition B, while it can be 37% higher under Condition A.

Olefin Reincorporation. The major assumption of the above discussion is that all of the products are non-reactive paraffins. This assumption significantly simplifies the development of reaction and mass transfer models. Also, comparison of the concentration profile of

hydrocarbon products in the catalyst pores becomes straightforward. In practice, however, olefins are also produced and these have been confirmed experimentally to be reactive. In other words, the pathway for termination to olefins is reversible. As a supplement to this work, the following sections present the hydrocarbon concentration profile in the catalyst pores when olefin reincorporation is also taken into account.

The chemical potential of a species is its partial molar Gibb's free energy in a mixture. It is the contribution of such species to the total free energy of the mixture. The chemical potential of species i in an ideal gas mixture (μ_i^v) and in an ideal solution (μ_i^L) can be described using Equations (17) and (18), respectively.

$$\mu_i^v = G_i^v + RT \ln y_i \quad (17)$$

$$\mu_i^L = G_i^L + RT \ln x_i \quad (18)$$

In these two equations, G_i^v and G_i^L are Gibb's free energies of pure gas and pure liquid of species i at the mixture temperature and pressure, respectively. y_i and x_i are molar fractions of species i in the gas phase and in the liquid phase, respectively. For a vapor-liquid system in equilibrium, the chemical potential of a species is identical in both phases, i.e., $\mu_i^v = \mu_i^L$. Thus, the following two equations can be derived.

$$RT \ln \frac{y_i}{x_i} = G_i^L - G_i^v = RT \ln \frac{P_i^s}{P} \quad (19)$$

$$y_i P = x_i P_i^s \quad (20)$$

Equation 15 is Raoult's law and the detailed derivation is available, such as the text by Smith and Van Ness (10).

In Fischer-Tropsch synthesis, the reversible reactions of olefins are considered when modeling the product distribution. The absolute reversible rate of an olefin species depends on its concentration (or activity if considering real solution) in the phase where reactions take place. Therefore, it is important to know how the olefin concentration changes with carbon number in different phases, even though these phases are in equilibrium. If the reaction takes place in gas phase, in which the hydrocarbon concentration decreases with increasing carbon number, it is obvious that the reversible reaction rate of olefin has to follow the same trend, assuming that the rate constant does not depend on carbon number. When there is vapor-liquid separation and the reactions take place in the liquid phase, liquid phase composition should be used to characterize the reaction rates. For two components with successive carbon number in the system, we have

$$\frac{x_{i+1}}{x_1} = \frac{y_{i+1}}{y_i} \frac{P_i^s}{P_{i+1}^s} \quad 21)$$

The dependency of hydrocarbon concentration on carbon number in the liquid phase does not necessarily follow the same trend as that in the vapor phase. In a typical low temperature Fischer-Tropsch reaction, the liquid concentration increases with increasing carbon number in the low carbon number range, because the vapor pressure rapidly decreases with increasing carbon number.

Additional assumptions are required since little quantitative data are available for olefin reactions under Fischer-Tropsch synthesis conditions. It is assumed that chain growth on the catalyst surface follows a single α rule. For each chain growth intermediate, the same olefin fraction is generated among the total hydrocarbons of that carbon number before considering the

reversible reaction of olefins. To simplify, it is further assumed that all of the products are olefins. The olefin reaction kinetics to higher hydrocarbons follows $k_r C_i$, in which k_r is the rate constant that is independent of carbon number. Finally, it is also assumed that the primary reaction of CO and H₂ are not affected by the olefin reaction.

Any hydrocarbon component i is generated from CO and H₂, from lighter olefins ranging from carbon 2 to carbon $i-1$, and is decreased by conversion to higher hydrocarbons at a rate of $k_r C_i$. The material balance of component i in the catalyst pores is shown in Equation (22).

$$D_i \frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dC_i}{dr} \right) = -k_i C_H - \sum_{j=2}^{i-1} k_r (1-\alpha) \alpha^{i-j-1} C_j + k_r C_i \quad (22)$$

The analytical solution to Equation (22) is

$$\frac{C_i}{C_{i,s}} = \left(1 - \sum_{j=1}^{i-1} B_{ij} \right) \left(\frac{R_p}{r} \right) \frac{\sinh(\phi_{ir} r / R_p)}{\sinh(\phi_{ir})} + \sum_{j=1}^{i-1} B_{ij} \left(\frac{C_j}{C_{j,s}} \right) \quad (23)$$

where

$$B_{ij} = \frac{1-\alpha}{\alpha} \frac{\phi_{jr}^2}{\phi_{ir}^2 - \phi_{jr}^2} \left(\frac{\phi_i^2}{\phi_j^2} - \sum_{k=j+1}^{i-1} B_{ik} \frac{\phi_k^2}{\phi_j^2} \right) \quad B_{i1} = \frac{\phi_H^2}{\phi_{ir}^2 - \phi_H^2} \left(\frac{\phi_i^2}{\phi_H^2} - \sum_{j=2}^{i-1} B_{ij} \frac{\phi_j^2}{\phi_H^2} \right)$$

$$\phi_i = R_p \sqrt{\frac{k_i}{D_i} \frac{C_{H,s}}{C_{i,s}}}$$

$$\phi_{ir} = R_p \sqrt{\frac{k_{ir}}{D_i}}$$

$$\phi_H = R_p \sqrt{\frac{k_H}{D_H}}$$

These equations are too complicated to allow visual examination on how pore concentrations change with carbon number. Condition A was used to illustrate the product concentration profile with Thiele modulus of H₂ = 2.0, and $k_r/k_H = 0.025$. The latter corresponds

to about 10% of the olefins generated in the primary termination step being reincorporated into growing chains. Figure 6 shows the dependence of the volumetrically average concentration of product in the catalyst pores on the carbon number. When considering the reversible olefin reaction, the relative concentration of light products decreases even more rapidly than the situation of non-reactive paraffin products. It is clear that, with or without considering olefin reaction, the relative concentration of light hydrocarbons (C_{20-}) decreases with increasing carbon number in the catalyst pores, indicating decreasing severity of internal diffusion limitation with increasing carbon number.

To distinguish among the models predicting the impact of diffusion on FTS is a demanding task. On the one hand, diffusion effects that arise after the reactant enters the bulk liquid phase can be defined with certainty by adding isotopically tracers. Once the product becomes a part of the bulk liquid-gas phases that are present external to the catalyst particle, the labeled and unlabeled compounds must become identical with respect to the impact of diffusion on secondary reactions. Such studies are being conducted in our lab. To establish the impact of diffusion on the primary and secondary reactions that occur within the catalyst particle prior to equilibrating with the bulk liquid-gas phases is a demanding task. One approach that has been used is to vary the size of the primary catalyst particle and to show that the experimental data match the values predicted from diffusion models. In principle this would be easy to do in the slurry phase; however, it is likely that catalyst particles small enough to cover the required size range agglomerate in the slurry phase.

One approach that has potential is to use the same catalyst particle under conditions where different amounts of liquid phase are present during the synthesis. At least in theory this is possible using supercritical conditions. Using a cobalt catalyst in a fixed-bed reactor, FTS was conducted using identical conditions except that the inert gas was argon in one case and a

mixture of pentane and hexane in the other (11). Thus, space velocity, partial pressure of reactants and temperature remained constant while the density of the inert diluent was varied. With argon dilution the density was low and at, or near, that of a gas whereas the mixture of pentane and hexane provided a liquid-like density (ca. 80% of the density of a liquid). The conditions were adjusted so that a conversion of CO was established at about 40% when the inert gas was a mixture of pentane and hexane. When argon replaced the hydrocarbon mixture the CO conversion gradually declined during seven days, ending at about 20% conversion. During the period of operating with argon, less non-volatile products were collected in the receiver than was calculated, based on the material balance. When the argon was replaced by the hydrocarbon mixture, the CO conversion increased to the 40% level. In addition, the amount of wax collected the first day of operation with the hydrocarbon mixture exceeded the amount calculated from mass balance. During the next eight days of operation with the hydrocarbon mixture the conversion remained constant and the amount of excess wax that was collected declined each day to approach that calculated for mass balance. However, the alpha value for the wax products was essentially the same whether argon or hydrocarbon mixture was added. Thus, while it appears that diffusion within the catalyst particle materially impacted CO conversion, it did not have a measurable impact upon hydrocarbon carbon number.

A key point of this paper is that one should use the Thiele module, rather than simply diffusivity, to justify diffusion limitation. Diffusivity is only one of the parameters contributing to diffusion limitation. Other factors, such as solubility or catalyst surface concentration, also contribute. This work shows that diffusion limitation is due to the competition between relative diffusivity and relative solubility; under most FT conditions, solubility dominates as in equation (16).

Conclusion

Due to the effect of vapor liquid separation in the Fischer-Tropsch reactor under steady state, the relative concentration of a hydrocarbon product in the catalyst pores decreases with increasing carbon number until about C_{20} . This indicates that, in this carbon number range, the heavier the hydrocarbon, the less severe the internal diffusion limitation. The impact of internal diffusion of a product may become significant only when there is internal diffusion limitation of reactants, and this significance decreases with increasing carbon number. It is thus deduced that the two alpha product distribution in Fischer-Tropsch reactions is not due to the effect of product diffusion limitation, even if it exists under some reaction conditions.

The view advanced here is that diffusion limitation should be based on a concentration profile in the catalyst pores, or Thiele Module, not simply diffusivity. For any species, diffusion limitation is based on a comparison of its generation rate (products) or disappearance rate (reactants) with its diffusion rate, and the latter is a function of its surface composition which depends on vapor-liquid separation.

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Nomenclature

C	molar concentration
D	diffusivity
G	Gibb's free energy
H	vapor liquid equilibrium constant
k	reaction rate constant
$\bar{n}$	average carbon number of hydrocarbon product mixture
P	pressure
P^s	saturated vapor pressure of hydrocarbon
r	reaction or generation rate (with subscription), radial position in a catalyst particle
R	gas constant
R_p	catalyst particle radius
T	temperature
x	liquid phase molar fraction
y	vapor phase molar fraction
α	chain propagation probability on surface, a function of carbon number
ϕ	Thiele Module
μ	chemical potential

subscript

H	hydrogen
HC	hydrocarbon
i	carbon number
r	olefin reaction rate constant
s	surface

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Figure 1 Thiele Modulus of Hydrocarbons with products in single phase

Figure 2 Liquid compositions in CSTR reactor (see reactor modeling and simulation section for definition of conditions of A, B and C).

Figure 3 Thiele Modulus of Hydrocarbons with VLE
and $D_n = D_0 e^{-0.3n}$

Figure 4 Hydrocarbon Concentration Profile in Catalyst Pores at Condition A with $\phi_H = 1.0$ ($\eta_H = 94\%$)

Figure 5 Effect of Hydrogen Thiele Modulus on Average Concentration of C_2 in Catalyst Pores

Figure 6 Average Concentration of Hydrocarbon Products in the Catalyst Pores with Olefin Reincorporation

E. Product Distribution of Fischer-Tropsch Synthesis

Abstract

Fischer-Tropsch product distribution models available in the open literature are discussed. It is concluded that the effect of vapor-liquid separation is the most probable reason for the observation of a two alpha product distribution. A mathematical model has been developed to describe the product distribution, based on the recognition that the termination path to olefin products is reversible. The observed product distribution at the reactor outlet consists of the contributions from the intrinsic chain propagation on the catalyst surface and the effect of olefin reactivity. The reaction product does not follow an Anderson-Schulz-Flory single alpha distribution even on the catalyst surface. The effect of olefin “reincorporation” is significant only for the low carbon number range when there is a high fraction of olefins. In the high carbon number range, alpha appears to be constant because there is a small or no olefin reincorporation effect. An excellent fit between the values predicted by the model and experimental data has been demonstrated.

Introduction

Fischer-Tropsch (FT) synthesis can be conducted in either vapor phase or vapor-liquid reactors depending on the product demand and the catalyst performance. Vapor phase reactors feature high temperature operation ($>300^{\circ}\text{C}$) and low alpha products (e.g., light olefins and gasoline). Alpha is related to the rates of termination and propagation steps, and therefore the average molecular weight of the products. Single alpha product distribution is a common observation with this type of operation. When high alpha products are the goal (e.g., diesel, wax), the synthesis is typically carried out in fixed-bed and slurry bubble column reactors at low temperatures ($<250^{\circ}\text{C}$). In these reactors, products separate into vapor and liquid phases. A two alpha product distribution has been observed in both laboratory and pilot scale tests (1), in

contrast to the so-called Anderson-Schulz-Flory (ASF) single alpha distribution. Several models have been proposed to explain the two alpha observation, including: two active sites responsible for different chain growth pathways (2-4), diffusion enhanced olefin readsorption in catalyst pores (5-9), and the effect of vapor-liquid-equilibrium (VLE) which causes accumulation of heavier products in the reactor and thus enhances olefin reactivity (10-13). An extensive review in this area has recently been made by Van Der Laan and Beenackers (14).

In most FT reactors, when vapor liquid separation is involved, the sample taken is actually not representative of what is produced during the sampling period, unless an impractically long time is taken for the reactor to reach “steady state”. This sampling behavior has been suspected to be responsible for the two alpha product distribution due to VLE of products in the reactor. Recently, we have proved that, without considering the reactivity of olefin products, simple accumulation effect of heavier products by VLE cannot be responsible for the two alpha observation in a slurry reactor under normal operating conditions (15)

It is generally agreed that the reversible olefin termination path is responsible for the two alpha product distribution. Yet, there is still significant uncertainty about how this reversible reaction works. The diffusion enhanced olefin readsorption model attributes the two alpha observation to increasing internal diffusion limitations of the olefin products due to reduced diffusivity with increasing carbon number. However, this model ignores the presence of a liquid phase in which the catalyst resides. Our recent work indicated that the internal diffusion limitation of hydrocarbon products does not necessarily exist in catalyst pores unless there is also an internal diffusion limitation of reactants (16). In addition, due to the effect of vapor-liquid separation of hydrocarbon products in the FT reactor, the severity of diffusion limitation of light hydrocarbons (C_{20} .) actually decreases with increasing carbon number, just opposite to the cornerstone assumption of the diffusion model. Consequently, it was concluded that internal

diffusion limitation of the hydrocarbon products could not be responsible for the two alpha distribution, even though it might alter the observed alpha value (16).

The effect of VLE on the two alpha product distribution has been proposed by a few researchers, although it was also rejected by other researchers (17-18). The basic idea of this model is that the higher olefin carbon number, the longer the residence time in the reactor and therefore the greater the contribution of the reversible olefin reaction. As a result, product distribution appears as a function of carbon number. However, these studies are based on their conclusion of single α chemistry for surface chain growth. The olefin reactions were then treated separately in terms of so-called secondary reactions. In addition, some other common experimental observations were not properly predicted or explained. In this work, we demonstrate conceptually that the two alpha observation could be due to the effect of VLE when considering olefin reactivity. For simplicity of discussion, a continuously stirred tank reactor (CSTR) is used for this modeling study.

Reaction Pathway and Model Development

The Fischer-Tropsch synthesis is a very complicated reaction and the details of reaction mechanism remain to be defined. Over the years it has been recognized that a simple polymerization mechanism should describe the product distribution, with the surface chain growth intermediate being an olefinic (19) or a paraffinic species (20). For the purpose of qualitatively understanding the product distribution, it is unimportant to distinguish the type of surface intermediate because both of them lead to the same dependency on carbon number. In this work, it is assumed that the chain growth follows the pathways shown in Figure 1, ignoring minor side reactions such as alcohol production. It is also assumed that there is only one type of active site on catalyst surface on which any surface process takes place. According to this scheme, the surface intermediate grows by addition of a surface methylene species, and

terminates to paraffin by hydrogenation or to olefin by β -elimination of hydrogen. The termination path to paraffin is irreversible since paraffins are non-reactive under typical FT conditions, while the pathway to olefin is reversible. Surface olefin species can undergo half-hydrogenation reversibly to form a surface chain growth intermediate or desorption as a free olefin molecule within the catalyst pores. The latter can adsorb reversibly on the catalyst surface or diffuse out of the catalyst pore and be removed as a reaction product. This reversible path eliminates the necessity and confusion of inventing terminologies such as readsorption, reinsertion, reinitialization, or reincorporation. These “re-“ concepts are sometimes misleading as they give an impression that they are separate processes from the forward dehydrogenation and desorption processes. In fact, inertness of the paraffins and the reversibility of olefin adsorption/ desorption and hydrogenation/dehydrogenation has been well documented (21).

The physical adsorption of olefins on the catalyst surface was taken into account by some researchers when modeling FT product distribution (10, **also chevron group** 22). This factor is not considered in this work since the effect of physical adsorption is virtually the same as that of liquid condensation and wetting. In the presence of vapor-liquid separation, the catalyst pores are filled with liquid which causes the physically adsorbed layer in the vicinity of catalyst surface to vanish. Nevertheless, chemisorption of the olefin may have a significant effect on product distribution. As a rule of thumb, other factors being equal, one may expect that the degree of chemical adsorptivity will increase with increasing molecular weight. However, since very little quantitative data are available for olefin chemisorption and the objective of this work is solely aimed at the effect of VLE, the olefin adsorption and desorption rate constants are assumed to be independent of carbon number.

Figure 2 shows schematically a typical CSTR slurry reactor, in which unconverted reactants and hydrocarbon products are separated into two phases, liquid and vapor. Both liquid

and vapor products are removed continuously to maintain a constant liquid level in the reactor.

With the assumption that there is no internal diffusion limitation of reactants, which is essentially true in a slurry reactor with small catalyst particles, the diffusion of hydrocarbon products in the catalyst pores is not considered, as has been proven to be absent (16). Based on the reaction mechanism of Figure 1, the steady state material balance of each surface species of carbon number n is as follows, assuming that the reaction rate constants are independent of carbon number:

$$\text{Chain growth intermediate, } C_n^* : \quad k_p S_1 S_{n-1} + k_o' S_H S_n = (k_p S_1 + k_H S_H + k_o) S_n \quad (1)$$

$$\text{Surface olefin, } C_n^* : \quad k_o S_n + k_a x_{n,o} = (k_o' S_H + k_d) S_n \quad (2)$$

$$\text{Olefin, } O_n : \quad V_R k_d S_n = V_R k_a x_{n,o} + V y_{n,o} + L x_{n,o} \quad (3)$$

$$\text{Paraffin, } P_n : \quad V_R k_H S_H S_n = V y_{n,p} + L x_{n,p} \quad (4)$$

From the above material balance equations, the concentration ratios of olefin to paraffin in the liquid phase (f_n) and the chain propagation probability on the catalyst surface (α_n) can be derived as Equations (5) and (6), respectively.

$$f_n = \frac{x_{n,o}}{x_{n,p}} = \frac{k_o k_d}{k_H S_H (k_d + k_o' S_H (1 + \tau_n k_a))} \quad (5)$$

$$\alpha_n = \frac{S_n}{S_{n-1}} = \frac{1}{1 + \beta(1 + f_n)} \quad (6)$$

where

$$\tau_n = \frac{V_R}{VH_n + L}; \quad H_n = \frac{y_{n,o}}{x_{n,o}} = \frac{y_{n,p}}{x_{n,p}} = \frac{P_n^s}{P}; \quad \beta = \frac{k_H S_H}{k_p S_1} \quad (7)$$

In Equation (7), τ_n is the average residence time of hydrocarbon product species n in terms of reactor size, H_n is the ideal vapor-liquid equilibrium constant of hydrocarbon product species n , and β is characteristic of surface chain propagation probability at high carbon numbers when olefin production rates approach zero. Under the latter situation, the product propagation probability (α_∞) appears to be independent of carbon number, as shown in Equation (8).

$$\alpha_\infty = \frac{k_p S_1}{k_p S_1 + k_H S_H} = \frac{1}{1 + \beta} \quad (8)$$

It is clear from Equation (6) that, due to the effect of vapor liquid separation and olefin reactivity, the surface chain propagation probability does not remain constant as proposed by Anderson (23, 24). Instead, it is a decreasing function of olefin to paraffin ratio or an increasing function of carbon number. Generally, the higher the carbon number, the lower the vapor-liquid equilibrium constant (H_n), the higher the average residence time (τ_n), the lower the olefin to paraffin ratio (f_n), and thus the higher the surface propagation probability (α_n).

In practice, it is impossible to collect hydrocarbon products directly from the catalyst surface. The product distribution is obtained by measuring vapor and liquid products collected at the reactor outlet. The production rate of a hydrocarbon species, n , including both olefin and paraffin in both vapor and liquid phases, is

$$r_n = V(y_{n,p} + y_{n,o}) + L(x_{n,p} + x_{n,o}) = V_R k_H S_H (1 + f_n) S_n \quad (9)$$

and the observed product distribution is thus defined as:

$$\alpha'_n = \frac{r_n}{r_{n-1}} = \frac{1 + f_n}{1 + f_{n-1}} \frac{S_n}{S_{n-1}} = \frac{1 + f_n}{1 + f_{n-1}} \frac{1}{1 + \beta(1 + f_n)} = \lambda_n \alpha_n \quad (10)$$

Equations (5), (6), and (10) completely describe the observed product distribution of Fischer-Tropsch synthesis in a CSTR reactor. Nonetheless, the same method can be applied to any type of reactor, as long as there is vapor-liquid separation of products. In integral reactors, such as a fixed-bed reactor, the molar flowrates of liquid and gas are local values but this model still holds. In fact, this model is valid for any type of reactor since the molar flowrate will cancel each other as far as the product distribution is of concern.

Model Simulation and Discussion

The observed alpha value, defined in Equation (10), is the one that is widely used to measure FT product distribution. It consists of two parts: the surface chain propagation probability (α_n) and the effect of olefin reactivity (λ_n). Both of these factors increase with increasing carbon number, leading to the observed two alpha distribution. In the high carbon number range, f_n approaches zero and λ_n approaches unity. Thus, α'_n appears as a constant, α_∞ . This is the so-called second alpha, as it has been named by many researchers. It should be noted that olefin reactivity affects the product distribution in the low carbon number range rather than that in the high carbon number range. The so-called “second alpha”, α_∞ in this work, reflects the “true” product distribution rather than the result of reversible olefin reactions. For instance, for those catalysts having strong hydrogenation ability, f_n could be very small even for low carbon number species. The effect of olefin reactivity is insignificant under this situation since f_n is essentially much smaller than unity. As a result, the product distribution, α'_n , appears to follow a single alpha which is α_∞ .

Equation (10) indicates that the observed FT product distribution can be quantified simply by using two parameters: olefin to paraffin ratio (f_n) at each carbon number and the β value which can be determined from high carbon number data. These two factors are dependent on the catalyst and reaction conditions. In most cases, even at high conversions, the molar flowrate of liquid product at the reactor outlet is significantly lower than that of gas phase products (hydrocarbon, water, unconverted reactants). Simple flash calculation indicates that this ratio (L/V) is generally less than 0.03 even when CO conversion is 100%. It is even an order of magnitude lower at 50% CO conversion. Therefore, the residence time, τ_n , can be approximated with Equation (11) by ignoring the liquid flow rate.

$$\tau_n = \frac{V_R}{VH_n} = \frac{V_R P}{VP_n^s} \quad (11)$$

At high carbon numbers, H_n becomes so small that the magnitude of VH_n could be comparable with that of L . However, ignoring L has negligible effect on α_n' since the magnitude of VH_n is very small and f_n is close to zero. The saturated vapor pressure of hydrocarbons in Equation (11) can be calculated using Antoine's equation (25) or an empirical correlation for FT products (26).

For simplicity of simulation, it is further assumed that olefin adsorption/desorption ($C_{n=}/C_{n=}^*$) and hydrogen elimination of chain growth intermediate/half hydrogenation of surface olefin ($C_{n=}^*/C_{n=}^*$) steps are in equilibrium (Figure 1). This is particularly true at high conversions when the total flow rate at the reactor outlet is lower. With these assumptions, the product removal is slow ($1/\tau_n \ll k_o, k_o', k_a, k_d$) and Equation (5) reduces to Equation (12), suggesting that the olefin to paraffin ratio is simply proportional to the reciprocal of the average residence time τ_n . In other words, f_n decreases exponentially with carbon number as it is related to the saturated vapor pressure.

$$f_n = \frac{x_{n,o}}{x_{n,p}} = \frac{K_E}{k_H S_H^2 K_{ad} \tau_n} \quad (12)$$

If the above mentioned equilibria are not valid, the dependency of f_n on carbon number will be weaker than exponentially for low carbon numbers, as can be seen from Equation (5). The higher the carbon number, the more τ_n dominates the denominator of Equation (5), and therefore the closer the dependency of f_n on carbon number to the exponential rule.

The model described with Equations (10)-(12) were tested using data obtained from the literature (7) and generated in our laboratory. The reaction conditions and major results are summarized in Table 1. The model simulation was performed with experimental data of temperature, α_∞ , and f_3 . As shown in Figures 3 and 4, there is a tight fit between model prediction and experimental data for both olefin to paraffin ratio (Figure 3) and product distribution (Figure 4) at CO conversions higher than 50%.

A common experimental observation of FT product distribution is that higher temperature, higher H_2/CO ratio, and/or lower pressure give lower alpha values. Table 2 shows that these general features can be qualitatively predicted using the model developed in this work. Another common experimental observation is that the deviation from a single α plot occurs in the range of carbon number 8 to 14 (1). This phenomenon has not been properly explained with any of the existing models. The only related work is the two active sites model by Donnelly and Satterfield (4), in which the break point was calculated from experimental data since this parameter was required in their model. Nevertheless, a potentially reliable model also should be able to predict, not only to explain, this feature of the product distribution. According to the model developed in this work, the product distribution deviates from single alpha rule for light

hydrocarbon products due to the effect of vapor-liquid separation of hydrocarbon products. The deviation becomes weaker and weaker with increasing carbon number. Starting at some carbon number and thereafter, the alpha value appears to be constant (α_{∞}) when the olefin to paraffin ratio approaches zero. The general feature is that the α value increases with increasing carbon number and then levels off at α_{∞} . The deviation point is thus defined as the carbon number at the intersection of the α_{∞} line and the linear regression line of the data for the first three carbon numbers (C_4 - C_6), as shown in Figure 5. The physical meaning of the deviation point is the carbon number above which the effect of olefin reactivity on product distribution becomes insignificant.

The observed product distribution, as described above, depends on the value of β (or α_{∞}) and the olefin to paraffin ratio (f_n) at each carbon number. With some assumptions described above, f_n can be simplified to be directly proportional to the vapor pressure. Consequently, with information of reaction temperature, α_{∞} , and f_3 (depending on reaction condition and catalyst), the dependency of α_n on carbon number can be simulated and the deviation point can be determined. Table 3 summarizes the effect of temperature and f_3 on the deviation point with $\alpha_{\infty}=0.9$ and 0.8 . The effect of α_{∞} is insignificant except at high f_3 and high temperatures. At 300°C and $f_3 = 10$ with $\alpha_{\infty}=0.8$, the deviation point is 15.1, which is only 1.5 higher than that with $\alpha_{\infty}=0.9$. The temperature and f_3 value used in Table 3 pretty much represent the conditions and results of a typical FT reaction. Therefore, the current VLE model predicts the deviation point to be within carbon number 8-14 which is in agreement with generally experimental observations.

In this work, it is assumed that the vapor and liquid are in equilibrium following Raoult's law. One may argue that in practice, non-ideal vapor/liquid system should be considered since hydrocarbons of different molecular weight deviate from ideal behavior differently. For instance, the activity coefficient may increase exponentially with increasing carbon number,

which retards the dependency of olefin to paraffin ratio on carbon number (12-14). However, it should be noted that the non-ideal behavior of a hydrocarbon affects not only its vapor-liquid equilibrium constant (partition coefficient), but also its chemical reactivity in the liquid phase. If the vapor liquid system is taken as non-ideal, the reaction rate of a chemical species in the liquid phase also should be taken as proportional to its activity instead of its concentration. If not, the reaction rate constants of olefins cannot be assumed to be independent of carbon number. As a result, the non-ideal effect (activity coefficient) on olefin to paraffin ratio and product distribution cancels out when ignoring other minor factors, such as the impact of pressure on liquid (Poynting factor), although the average residence time of each hydrocarbon species, as defined in this work, deviates from that of ideal system. Therefore, when modeling the effect of VLE on product distribution, it is essentially unnecessary to account for the thermodynamic deviation of hydrocarbon products from ideal system.

Some researchers attribute the two- α distribution to physisorption of hydrocarbons on catalyst surface in the presumed gas-solid reactions, although the reactions were actually carried out at temperatures lower than the dew point of products. Typically, when the alpha value is higher than about 0.7 (actually depending on reaction temperature, pressure, conversion), there is inevitable formation of liquid phase on catalyst surface. Under these circumstances, the FT reaction actually takes place in the liquid phase. Physisorption should be taken into account only when the reaction is in gas phase, which typically involves high temperature operations. However, high temperature operation in turn does not favor the existence of a physisorption layer. If the products are entirely in the vapor phase, it is not difficult to prove that, without accounting for the effect of physisorption or diffusion, the product should follow a single alpha distribution, even when the olefin reactivity is taken into account. Since the effect of

physisorption, if it exists, on the FT product distribution is essentially the same as that of vapor-liquid separation, no further discussion is attempted here.

From the above discussion, it is clear that the $2-\alpha$ distribution could be attributed to the effect of vapor-liquid separation of hydrocarbon products in the reactor. In addition, ideal gas and ideal solution assumptions are adequate to approximate the thermodynamic behavior of this system because non-ideal factors, such as activity coefficients, tend to cancel out with each other when evaluating olefin to paraffin ratio.

It has been argued that, in the presence of vapor-liquid equilibrium, the chemical potential of a given species is identical in both liquid and vapor phases and thus the rate of a chemical reaction cannot depend on the identity of the phase and the hydrocarbon solubility in the liquid phase (17, 18). This concept is incorrect unless the impacts of thermodynamics and kinetics are clearly defined. As a thermodynamic intensive property, the chemical potential tells us the processing direction and the processing limit. It does not tell us the processing rate which is the scope of kinetics. According to the standard definition, the chemical potential of a species in a phase is the sum of its standard free energy and the contribution of such species in its current mixture, and the latter is a function of its composition. The fundamental difference between vapor and vapor/liquid systems lies in the fact that the standard free energy of a species in the liquid phase is different from that in the vapor phase; the difference can be quantified as a function of its vapor pressure. For an ideal vapor/liquid system in equilibrium, the relationship between vapor and liquid can be described using Raoult's law. Therefore, the concentration of a species in the liquid phase depends not only on its vapor composition but also its vapor pressure under the processing conditions. For two species whose chemical potentials are identical in both vapor and liquid phases, the component having a lower concentration in the vapor phase may have a higher concentration in the liquid phase, simply because it has lower vapor pressure. In a

Fischer-Tropsch reactor, due to the effect of vapor-liquid separation (if it exists), the hydrocarbon concentration in the liquid phase increases with increasing carbon number in the lower carbon number ranges (say C_{20-}), in contrast to the opposite trend in the vapor phase (15). As a result, product concentration profiles in the catalyst pores are totally different in these two systems; that is, a gas phase system and a gas-liquid phase system.

In a multi-phase reactor, the rate of chemical reaction definitely depends on the phase in which the catalyst resides. The chemical reaction is only affected by the changes in the phase which the catalyst is directly in contact with. Any impact resulting from the others phases has to go through this phase and affects the chemical reaction indirectly. If the catalyst is in the liquid phase, a gas reactant has to dissolve in liquid phase before it can participate in reactions. The so-called residence time must be the one in the liquid phase rather than in the gas phase because there is no reaction taking place in the gas phase. In a typical Fischer-Tropsch reaction, although most of the light hydrocarbons (C_{20-}) are removed from gas phase, it does not change the fact that the catalyst can only sense the amount of molecules in the liquid phase rather than those in the vapor phase. An active site on the catalyst surface does not know where the reactant molecule comes from -- liquid or vapor phase; however, it does know how many molecules are in the phase in contact with the catalyst. According to the collision theory, the nature of a chemical reaction is nothing more than the effective collisions between reactant molecules. It is obvious that a higher population will lead to a higher probability of effective collisions and, thus, higher reaction rates. Generally, the assumption of vapor phase operation should not be made when there is vapor-liquid separation and the catalyst is in liquid phase, especially when the reaction rate is of concern.

Conclusion

A mathematical model has been developed to describe the product distribution of Fischer-Tropsch synthesis, based on the recognition that the termination path to olefin is reversible. The observed product distribution at the reactor outlet consists of the contribution from intrinsic chain propagation on the catalyst surface and the effect of olefin reactivity. The 2-alpha distribution can be attributed to the effect of vapor-liquid separation of hydrocarbon products. The reaction product does not follow a ASF single alpha distribution even on the catalyst surface. A tight fit between model prediction and experimental data has been demonstrated. Also, the deviation point of product distribution is predicted to be within carbon number 8-14 under typical FT conditions.

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Nomenclature

f	olefin to paraffin ratio
H	vapor liquid equilibrium constant
k_a	olefin adsorption rate constant
k_d	olefin desorption rate constant
k_o	hydrogen abstraction rate constant of chain growth intermediate
k_o'	olefin half hydrogenation rate constant
k_p	propagation rate constant of chain growth intermediate
k_H	hydrogenation rate constant of chain growth intermediate
K_E	reaction equilibrium constant of olefin half hydrogenation ($K_E = k_o/k_o'$)
K_{ad}	adsorption equilibrium constant ($K_{ad} = k_a/k_d$)
L	liquid molar flow rate at reactor outlet
P	total operating pressure
P^s	saturated vapor pressure of hydrocarbon
r	reaction rate
R	gas constant
S	concentration of surface species
T	temperature
V	vapor molar flow rate at reactor outlet
V_R	reactor size (catalyst volume, catalyst weight)
x	molar fraction in liquid phase
y	molar fraction in vapor phase
α	chain propagation probability on surface, a function of carbon number
α'	observed product distribution, a function of carbon number

α_{∞} chain propagation probability on surface at high carbon numbers, a constant

λ factor of olefin reactivity ($\lambda_n = (1+f_n)/(1+f_{n-1})$)

τ average residence time of hydrocarbon species in the reactor

subscript

= olefin

H hydrogen

n paraffin, olefin, or chain growth intermediate of carbon number n

o olefin

p paraffin

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Table 1		
Reaction Conditions and Results from Literature and In-house		
	Reaction 1	Reaction 2
Source	Exxon (7)	CAER
Catalyst	Co/TiO ₂	Co-Pt/Al ₂ O ₃
Temperature, °C	200	210
Pressure, kPa	2000	2000
CO Conversion, %	72	53
α_{∞}	0.92	0.85
f ₃ (olefin/paraffin of C ₃)	2.15	1.84
f ₄ (olefin/paraffin of C ₄)	1.3	0.98

Table 2 Model Prediction on the Effect of Reaction Conditions on Product Distribution		
Condition	Effect on α_{∞}	Effect on α_n
$T \uparrow$	$(S_H \downarrow + S_I \downarrow) \Rightarrow \beta \uparrow \Rightarrow \alpha_{\infty} \downarrow$	$(P_n^s \uparrow + S_H \downarrow) \Rightarrow f_n \uparrow \Rightarrow \alpha_n \downarrow$
$P \uparrow$	$(S_H \uparrow + S_I \uparrow) \Rightarrow \beta \downarrow \Rightarrow \alpha_{\infty} \uparrow$	$(f_n \downarrow + S_H \uparrow) \Rightarrow \alpha_n \uparrow$
$H_2/CO \uparrow$	$S_H \uparrow \Rightarrow \beta \uparrow \Rightarrow \alpha_{\infty} \downarrow$	$V \uparrow \Rightarrow f_n \uparrow \Rightarrow \alpha_n \downarrow$

Table 3 Deviation Point of Alpha Value at $\alpha_{\infty}=0.9$ ($\alpha_{\infty}=0.8$)			
T, °C f₃	1	5	10
200	8.4 (8.3)	10.6 (10.4)	11.6 (12.0)
250	9.1 (9.0)	11.4 (11.4)	12.5 (13.4)
300	10.0 (9.8)	12.4 (12.6)	13.6 (15.1)

Figure 1 Reaction pathway of Fischer-Tropsch synthesis

Figure 2 Schematic diagram of a CSTR reactor

Task 11. University of California, Berkeley (Subcontract)

Final Research Report

October 1, 1998 to September 30, 2001

**Structural and Catalytic Characterization of the Mechanism and
Site Requirements in Fischer-Tropsch Synthesis on Fe and Co Catalysts**

Principal Investigator

Enrique Iglesia
Laboratory for the Science and Application of Catalysis
Department of Chemical Engineering
University of California at Berkeley
Berkeley, CA 94720

Project Personnel

Sundaram Krishnamoorthy (UC-Berkeley)
Anwu Li (UC-Berkeley)
Senzi Li (UC-Berkeley)
Wei Li (UC-Berkeley)
George D. Meitzner (Edge Analytical, Inc.)
Dario Pinna (UC-Berkeley)
Juston Smithers (UC-Berkeley)
Peter Szedlacsek (UC-Berkeley)
Mai Tu (UC-Berkeley)

I. FISCHER-TROPSCH SYNTHESIS ON IRON CATALYSTS

1. Background
  - 1.1. *Structure and Function of Active Phases in Fischer-Tropsch Synthesis*
2. Synthesis Procedures for Fe-Zn-K-Cu(Ru) samples
3. Structure and Site Evolution of Iron Oxide Catalyst Precursors during the Fischer-Tropsch Synthesis
  - 3.1. *Methodology*
  - 3.2. *X-ray absorption sample preparation*
  - 3.3. *In situ X-ray absorption microreactor cell*
  - 3.4. *Measurement of X-ray absorption spectra, FTS rates and data analysis*
  - 3.5. *Fe K-edge XANES of reference compounds*
  - 3.6. *In situ Fe K-edge XANES during reactions of Fe oxide precursors in CO*
  - 3.7. *In situ Fe K-edge XANES of Fe-K-Cu oxide precursors in synthesis gas*
  - 3.8. *Effects of K and Cu on catalyst structure and on FTS rates*
  - 3.9. *CO chemisorption and surface area measurements*
4. Effect of Zn, Cu, and K promoters on the reduction/carburization/catalytic performance of Fe oxides
  - 4.1. *Methodology*
  - 4.2. *Crystal structure*
  - 4.3. *Surface areas of Fe₂O₃-Zn-K-Cu oxide precursors*
  - 4.4. *Zn promotion effects on Fischer-Tropsch Synthesis rates and selectivity*
  - 4.5. *Reduction kinetics of Fe₂O₃-Zn-K-Cu precursors in H₂*
  - 4.6. *Reduction and carburization kinetics of Fe₂O₃-Zn-K-Cu in CO*
  - 4.7. *Effects of K and Cu on Fischer-Tropsch Synthesis rate and selectivity*
5. Design of high activity Fe Fischer-Tropsch Synthesis catalysts by promotion with Cu, Ru and by synthesis of high surface area Fe-Zn precursors
  - 5.1. *Introduction*
  - 5.2. *Comparison of the Reduction and Carburization Behavior of Fe-Zn-K oxides Promoted with Ru or Cu*
  - 5.3. *Effect of Ru and Cu on Fischer-Tropsch Synthesis Rate and Selectivity*
  - 5.4. *Surface areas and CO chemisorption site densities on fresh and activated Fe-Zn-K-Cu(Ru) oxides*
  - 5.5. *Structural characterization of Fe-Zn-K-Cu(Ru) catalysts during Fischer-Tropsch Synthesis using X-ray absorption spectroscopy*
  - 5.6. *Isothermal transient analysis of reduction, carburization, and Fischer-Tropsch Synthesis products during activation of Fe-Zn-K-Cu(Ru) catalysts*
  - 5.7. *Synthesis of Fe-Zn-K-Cu oxide precursors with high surface area*
  - 5.8. *Site density of active species and promoters and effects on the Fischer-Tropsch Synthesis*

- 5.9. *Fischer-Tropsch Synthesis Rates and Selectivities on Fe-based catalysts – A comparison*
6. Comparison of the performance of a Fe-Zn-K-Cu and Co/SiO₂ catalysts at Co conditions
7. Structural analysis of unpromoted Fe-based FTS catalysts using X-ray absorption and Mössbauer emission spectroscopy
  - 7.1. *Introduction*
  - 7.2. *Catalyst preparation*
  - 7.3. *Activation and FTS reactions*
  - 7.4. *Mössbauer emission spectroscopy measurements*
  - 7.5. *Mössbauer structural analysis*
  - 7.6. *Fe K-edge XANES*
  - 7.7. *Fe K-edge fine structure*
  - 7.8. *Comparison of the results from Mössbauer emission and X-ray absorption spectroscopy*
  - 7.9. *Discussion*
  - 7.10. *Conclusions*
8. Pathways for CO₂ formation and conversion during FTS reactions on Fe-based catalysts
  - 8.1. *Introduction*
  - 8.2. *Experimental methods*
  - 8.3. *Role of CuO and K₂CO₃ promoters on CO₂ formation pathways*
  - 8.4. *Effects of CO₂ addition to synthesis gas on Fe-based catalysts*
  - 8.5. *The role of CO₂ in the initiation and growth of hydrocarbon chains*
9. Investigation of the kinetic isotope effects during FTS reactions on Fe-based catalysts
  - 9.1. *H₂/D₂ effects on FTS rates*
  - 9.2. *H₂/D₂ effects on α -olefin/n-paraffin ratios*

II. FISCHER-TROPSCH SYNTHESIS ON COBALT CATALYSTS

1. Background
2. Catalyst synthesis and characterization
3. FTS activity and selectivity measurements
4. Effect of water on FTS rate and selectivities on Co catalysts
5. Kinetic studies to explore effect of water on the reaction mechanism
  - 5.1. *D₂-H₂ Exchange and D₂O Tracer experiments*
  - 5.2. *Formulation of reaction mechanisms and derivation of rate expressions*

- 5.3. *Kinetic studies and mathematical fitting of data to rate expressions*
- 6. Determination of the kinetic isotope effects on Co-based catalysts
- 7. Possible effects of water on the number of CO-binding sites available during FTS
  - 7.1. *Introduction*
  - 7.2. *FTS activity and selectivity measurements at 0.5 MPa*
  - 7.3. *In situ FTIR spectra during FTS*
  - 7.4. *In situ X-ray absorption spectroscopy during reactions of CO/H₂ and CO/H₂/H₂O on Co/SiO₂*
  - 7.5. *Carbon coverage measurements during FTS*
    - 7.5.1. Introduction
    - 7.5.2. Catalyst synthesis and measurement of steady state and transient FTS kinetics
    - 7.5.3. Measurement and estimation of carbon coverage

III. APPENDIX

- 1. References

I. FISCHER-TROPSCH SYNTHESIS ON IRON CATALYSTS

1. Background

1.1. *Structure and Function of Active Phases*

Fe-based oxides have been used as commercial catalysts for Fischer-Tropsch synthesis (FTS) to produce a large variety of paraffin and olefin products, ranging from methane to high molecular weight waxes [1]. During activation by synthesis gas and subsequent FTS reaction, several phases including metallic iron, iron carbides and iron oxides are known to co-exist at steady-state conditions [2-5]. The distribution and amounts of these phases depend on exposure to various activation and reaction conditions, leading to different catalytic performances in FTS. Some researchers have proposed that surface iron atoms are responsible for FTS activity [6], while some others considered surface carbides or a mixture of carbides [7,8] and metallic iron [9] to be the active phase. There are several reports that suggest that magnetite Fe_3O_4 is the active phase in FTS [10-12]. Although these studies have each provided some evidence to support their specific proposals about the active phase, the available information remains phenomenological, and a method to identify the active phase during reaction and to count the number of active sites has not yet been established.

This project is aimed at building on our previous research on structure-function roles for FTS reactions on catalysts based on Co [13,14] and Fe [15,16]. It addresses the characterization of the structure and function of the active sites involved in the Fischer-Tropsch synthesis on these multi-component Fe-based catalysts. It involves the use of characterization techniques such as X-ray absorption spectroscopy, X-ray diffraction, and temperature programmed reaction, monitoring of isothermal product transients under FTS reaction conditions using mass spectrometry, as well as activity and product selectivity measurements in a high pressure reactor under FTS conditions, in order to obtain a complete picture of the structure-function relationships of the active sites on Fe catalysts. In Section 2, we address the structure and site evolution of iron oxide precursors during FTS. The effect of Zn, Cu, K as promoters for FTS is discussed in Section 3 while the effects of Cu and Ru as well as surface area of precursors, as site density enhancers are illustrated in detail in Section 4. We also demonstrate that the high activity Fe-Zn-Cu-K catalysts are comparable in performance with typical Co/SiO₂ catalysts at low temperatures.

1.2. *Effect of Zn, K and Cu*

Many components have been added to Fe catalysts in order to improve their mechanical and catalytic properties. Our previous studies have shown that zinc, alkali and copper [16,17] promote the catalytic properties of Fe oxides. Zinc oxide, as a non-reducible oxide in FTS conditions, appears to stabilize the surface area of Fe oxide. Alkali, as an apparent modifier of the adsorption enthalpies of H₂ and CO, increases the selectivity to desired C₅₊ products [18]. Copper promotes the carburization processes and decreases the temperature required for the activation of iron oxide. Here, our initial efforts have

focused on Fe-Zn-K-Cu catalysts. We have prepared a series of Zn and Fe co-precipitated oxides with varied Zn/Fe ratios and then introduced varying amounts of K and Cu. We have examined the surface area, bulk structure, required reduction and carburization temperatures as well as the catalytic behavior of these catalysts, in order to identify optimum Zn/Fe ratios and Cu and K contents that give maximum site density and catalytic activity. Finally, as part of our attempt to design a high activity Fe-based FTS catalyst, we have also investigated the use of Ru as a promoter in place of Cu, based on the high activity of Ru-based catalysts for CO hydrogenation reactions [19], as well as by the synthesis of higher surface area Fe-Zn precursors. The performance of Fe catalysts thus prepared, have been evaluated at conditions typically used for Co-FTS reactions (473 K and 2 MPa) for comparison with a typical Co/SiO₂ catalyst.

2. Synthesis Procedures for Fe-Zn-K-Cu(Ru) Samples

Fe-Zn oxide precursors were prepared by co-precipitation from a mixed solution of Fe and Zn nitrates using ammonium carbonate using a procedure reported previously [16]. A solution containing Fe(NO₃)₃ (Aldrich, 99.9+%, 3.0 M) and Zn(NO₃)₂ (Aldrich, 99.9+%, 1.4 M) at a Zn/Fe atomic ratio of 0.1 was added into a large flask containing deionized water at 353 K (~100 cm³) at a rate of 120 cm³h⁻¹ using a liquid pump. (NH₄)₂CO₃ (Aldrich, 99.9%, 1 M) was added separately to this flask at the rate required to maintain the pH at a constant value of 7.0±0.1, measured by a pH meter (Omega, PHB-62). The precipitates (~20 g) were washed five times with doubly distilled deionized water (~200 cm³/g each time), dried in ambient air at 393 K overnight, and then treated in flowing dry air at 623 K for 1 h. The K, Cu, and Ru promoters were added to these Fe-Zn oxide precursors by incipient wetness impregnation with aqueous solutions of K₂CO₃ (Aldrich, 99.99%, 0.16 M), Cu(NO₃)₂ (Aldrich, 99.99%, 0.16 M), or ruthenium (III) nitrosyl nitrate [Ru(NO)(NO₃)_x(OH)_y (x+y=3)] (Aldrich, dilute nitric acid solution, Ru 1.5%) at the concentrations required to obtain the desired K/Fe, Cu/Fe, or Ru/Fe atomic ratios (K/Fe=0.02, Cu,Ru/Fe=0.01). The impregnated samples were then dried 373 K in ambient air. Finally, the samples were treated in flowing dry air at 673 K for 4 h. The resulting oxide precursors are denoted throughout as Fe-Zn-K₂, Fe-Zn-K₂-Cu₁ and Fe-Zn-K₂-Ru₁, respectively. The subscripts denote the atomic content of the corresponding promoter divided by the Fe atomic content and multiplied by 100. These catalysts were pressed at 443 MPa into pellets, lightly crushed, and then sieved to retain the 80 - 140 mesh fraction for FTS reaction. Pure Fe oxide precursors were prepared in an identical manner and promoted with Cu and K for the initial characterization studies.

High surface area Fe-Zn-K-Cu oxide precursors were prepared using surface-active components, such as alcohols, in order to minimize pore mouth pinching as intrapore liquids with high surface tension are removed by drying. These processes lead to a decrease in pore volume and surface area. Fe-Zn-K₄-Cu₂ oxides were prepared by the procedure described above, except that alcohols (isopropanol or ethanol) were used to replace the water retained within pores during precipitation before the drying step. After co-precipitation, the powders were washed with isopropanol or absolute ethanol (Fischer Chemical) five times (~200 cm³/g each time) at ambient temperature. Magnetic stirring was used during alcohol washing in order to increase the rate at which liquid water within

pores was replaced by the alcohol. In order to maintain similar promoter surface densities on these higher surface area oxides, proportionally higher concentrations of K (K/Fe=0.04) and Cu (Cu/Fe=0.02) were introduced by incipient wetness impregnation.

3. Structure and site evolution of iron oxide catalyst precursors during the Fischer-Tropsch Synthesis

3.1. Methodology

Several of the Fe phases described in Section 1 have been detected in freshly activated or used Fe-based FTS catalysts. Most of these phases have been proposed at various times to be the active species for FTS reactions. The relative abundance of these phases depends on reaction conditions. Even after many *ex situ* characterization studies, the composition of Fe-based FTS catalysts during reaction and the identity of the active phase remain controversial. Fe-based catalysts have been investigated by Mössbauer spectroscopy [7,20]; the time resolution of Mössbauer spectroscopy (>1 h for typical samples) precludes its use for *in situ* transient measurements during initial phase transformations. Also, Mössbauer spectroscopy is sensitive only to the recoil-free fraction, which depends on the structure of the Fe-containing phase. This recoil-free fraction must be accurately measured as a function of temperature for precise structural assessments using Mössbauer spectroscopy. X-ray diffraction (XRD) cannot detect inorganic structures without long-range periodicity; as a result, it is not sensitive to amorphous or well-dispersed Fe species, which tend to account for a large fraction of the surface area and the active sites available for FTS. X-ray photoelectron spectroscopy (XPS) [11,21] has been used to examine catalytic solids before and after reaction, but it cannot be used during FTS. It requires quenching and catalyst cleansing procedures that influence the state of the surface layers meant to be probed by XPS. Recent high resolution transmission electron microscopy (HRTEM) studies have addressed the active phase of working Fe catalysts after different activation and reaction treatments; these studies have provided useful, but occasionally misleading insights about the nature of the working Fe catalysts [22,23]. However, none of these measurements were performed during reaction or even within the FTS reactor. Therefore, the relevant catalytic surfaces may have become restructured or contaminated, even with careful handling and controlled passivation, as a result of the indispensable quenching and cleansing procedures.

X-ray absorption spectroscopy (XAS) can probe the local structure of inorganic structures, even as catalytic reactions occur, by using *in situ* spectroscopic cells with realistic and well-defined hydrodynamics. The X-ray absorption near-edge spectrum (XANES) is sensitive to the oxidation state and to the symmetry of the absorber atom [24]. Comparisons between these features and those in compounds with known local structure can be used to quantify the fraction of each absorber present within each type of local coordination environment using principal component analysis (PCA) [25] and linear combination [26] methods. The region beyond the absorption edge contains oscillations in absorbance, which arise from the scattering of the emitted photoelectrons by the atoms surrounding the absorber. This extended X-ray absorption fine structure (EXAFS) region

of the spectrum contains information about the identity and the location of neighboring atoms coordinated to the absorber directly or through other atoms [24]. Therefore, X-ray absorption methods are ideally suited for *in situ* characterization of Fe-based FTS catalysts. We are not aware of its previous use for the structural characterization of Fe catalysts during FTS. Several reaction cells have been reported previously for *in situ* XAS measurements [27,28]. Here, we report a cell design based on modifications of one of these previously described cells [28], and use it to probe the local structure of Fe catalysts derived from Fe₂O₃ precursors during FTS. This study focuses on the evolution of the Fe₂O₃ component in the precursor materials during FTS reactions, on the effect of various promoters (Cu, K), and on the extent and rate of structural transformations occurring as Fe oxide catalyst precursors activate during contact with synthesis gas and as FTS reactions approach steady-state.

3.2. X-ray absorption sample preparation

Fe K-edge X-ray absorption spectra were measured for reference compounds with known local structures and for catalyst precursors consisting of Fe-K-Cu oxides (K/Fe=0.02, Cu/Fe=0.01) during their reduction and carburization in CO and in synthesis gas. Fe₂O₃ (Alfa AESAR, 99.998%), Fe₃O₄ (Alfa AESAR, 99.997%), and FeO (Alfa AESAR, 99.5%) were used as reference crystalline oxides. Fe₃C, which can form during FTS reactions, was prepared by temperature-programmed reaction (0.167 K/s) of Fe₂O₃ up to 973 K using CO (Matheson, 99.99%, 107 mol CO/g-atom Fe-h) as the reduction and carburization agent [3]. The resulting Fe₃C powder was passivated in flowing 1 % O₂/He (Matheson, 99.999%, 0.05 mol/h) at room temperature (RT) for 1 h before removing from the synthesis cell. X-ray diffraction measurements confirmed the exclusive presence of Fe₃C in this sample.

The Fe₂O₃ used for *in situ* XAS measurements was prepared by precipitation from an aqueous solution of Fe(NO₃)₃ (Aldrich, 99.99%, 3.0 M) with (NH₄)₂CO₃ (Aldrich, 99.9%, 1 M) at 353 K and a constant pH of 7.0. The precipitate was dried at 393 K overnight and treated in dry air at 643 K for 4 h. These oxide precursors were impregnated with aqueous solutions of K₂CO₃ (Aldrich, 99.99%,) and/or Cu(NO₃)₂ (Aldrich, 99.99%) to incipient wetness in order to give K/Fe and Cu/Fe atomic ratios of 0.02 and 0.01, respectively. These compositions were found to give the best catalytic performance in the Fischer-Tropsch synthesis described in subsequent sections.

All samples used in spectroscopic measurements were diluted to 10 wt.% Fe using graphite powder (Alfa AESAR, 99.9995%, S_g < 1 m²/g), pressed at 10 MPa, sieved to retain 180-250 μ particles, and placed within a quartz capillary cell [29]. The inertness of graphite was tested by flowing H₂ over Fe oxides mixed with graphite up to 873 K without any detectable formation of FeC_x. Also, no carbon oxide products were detected by mass spectrometry, indicating that neither FeO_x nor the Fe metal formed during reduction reacted with graphite at typical FTS temperatures (473-773 K). The maximum sample thickness was set by the inner diameter of the quartz capillary (0.8 mm). Reference compounds were also diluted with graphite to 10 wt.% Fe and held using a Prolene^{TM} film against an Al plate containing a beam slit.

3.3. *In situ* X-ray absorption microreactor cell

Figure 1. X-ray absorption cell: (A) picture, (B) front view, (C) top view with the heating unit removed.

An *in situ* X-ray absorption reaction cell was designed as a modified version of a previously reported reaction cell [29]. The modifications consisted of a finned heated block designed to replace the temperature control by heated air used in the earlier design. The cell consists of a quartz capillary (0.8 mm inner diameter, 0.1 mm wall thickness, 100 mm length) mounted horizontally into a stainless steel base using metal fittings and graphite ferrules (Figure 1). Samples with 180-250 μ particles formed a dense bed through which gas flows with negligible pressure drop and plug-flow hydrodynamics. Heat is supplied by four cartridges heaters mounted into a finned copper block. The copper block was insulated using a ceramic foam casing. A 20 $\times$ 4 mm beam path was cut into the finned copper block and the ceramic insulation in order to provide a clear path for the X-ray beam (10 $\times$ 0.2 mm) at a 45° angle through the middle section of the capillary.

Gases were introduced into the cell from lecture bottles mounted in a portable gas manifold unit with built-in gas purifiers (O₂ remover; 13X molecular sieve; Matheson) and mass flow controllers (Porter Instruments). Features of this XAS cell include small sample loadings (1-10 mg), low flow rates (1.3-13.4 mmol/h), and plug-flow hydrodynamics, as well as the ability to attain conversions and space velocities similar to those typical of laboratory tubular microreactors. The capillary microreactor can reach temperatures of $\sim$ 973 K and pressures up to 1.0 MPa. It also provides efficient heat transfer and accurate temperature control and measurement. A thermocouple (0.5 mm outer diameter) inserted into the outlet side of the capillary using a metal T-union provides accurate temperature measurements and prevents the sample from being dislodged from the capillary by the flowing gas. Temperature uniformity was confirmed by measuring the temperature profile along the sample bed under conditions identical to those used for the *in situ* experiments. The typical temperature variation along the sample bed is within $\pm$ 0.5 K. During *in situ* measurements, the cell temperatures can be controlled within $\pm$ 0.5 K in either temperature-programmed or isothermal modes using a temperature controller (Series 982, Watlow). For the quench experiments described below, the capillary cell can be cooled to ambient temperature within a few seconds by simply sliding the heating block away from the capillary cell.

3.4. Measurements of X-ray absorption spectra, FTS rates and data analysis

Fe K-edge X-ray absorption spectra were measured at the Stanford Synchrotron Radiation Laboratory (SSRL) on a wiggler side-station (beamline 4-1). During these measurements, the storage ring was operated at 30-100 mA and 3.0 GeV. Two Si (111) crystals were used in the monochromator, which was detuned by 20% in order to eliminate harmonics from the monochromatic beam. Three N₂-filled ion chambers were used in order to measure the intensity of the X-ray beam incident on the sample (I_0), after the sample (I_1), and after a 5 μ Fe calibration foil (I_2). In this manner, the sample spectrum (I_0/I_1) and a reference spectrum (I_1/I_2) were obtained simultaneously. The most restrictive aperture along the beam path was the 0.2 $\times$ 12 mm slit within the hutch, which provided a resolution better than 2 eV at the Fe K-edge (7.112 keV) [30].

In order to achieve the required time resolution for spectrum measurements during temperature-programmed reduction and carburization in CO, a slow heating rate was used (0.017 K/s) and only the near-edge spectra were measured (6.900-7.350 keV; 120 s per spectrum). After isothermal exposure to synthesis gas for 8-14 h, the spectra were recorded in the full energy range (6.900-8.120 keV; 0.33 h per spectrum) in order to measure accurate spectra in both the near-edge and the fine structure regions.

X-ray absorption data were analyzed using WinXAS (version 1.2) [31]. Raw spectra were shifted in energy in order to align the first inflection point in the Fe foil calibration spectra with the known absorption energy of Fe metal (7.112 keV) [30]. Linear fits to the pre-edge region (6.900-7.100 keV) were subtracted from the spectra, and the spectra were normalized by a sixth-order polynomial fit of the post-edge region (7.240-8.120 keV). Principal component analysis [25] and linear combination methods [26] were used to calculate the relative abundance of the various Fe phases using the near-edge spectral region between 7.090 and 7.240 keV for each sample and for the Fe reference compounds.

The approach used to identify chemical species and to measure their relative abundance involves using linear combinations of the spectra from reference compounds, which include the structures thought to be present in the sample, in order to fit the experimental near-edge spectra of each sample. In the present case, it is difficult to anticipate which of the many possible Fe carbides, oxides, and oxycarbides may be formed during reactions with CO or with synthesis gas. Moreover, some species may be stable only under FT synthesis conditions. Thus, they are not necessarily available as structurally pure references. In view of this, we have used principal component analysis (PCA) in order to identify sets of spectral features that increase or diminish in synchrony as the spectral series progresses. These sets of features comprise contributions from the spectra of chemical species that change in concentration as the sample evolves under *in situ* treatments.

During the reduction and carburization of Fe oxides in CO or in synthesis gas, PCA identified three major components involved in the phase changes; these components were Fe₂O₃, Fe₃O₄ and a carbide resembling Fe₃C. Therefore, *in situ* spectra were described using a linear combination of the near-edge spectra of these three reference compounds. Fe and FeO were specifically rejected by the PCA analysis, and their presence in linear combinations did not improve the spectral fits, suggesting that Fe and FeO do not occur as intermediates during reduction and carburization of Fe₂O₃ precursors. The target-transform application of the PCA led to an excellent fit quality to Fe₃C, using components generated from our catalyst spectra. The analysis of the fine structure, however, indicated that the carburized Fe catalyst did not achieve sufficient long-range order to be rigorously described as a specific crystallographic phase of Fe carbide; therefore, we refer to it only as FeC_x throughout the rest of this report.

Isothermal transient experiments to measure rates of product formation at FTS conditions similar to those for *in situ* XAS measurements, were carried out using on-line mass spectrometric analysis. A 0.2 g sample diluted with graphite (0.5 g, 180-250 μ , Alfa

AESAR, 99.998%) was loaded into a quartz microreactor and treated in He (Matheson, 99.999%, 0.268 mol/h) at temperatures up to 573 K and cooled under the same flow of He to 523 K. The He stream was switched to a flow of synthesis gas in Ar ($\text{H}_2/\text{CO}/\text{Ar}=40/20/40$ kPa, Matheson, 99.999%, total molar rate 0.268 mol/h) at 523 K. The resulting isothermal transients in the rate of evolution of several FTS products (CH_4 , H_2O and CO_2 , etc.) were measured as a function of time using on-line mass spectrometry (Leybold Inficon, Transpector Series). The rate of formation of CH_4 was used as a surrogate measure of the total FTS rates, because it can be measured accurately and changes with time on stream in parallel with the rate of formation of other hydrocarbon products. CH_4 selectivities change with time on stream by less than 5%; therefore, CH_4 formation rates accurately reflect the total rate of hydrocarbon synthesis.

3.5. Fe K-edge XANES of reference compounds

Figure 2 shows the near-edge spectra for the Fe_3C , FeO , Fe_3O_4 , and Fe_2O_3 reference compounds. The absorption edge at ~ 7.120 keV is caused by the ejection of Fe $1s$ electrons after absorption of a photon. The measured absorption edge energies for all reference compounds are listed in Table 1. These binding energies of $1s$ electrons increase with increasing Fe valence. The weak pre-edge features in the spectra of Fe oxides reflect electronic transitions from $1s$ atomic orbitals to unoccupied p - d hybrid molecular orbital final states; these transitions are dipole-forbidden in non-centrosymmetric structures.

Figure 2. Normalized Fe K-edge X-ray absorption spectra for Fe oxides and carbide.

Table 1. Absorption edge energies for Fe compounds with known structure and oxidation state.

Compound	Fe	Fe_3C	FeO	Fe_3O_4	Fe_2O_3
Binding Energy (keV)	7.112	7.112	7.119	7.123	7.124

3.6. *In situ* Fe K-edge XANES during reactions of Fe oxide precursors with CO

Figure 3 shows Fe near-edge spectra for the Fe_2O_3 sample during exposure to CO. No detectable changes in the spectra occurred below 450 K. Gradual changes occurred at temperatures between 450 K and 600 K, but the spectra then remained unchanged at higher temperatures. Thus, it appears that the formation of a stable compound is complete by ~ 600 K. A qualitative comparison of the reference spectra (Figure 2) with those of the samples after exposure to CO (Figure 3) suggests that structural transformations involve the intermediate formation of Fe_3O_4 and its ultimate conversion to FeC_x .

Figure 3. *In situ* Fe K-edge XANES spectra for Fe oxide in CO as a function of temperature. (1 mg precipitated Fe_2O_3 , CO flow rate=107 mol/g-atom Fe h)

A more quantitative assessment of these transformations is shown in Figure 4, which shows the relative abundances of the various phases required to describe the experimental near-edge spectra during reduction and carburization of Fe_2O_3 in CO. The reduction of Fe_2O_3 did not start until ~ 450 K. Above 450 K, the relative abundance of Fe_3O_4 increased, and then it decreased above 550 K, as Fe_3O_4 was converted to FeC_x . The concentration profiles for Fe_2O_3 , Fe_3O_4 , and FeC_x suggest that these transformations occurred in a sequential manner. The evidence for the rapid conversion of Fe_3O_4 to FeC_x (Figure 4) was provided by detailed temperature-programmed reduction and carburization studies of Fe_2O_3 in CO (Section 5) with concurrent measurements of the amounts of CO_2 evolved and of CO consumed using mass spectrometry. The reduction and carburization of Fe_2O_3 in synthesis gas ($\text{H}_2/\text{CO}=2$) followed the same reaction sequence as in CO, except that all structural changes occurred at slightly higher temperatures (~ 20 K).

Figure 4. *In situ* evolution of Fe_2O_3 in CO as a function of temperature. Fe_2O_3 (dot), Fe_3O_4 (square), FeC_x (triangle). (1 mg precipitated Fe_2O_3 , CO flow rate=107 mol/g-atom Fe h)

3.7. *In situ Fe K-edge XANES of Fe-K-Cu oxide precursors in synthesis gas*

Previous studies have shown that both K and Cu markedly increase FTS and water-gas shift reaction rates [1,4]. K also increases the olefin content and the molecular weight of FTS products [18,32]. The evolution of the Fe near-edge spectral features in Fe and Fe-K-Cu oxide precursors during exposure to synthesis gas was used in order to examine the effects of H_2 in modifying the structural details detected during carburization in CO, as

well as the role of the K and Cu on the rate and products of the transformation that occurs during the initial exposure of these oxide precursors to synthesis gas.

Figure 5 shows the near-edge spectra for Fe, Fe-Cu, Fe-K, and Fe-K-Cu oxide precursors measured *in situ* after contact with synthesis gas at 523 K for 5 h. The absorption edge energy was lower and the spectra resembled the Fe carbide spectrum (Figure 2) more closely when K or Cu was present in the sample. These effects of Cu or K were even stronger when both promoters were present.

Figure 5. *In situ* Fe K-edge spectra of Fe-K-Cu oxides in synthesis gas at 523 K for 5 h. (1 mg precipitated Fe_2O_3 , $\text{H}_2/\text{CO}=2$, synthesis gas flow rate=107 mol/g-atom Fe h).

3.8. Effects of K and Cu on catalyst structure and on FTS rates

The spectra of Fe, Fe-Cu, Fe-K, and Fe-K-Cu oxide precursors during exposure to synthesis gas at 523 K were described by linear combinations of the near-edge spectra of reference compounds. The structural evolution of unpromoted Fe_2O_3 as a function of time is shown in Figure 6. The Fe_3O_4 and FeC_x contributions approached constant values of ~70% and ~30%, respectively, after ~4 h. Carburization rates then decreased as the remaining Fe oxides became covered by a dense Fe carbide coating, which appears to inhibit the rate-determining oxygen diffusion step required for carburization processes. At 543 K, the FeC_x contribution increased to ~45% after 4 h, apparently because of faster oxygen diffusion at higher temperatures. Previous studies have suggested that the reduction and carburization (or nitridation) of transition-metal oxides are limited by the bulk diffusion of oxygen in the lattice of the corresponding oxide [33,34]. This was

inferred from the excellent agreement between the activation energies for the synthesis of transition-metal carbides or nitrides and those for the diffusion of oxygen in the oxides. The absence of Fe metal or FeO in the near-edge spectra of these samples confirms the rate-determining nature of oxygen diffusion steps. If the removal of oxygen atoms at crystallite surfaces or at oxide-carbide interfaces had occurred without the immediate availability of carbon to react with the resulting reduced species, nucleation of Fe metal and FeO crystallites would have occurred and such phases would have been detectable by X-ray absorption.

Figure 6. Phase evolution of Fe₂O₃ with time on stream after exposure to synthesis gas at 523 K (1 mg precipitated Fe₂O₃, H₂/CO=2, synthesis gas flow rate=107 mol/g-atom Fe h).

Figure 7 shows the structural evolution of Fe-Cu oxide precursors (Cu/Fe = 0.01) during exposure to synthesis gas (H₂/CO=2) at 523 K for 14 h. These data show that Fe₂O₃ converts to Fe₃O₄, and subsequently to FeC_x more rapidly than for the pure Fe oxide samples (Figure 6). CuO reduces to Cu readily in H₂ at 523 K; once reduced, it provides sites for H₂ dissociation, which in turn lead to adsorbed hydrogen species that reduce Fe₂O₃ to Fe₃O₄ at lower temperatures than for unpromoted Fe₂O₃.

The ultimate extent of carburization after long contact times (8 h) was also higher for Fe-Cu oxides (~45%; Figure 7) than for unpromoted Fe oxide samples (~30%; Figure 6). The more complete carburization of Cu-containing Fe₂O₃ precursors would be unexpected without changes in the size of the crystalline structures, because carburization rates become ultimately controlled by the rate of oxygen diffusion. Oxygen diffusion rates cannot be influenced by the mere presence of Cu metal sites at the surface of such structures. Instead, it appears that the presence of Cu metal species at Fe₂O₃ surfaces

leads to the simultaneous formation of a larger number of Fe_3O_4 or FeC_x nuclei, which then grow to consume a large fraction of the remaining Fe_2O_3 starting material. In contrast, the nucleation of these phases on pure Fe_2O_3 surfaces is likely to proceed through the formation of a uniform shrinking core of FeO_x encapsulated by a growing FeC_x layer or at least via the initial formation of a smaller number of nuclei. Our parallel XAS studies of the structural evolution of Fe_2O_3 during initial exposure to synthesis gas discussed in Section 5 have shown that Fe_2O_3 , once reduced to Fe_3O_4 , readily reduces and carburizes to FeC_x , at least in the near-surface regions, as indicated by the concurrent formation of Fe_3O_4 and FeC_x and the rapid attainment of steady-state FTS reaction rates.

The conversion of Fe_3O_4 to Fe_3C is accompanied by a substantial decrease in crystallite volume, because of the lower density of Fe_3O_4 (5.2 g/cm^3) compared with FeC_x (7.7 g/cm^3 for Fe_3C) [35]. The dense Fe carbide layers formed at pure Fe_3O_4 surfaces apparently provide an effective barrier to the diffusion of oxygen. In addition, the carburization of the shrinking oxide core cannot continue to completion without the nucleation of a void or the shattering of the carbide shell because of the density mismatch between the two phases. This shrinking core type of reduction is similar to the model proposed in previous studies, for the reduction behavior of transition-metal oxides [36].

Figure 7. Phase evolution of Fe-Cu oxide with time on stream after exposure to synthesis gas at 523 K (1 mg precipitated Fe_2O_3 , Cu/Fe=0.01, H_2/CO =2, synthesis gas flow rate=107 mol/g-atom Fe h).

The simultaneous formation of a larger number of FeC_x nuclei on Cu-promoted Fe_2O_3 leads to the growth of smaller carbide regions, which avoid both the longer diffusion

paths and the void nucleation or shell breakup required in pure Fe_3O_4 . This leads, in turn, to more complete carburization and to smaller FeC_x structures, with a higher surface area and a smaller oxygen diffusion distance, and with a larger density of sites for CO activation. The apparent correlation between FTS rates and the extent of carburization is not causal. Instead, both reflect the smaller size of the active carbide structures that form during FTS when Cu is present on the Fe_2O_3 precursors. This finding resolves the puzzling observed correlation between the extent of carburization and FTS rates, even when the formation of only a few near-surface layers of FeC_x is apparently sufficient to achieve steady-state FTS reaction rates. Although only the incipient conversion of Fe_3O_4 to FeC_x is required for Fe_2O_3 or Cu-containing Fe_2O_3 precursors to become active in FTS reactions, the smaller and more extensively carburized structures formed when Cu is present lead to the higher FTS rates observed on Cu-containing Fe_2O_3 precursors than on pure (Section 5). As we describe immediately below, K has a similar effect as Cu on FTS rates and on the rate and extent of carburization of Fe_2O_3 precursors.

Figure 8. Phase evolution of Fe-K oxide with time on stream after exposure to synthesis gas at 523 K (1 mg precipitated Fe_2O_3 , K/Fe=0.02, H_2/CO =2, synthesis gas flow rate=107 mol/g-atom Fe h).

Fe_2O_3 precursors modified by K (K/Fe = 0.02) reduce and carburize even more rapidly than Cu-promoted Fe_2O_3 (Figure 8), consistent with our reduction and carburization kinetic measurements on these samples using both CO and H_2/CO reactants. The similar reduction-carburization promotion introduced by K in both CO and H_2/CO suggests that the role of K is to increase the rate of CO activation on Fe_2O_3 surfaces (Section 5). In contrast, the effect of Cu is most evident when H_2 is also present with CO, because of the

role of Cu surfaces as H_2 dissociation sites. The presence of dispersed K species, probably as carbonates, also leads to the rapid incipient formation of multiple Fe_3O_4 and FeC_x nuclei and to the ultimate formation of smaller crystallites with carbided surfaces. In this manner, we reconcile the similar directional effects of Cu and K on FTS reaction rates and the apparent contradiction between the positive effects of the higher extents of carburization induced by K and Cu and the rate increase for FTS reactions, which appear to require only the near-surface conversion of Fe oxides to FeC_x (Section 5). During the incipient conversion of Fe oxides to carbides upon contact with synthesis gas, CH_4 formation rates initially increased rapidly as a layer of FeC_x formed, and then they increased at a slower rate as the surface area of the FeC_x structures continued to increase gradually with increasing extent of carburization (Section 5). Ultimately both the FeC_x content and the FTS rates reached their respective steady-state values.

Figure 9. Phase evolution of Fe-K-Cu oxide with time on stream after exposure to synthesis gas at 523 K (1 mg precipitated Fe_2O_3 , K/Fe=0.02, Cu/Fe=0.01, $H_2/CO=2$, synthesis gas flow rate=107 mol/g-atom Fe h).

Reduction and carburization processes were even faster when both Cu and K were present (Figure 9), than when samples were promoted by either K or Cu (Figures 7 and 8). Apparently, the presence of a larger number of "activation sites" provided by the combined contributions of both Cu and K at Fe_2O_3 surfaces, leads to an even larger number of incipient nucleation points than when only one of these promoters is present. The resulting higher density of FeC_x nuclei ultimately grow into even smaller crystallites, which provide a larger number of sites for CO and H_2 activation, leading to even faster

reduction and carburization, shorter diffusion distances required for complete carburization, and higher FTS reaction rates than on singly-promoted samples.

3.9. *CO chemisorption and surface area measurements*

Precipitated Fe oxides (0.2 g; diluted with graphite) were treated in flowing He (0.268 mol/h) up to 573 K and then cooled down to 523 K. The He stream was switched to a H₂/CO/Ar stream (40/20/40 kPa; 0.268 mol/h) at 523 K for 1 h and flushed with He (0.268 mol/h) at this temperature for 1 h in order to remove any reversibly adsorbed species. The samples were then cooled to RT before CO chemisorption and BET surface area measurements.

Two sets of temperature-programmed desorption (TPD) experiments were performed. In one experiment, a flow of CO/Ar stream (20/80 kPa; 0.268 mol/h) was passed through the sample for 0.5 h. Physisorbed species were removed by flushing the sample using Ar (0.268 mol/h) for 0.5 h. The amount of carbon species CO_x (CO+CO₂) evolved as the samples were heated in Ar flow (0.268 mol/h) at 0.167 K/s to 1000 K was measured by mass spectrometry. Another set of experiments followed the same protocol but without a CO chemisorption after FTS reaction. The difference between the peak areas under these two TPD curves was taken as a measure of the availability of active sites capable of chemisorbing CO reversibly at FTS temperatures. This method allows us to subtract from the total CO evolved those CO species formed from irreversibly adsorbed carbon species during FTS, as well as the CO_x produced from reaction of FeC_x with residual Fe oxides at temperatures much higher than those of the FTS reaction.

BET surface area measurements were carried out on samples after FTS reaction at 523 K and quenching to RT by passivating catalyst samples in flowing 1 % O₂/He at RT. N₂ physisorption measurements were performed at its normal boiling point (77 K) using an Autosorb 6 system (Quantachrome, Inc.). Surface areas were calculated using the BET method.

The formation of smaller crystallites and of a higher density of active sites when K and/or Cu are present during activation is consistent with measurements of the BET surface area and the CO chemisorption capacity after FTS reactions for 1 h (H₂/CO=2, 523 K; Table 2). BET surface areas were higher on samples containing K and/or Cu, consistent with the formation of active catalysts containing smaller crystallites. CO chemisorption uptakes increased with increasing BET surface area. The site density available for CO chemisorption was higher on K- or Cu-containing samples. Chemisorption uptakes reached their highest value for samples prepared from the Fe-K-Cu oxide precursors. These values correspond to about one monolayer (~15 CO/nm²) of chemisorbed CO. This suggests that K and/or Cu promote the formation of smaller Fe carbide crystallites, which in turn increase the number of sites available for CO adsorption/dissociation and consequently for the initial reduction and carburization and for steady-state FTS turnovers.

Table 2. The surface area and CO chemisorption results after 1 h FTS reactions; Fe carbide concentrations obtained from *in situ* XAS, and CH₄ formation rates from transient experiments, after 5 h FTS reactions.

Oxide precursor	Fe	Fe-Cu	Fe-K	Fe-K-Cu
Surface area (m ² /g)	13	17	18	23
Amount of CO _x desorbed before CO chemisorption (mmol/g-atom Fe)	12.2	14.1	23.4	56.9
Amount of CO _x desorbed after CO chemisorption (mmol/g-atom Fe)	20.3	27.9	40.9	95.7
Amount of CO chemisorbed (mmol/g-atom Fe)	8.1	13.8	17.5	38.8
CO chemisorption site density (molecule /nm ²)	5	6	7	13
FeC _x concentration ^a (atom %)	28.8	32.4	60.8	88.0
CH ₄ formation rate ^b (mmol/g-atom Fe s)	0.061	0.070	0.11	0.19

^aFeC_x concentration measured after exposure to synthesis gas at 523 K for 5 h (1 mg precipitated Fe₂O₃, K/Fe=0.02, Cu/Fe=0.01, H₂/CO=2, synthesis gas flow rate=107 mol/g-atom Fe h).

^bCH₄ formation rates measured after exposure to synthesis gas at 523 K for 5 h (0.2 g precipitated Fe₂O₃, K/Fe=0.02, Cu/Fe=0.01, H₂/CO=2, synthesis gas flow rate=64.3 mol/g-atom Fe h).

In order to explore the relation between the structure of the working catalysts and their catalytic performance, FTS rates were measured during exposure to synthesis gas at the same conditions (H₂/CO=2, 523 K) as the XAS experiments. Figure 10 shows the Fe carbide concentrations obtained from *in situ* XAS and the CH₄ formation rates measured in the corresponding transient FTS experiments on unpromoted precipitated Fe₂O₃ as a function of time. The rate of formation of CH₄ increased with increasing FeC_x content. This indicates that Fe carbide (FeC_x) is the stable Fe phase during FTS and provides the active surfaces required for FTS turnovers. On samples containing K and/or Cu (Table 2), FTS rates increased proportionally with the observed increase in FeC_x content (at long contact times) and in CO chemisorption uptakes. This supports the conclusion that the effect of K and Cu on the structure of catalysts is to provide a larger number of active Fe carbide sites for FTS reactions. The chemical promotion effects by K and/or Cu do not appear to be necessary in order to account for the increase in reaction rates observed

when Fe_2O_3 precursors are impregnated with these components. Cu does not influence the selectivity; the effects of K on FTS selectivity will be discussed in the next Section.

Figure 10. Fe carbide concentration (dots) obtained from XAS ($\text{H}_2/\text{CO}=2$, 523 K, synthesis gas flow rate=107 mol/g-atom Fe h), and CH_4 formation rate as function of time on unpromoted precipitated Fe_2O_3 ($\text{H}_2/\text{CO}=2$, 523 K, synthesis gas flow rate=64.3 mol/g-atom Fe h).

Clearly, K and Cu lead to the formation of FeC_x structures with higher specific surface area and smaller size. A consequence of their smaller size is their more complete carburization, which is not the direct cause of the higher FTS rates observed in the presence of K and/or Cu. Their more complete carburization reflects the shorter diffusion paths for lattice oxygen species in the smaller crystallites, but the attainment of steady-state FTS rates appears to require only the formation of FeC_x near surface layers, the FTS activity of which does not depend on the existence or chemical identity of a separate oxide phase residing within the carbide shell.

4. Effect of Zn, Cu and K on the reduction/carburization and catalytic performance of Fe catalysts

4.1. Methodology

We examine here a series of co-precipitated Fe and Zn oxides containing Zn, Cu and K (Zn/Fe=0-0.4, K/Fe=0-0.04, Cu/Fe=0-0.02; atomic ratios) in order to probe the roles of these additives on the structure, reduction/carburization behavior, and catalytic properties of Fe oxides. The surface area, bulk structure, and reduction and carburization behavior were systematically investigated using BET surface area measurements, X-ray diffraction (XRD) and temperature-programmed reaction (TPR) studies. In parallel, steady-state FTS rates and selectivities were measured as a function of the Zn, K and Cu contents at typical FTS conditions (493 K, 3.16 MPa) using a tubular reactor with plug-flow hydrodynamics in order to relate the observed catalytic promotion to the active structures formed during activation of the oxide precursors in H₂/CO mixtures.

4.2. Crystal structure

Powder X-ray diffraction (XRD) measurements were carried out using a Siemens Diffractometer D-5000 and Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$). X-ray powder diffraction patterns for Fe₂O₃-Zn precursors with Zn/Fe atomic ratios of 0-0.4 are shown in Figure 11. These diffraction data indicate that rhombohedral hematite (Fe₂O₃) with a corundum-type structure, forms in samples with Zn/Fe < 0.2, while a ZnFe₂O₄ phase with a cubic franklinite spinel-type structure appears along with hematite at higher Zn/Fe ratios. Fe₂O₃ and ZnFe₂O₄ co-exist at intermediate Fe/Zn ratios. ZnFe₂O₄ is the only detectable phase in the sample with the highest Zn/Fe ratio (0.4); its broad diffraction peaks reflect the Zn-deficient nature of the Fe-Zn spinel structure, which requires a Zn/Fe ratio of 0.5 for the formation of stoichiometric ZnFe₂O₄. Precipitated Fe-Zn oxides appear to be present in the form of a mixture of Fe₂O₃ and ZnFe₂O₄. The only Zn-containing phase is ZnFe₂O₄, and it acts as a textural promoter that increases the surface area of Fe₂O₃-Zn precursors, as shown in the next section. At low Zn concentrations (Figure 11; patterns a-c), Zn is detected only as small ZnFe₂O₄ crystallites, which appear to inhibit the sintering of Fe₂O₃ at high temperatures (623-673 K). At higher Zn contents (Figure 11; patterns d and e), it is likely that ZnFe₂O₄ crystallites provide a matrix for the isolation of individual Fe₂O₃ crystallites. Zn also titrates Fe by forming ZnFe₂O₄, a less reducible compound than Fe₂O₃; this tends to weaken the structural promotion by Zn by preventing the reduction of some of the Fe and its contribution to the pool of active sites. Thus, intermediate Zn/Fe ratios are likely to lead to optimum catalytic performance. The impregnation of potassium and copper and the subsequent treatment in air did not influence the crystalline phases detected by X-ray diffraction. This shows that Fe-Zn oxide structures, once formed, remain stable during subsequent aqueous impregnation and thermal treatment.

Figure 11. X-ray diffraction patterns of Fe_2O_3 -Zn samples with different Zn/Fe ratios. (a) 0, (b) 0.05, (c) 0.1, (d) 0.2, and (e) 0.4.

4.3. Surface areas of Fe_2O_3 -Zn-K-Cu oxide precursors

The textural promotion effects of ZnFe_2O_4 on the surface area of Fe oxide precursors were examined by N_2 physisorption measurements for K- and/or Cu-promoted Fe_2O_3 -Zn samples. BET surface areas were measured using N_2 physisorption at its normal boiling point, after evacuating the samples at 393 K for 3 h. The BET surface area of Fe_2O_3 -Zn-K-Cu increased monotonically with increasing Zn/Fe ratio (Figure 12). The surface area for the sample with a Zn/Fe ratio of 0.4 is almost twice that for Zn-free Fe_2O_3 (96 vs 53 m^2g^{-1}). The addition of K and/or Cu to Fe-Zn oxides did not influence surface areas, suggesting that K and Cu reside at Fe oxide crystallite surfaces and that they do not influence the structure or the dispersion of the previously established Fe oxide phase. These data suggest that Zn, as a ZnFe_2O_4 phase, inhibits the sintering of Fe oxides, by keeping Fe oxides from migrating, and hence preventing sintering during treatments at high temperatures or by providing anchoring or nucleation sites for Fe oxides during precipitation or thermal treatment. However, it is not clear if this increase in surface area alone accounts for the higher FTS rates observed on Zn-promoted samples [16] or what

the optimum Zn/Fe ratio is; therefore, the catalytic behavior of on K- and Cu-promoted Fe oxides with different Zn/Fe ratios was examined in order to establish a suitable Zn concentration for maximum FTS reaction rates.

Figure 12. BET Surface areas of K- and/or Cu-promoted $\text{Fe}_2\text{O}_3\text{-Zn}$ (K/Fe=0.02; Cu/Fe=0.01) samples as a function of Zn/Fe ratios: (●) $\text{Fe}_2\text{O}_3\text{-Zn-K}_2\text{-Cu}_1$ sample, (○) $\text{Fe}_2\text{O}_3\text{-Zn-Cu}_1$ sample, (□) $\text{Fe}_2\text{O}_3\text{-Zn-K}_2$ sample.

4.4. Zn promotion effects on Fischer-Tropsch Synthesis rates and selectivity

Steady-state FTS rates and selectivities (493 K, 3.16 MPa) on $\text{Fe}_2\text{O}_3\text{-Zn-K-Cu}$ catalysts with a constant K and Cu content (K/Fe=0.02, Cu/Fe=0.01) but different Zn contents, were determined in a fixed-bed single-pass flow reactor with plug-flow hydrodynamics. This reactor was held within a three-zone furnace controlled by three temperature controllers (Watlow, Series 982 and 988). The tubular reactors were constructed of stainless steel (SS 304, 1.27 cm outer diameter and 1 cm inner diameter). Axial temperature profiles were measured using a type K movable thermocouple contained within a 0.32 cm thermowell. The temperatures at all bed positions were within ± 0.5 K of the average bed temperature. All lines after the reactor were kept at 433-553 K and a vessel placed immediately after the reactor was held at 408 K to collect liquid products. Another vessel was placed at ambient pressure and temperature after a sampling valve,

which collected gaseous components (at ambient pressure and 523 K) for injection into a gas chromatograph.

The catalysts (100-180 μ , 0.4 g) were diluted with 11 g of quartz granules (100-180 μ) in order to avoid temperature gradients. These quartz granules were washed with concentrated nitric acid and treated in air at 973 K before use. The Fe catalysts were activated using flowing synthesis gas ($H_2/CO=2$) at 0.1 MPa by increasing the temperature from 298 K to 423 K at a rate of 0.167 K/s and from 423 K to 543 K at 0.017 K/s. The catalyst was held at 543 K for 1 h, following which the reactor was set to the desired operating conditions.

Table 3. Effect of Zn loading on the surface area and the steady state performance of a Fe_2O_3 -K-Cu catalyst (K/Fe=0.02, Cu/Fe=0.01; $H_2/CO=2$, 493 K, 3.16 MPa, CO conversion=16-18%).

Sample	Zn/Fe=0	Zn/Fe=0.1	Zn/Fe=0.4
Surface area (m^2/g)	53	65	96
CO conversion rate (mol CO/h.g-at.Fe)	1.52	2.40	2.63
CO ₂ formation rate (mol CO/h.g-at.Fe)	0.19	0.30	0.21
Hydrocarbon formation rate (mol CO/h.g-at.Fe)	1.33	2.10	2.52
CO ₂ selectivity (%)	12.3	12.3	7.6
CH ₄ selectivity (%) ^a	1.7	1.8	2.3
C ₅₊ selectivity (%) ^a	86.6	87.6	85.6
<i>I</i> -C ₅ H ₁₀ / <i>n</i> -C ₅ H ₁₂ ratio	1.9	1.8	2.0

^a CH₄ and C₅₊ selectivities are reported on a CO₂-free basis.

A $H_2/CO/N_2$ mixture with N_2 being the internal standard (0.62/0.31/0.07 mole; Praxair: 99.9% H_2 , 99.9% CO, 99.99% N_2) was used as the reactant. This reactant mixture was purified using activated carbon (Sorb-Tech RL-13) to remove metal carbonyls and a molecular sieve trap (Matheson, Model 452A) to remove water. All flows were metered using electronic mass flow controllers (Porter, Model 201-AFASVCAA). Reactant and product streams were analyzed on-line using a gas chromatograph (Hewlett Packard, Model 5890 Series II) equipped with a 10-port sampling valve and two sample loops. The contents of one sample loop were injected into a cross-linked methyl silicone capillary column (HP-1, 50 m $\times$ 0.32 mm; 1.05 μ film). The contents of the other loop were

injected into a Porapak Q (15.2 cm $\times$ 0.318 cm) packed column. Ar, N₂, CO, CO₂, and light hydrocarbons eluting from the packed column were analyzed using a thermal conductivity detector (TCD). A flame ionization detector (FID) was used to analyze all hydrocarbon products as they eluted from the capillary column. The concentrations of all hydrocarbons up to C₁₅ were measured using these chromatographic protocols.

These results are shown in Table 3 at similar CO conversion levels. The presence of Zn at a Zn/Fe atomic ratio of 0.1 increased CO conversion rates (from 1.5 to 2.4 mol CO/h.g-at. Fe), but additional increases in the Zn/Fe ratio from 0.1 to 0.4 did not lead to higher FTS rates. The additional increase in surface area brought about by these higher Zn contents occurs at the expense of the reaction of some of the Fe oxide precursor to form less reducible ZnFe₂O₄. FTS selectivities (CH₄, C₅₊, and *l*-pentene/*n*-pentane ratios) were almost unchanged by the presence of Zn. It appears that Zn acts only as a textural promoter and that a Zn/Fe atomic ratio of $\sim$ 0.1 provides an optimum balance between a higher surface area and a decrease in the fraction of the Fe that is activated during contact with synthesis gas at FTS conditions. Therefore, a Zn/Fe atomic ratio of 0.1 was chosen to study the effects of Cu and K on FTS reaction rates and selectivities.

4.5. Reduction kinetics of Fe₂O₃-Zn-K-Cu precursors in H₂

The rates of reduction and carburization of K- and/or Cu-promoted Fe₂O₃-Zn were measured by using temperature-programmed reaction (TPR) methods with H₂ or CO as the reactant. Samples (0.2 g) were placed in a quartz cell (10 mm i.d.) and first treated in 20% O₂ in Ar (0.268 mol/h) to 673 K at 0.33 K/s, held at 673 K for 900 s, and then cooled to ambient temperature in Ar. The flow was then switched to 20% H₂ or 20% CO in Ar (0.268 mol/h) and the reactor temperature was increased to 1000 K at 0.167 K/s. The concentrations of reactants and products were measured using a mass spectrometer (Leybold Inficon Instruments Co., Inc.) equipped with a differentially pumped sampling system.

Figure 13 shows the rates of removal of lattice oxygen atoms during treatment of Fe₂O₃-Zn-K-Cu precursors using H₂ as the reductant. The areas under these reduction peaks were calibrated using CuO. The respective amounts of oxygen in the two reduction peaks in Figure 13 show that Fe₂O₃ reduces in two steps. Fe₃O₄ is first formed and then reduced to form Fe metal. The presence of Cu in Fe-Zn oxides (Zn/Fe=0.1) causes the reduction of Fe₂O₃ to Fe₃O₄ to occur at temperatures $\sim$ 140 K lower than in Cu-free samples (Figure 13b); these reduction processes occur at temperatures identical to those required for the reduction of CuO to Cu metal (Figure 13a). As CuO reduces, Cu crystallites nucleate and provide H₂ dissociation sites, which in turn lead to reactive hydrogen species capable of reducing Fe oxides at relatively low temperatures. Potassium, shown to be present as a carbonate by X-ray absorption spectroscopy [37], does not influence the reduction of Fe₂O₃, but it weakly inhibits the reduction of Fe₃O₄ to Fe metal. When both Cu and K are present, the reduction profile resembles that for Fe₂O₃-Zn-Cu; Fe₂O₃ reduces at temperatures characteristic of CuO reduction ($\sim$ 470 K), except for a small fraction of the Fe₂O₃, which is not affected by Cu, apparently because of inefficient contact between some of the Fe₂O₃ precursor and the CuO promoter. The presence of Cu or K does not strongly influence the reduction of Fe₃O₄ to Fe, because thermodynamics and the

nucleation of a new crystal structure, and not H₂ dissociation steps, control reduction rates at these higher temperatures [36,38]. The effects of Cu on the kinetics of removal of lattice oxygen from Fe-Zn oxides suggest that Cu increases the initial rate of nucleation of reduced Fe oxide phases. Consequently, a larger number of nuclei become available for crystallization of reduced FeO_x and FeC_x crystallites; as a result higher FTS rates would be expected when precursor activation occurs in synthesis gas in the presence of these promoters.

Figure 13. Oxygen removal rates of Fe₂O₃-Zn-K-Cu (Zn/Fe=0.1) in H₂. (a) CuO, (b) Fe₂O₃-Zn (c) Fe₂O₃-Zn-Cu₁, (d) Fe₂O₃-Zn-K₂, (e) Fe₂O₃-Zn-K₂-Cu₁ (0.2 g sample, 0.167 K/s ramping rate, 20% H₂/Ar, 0.268 mol/h flow rate).

4.6. Reduction and carburization kinetics of Fe₂O₃-Zn-K-Cu in CO

The rates of oxygen removal and of carbon introduction using CO were measured as a function of temperature on Fe₂O₃-Zn-K-Cu oxides by monitoring the concentrations of CO and CO₂ in the effluent stream. Two general stoichiometric reactions are involved in the carburization of Fe oxides. The removal of lattice oxygen occurs via the stoichiometry given by:

Initially Fe oxides reduce to form CO₂ and a Fe center with valence lower than in Fe₂O₃. In a sequential or alternate step, CO carburizes Fe oxides to form CO₂ and Fe carbides:

In this step, oxygen removal and carbon deposition occur concurrently. The excess amount of CO consumed relative to that of CO₂ produced provides a measure of the extent of carbon deposited. The different CO and CO₂ stoichiometries associated with these two steps, allows to decouple oxygen removal and carbon deposition steps using the following equations:

$$R_O = \text{Oxygen Removal Rate} = 2 R_{\text{CO}_2} - R_{\text{CO}} \quad (1)$$

$$R_C = \text{Carbon Introduction Rate} = R_{\text{CO}} - R_{\text{CO}_2} \quad (2)$$

where, R_{CO_2} is the rate of formation of the CO₂ product and R_{CO} is the rate of consumption of the CO reactant. We note that this approach remains rigorous even if the actual reactions do not proceed as written, because equations (1) and (2) merely reflect an oxygen and a carbon balance, respectively. Together with the structures detected by X-ray diffraction at various stages during reaction with CO, this approach probes the temperatures required, the rates of reduction and carburization, as well as the structure and stoichiometry of the carbides formed.

Figure 14. Rates of CO consumption (solid line) and CO₂ formation (dashed line) for the Fe₂O₃-Zn-K₂-Cu₁ sample (Zn/Fe=0.1) during the reduction and carburization in CO (0.2 g sample, 0.167 K/s ramping rate, 20% CO/Ar, 0.268 mol/h flow rate). Temperatures (dotted line) at which reactions were terminated for XRD measurements (Figure 15).

CO consumption and CO₂ formation rates are shown in Figure 14 for Fe₂O₃-Zn-K-Cu samples as a function of temperature. The stoichiometries for oxygen removal and carbon introduction measured from the areas under these peaks indicate that the reduction-carburization of Fe oxides proceeds in two sequential steps. Fe₂O₃ first reduces to Fe₃O₄ at ~543 K; then, Fe₃O₄ concurrently reduces and carburizes to a mixture of Fe_{2.5}C and Fe₃C in the 543-723 K temperature range. Above 723 K, CO disproportionation occurs via the Boudouard reaction, with the formation of excess amorphous carbon; this amorphous carbon is not present in the carbide structures prevalent at temperatures below 723 K. X-ray diffraction patterns at various stages in these processes (Figure 15) confirmed the sequential nature of the structural evolution from Fe₂O₃ to Fe₃O₄ and then to mixtures of Fe_{2.5}C and Fe₃C. Figure 6 shows oxygen removal and carbon introduction rates as a function of temperature for Fe₂O₃-Zn-K-Cu samples using CO as the reactant. The areas under the oxygen removal peaks for Fe₂O₃-Zn confirm that Fe₂O₃ is first converted to Fe₃O₄ without any detectable carburization.

Figure 15. X-ray diffraction patterns showing the phase evolution of the Fe₂O₃-Zn-K₂-Cu₁ oxide (Zn/Fe=0.1) during the reduction and carburization in CO at (a) 560 K, (b) 730 K, and (c) >730 K (0.2 g sample, 0.167 K/s ramping rate, 20% CO/Ar, 0.268 mol/h flow rate).

The temperatures required and the areas under the carbon introduction peaks show that reduced Fe₃O₄ species are then concurrently carburized to form FeC_x (Figure 16a). The addition of K and/or Cu to Fe₂O₃ did not influence this reduction-carburization sequence,

but the reduction-carburization rates increased and the required temperatures decreased when these promoters were present (Figure 16b-d). Cu increased oxygen removal rates and decreased the temperature required for the reduction and concurrent carburization of Fe_3O_4 by ~ 50 K. This effect of Cu on reduction rates was weaker than that observed when H_2 was used as the reductant, apparently as a result of the slower activation of CO relative to H_2 on Cu metal surfaces. The addition of K to Fe_2O_3 shifted the oxygen removal peak to higher temperatures (Figure 16c), but the rate of incipient carburization, indicated by the low-temperature shoulder in the carbon introduction peak, was slightly lower than on the unpromoted Fe oxide (Figure 16a). This may merely reflect a catalytic effect of K-promoted Fe oxides on CO activation rates or just the faster nucleation of FeC_x crystallites on oxide surfaces promoted with K carbonate. When both K and Cu were present in the catalyst, the combined effect of Cu in promoting the oxygen removal and K in CO activation leads to the highest reduction/carburization and Fe carbide nucleation rates, as indicated by the markedly lowered temperatures required for oxygen removal and carbon introduction (Figure 16d).

Figure 16. Oxygen removal and carbon introduction rates for the Fe_2O_3 -Zn-K-Cu (Zn/Fe=0.1) samples in CO. (a) Fe_2O_3 -Zn (b) Fe_2O_3 -Zn-Cu₁, (c) Fe_2O_3 -Zn-K₂, (d) Fe_2O_3 -Zn-K₂-Cu₁ (0.2 g sample, 0.167 K/s ramping rate, 20% CO/Ar, 0.268 mol/h flow rate)

In summary, K and Cu increased the rates of reduction and carburization of Fe-Zn oxide precursors when CO is used as the reactant. These faster rates of nucleation reflect a larger number of nuclei, which ultimately lead to smaller crystallites and to higher catalytic surface areas as determined by *in situ* X-ray absorption measurements shown in Section 3. These promotional effects of K and Cu, which appear to be mostly textural in nature, are confirmed by the FTS catalytic data described in the next section.

4.7. Effects of K and Cu on Fischer-Tropsch Synthesis rate and selectivity

The promotional effects of Cu and K on the behavior of Fe-Zn FTS catalysts were examined using a tubular reactor with plug-flow hydrodynamics. Fe₂O₃-ZnO catalysts (Zn/Fe=0.1) with varying K (K/Fe=0, 0.02 and 0.04) and Cu (Cu/Fe=0, 0.01, 0.02) contents were used to convert H₂/CO mixtures at 493 K and 3.16 MPa. FTS rates and selectivities are shown in Table 4.

Table 4. Steady state performance of Fe₂O₃-Zn catalysts (Zn/Fe=0.1) with different loadings of K and Cu (H₂/CO=2, 493 K, 3.16 MPa, CO conversion = 14-18%).

K/Fe atomic ratio (×100)	0	0	2	2	2	4
Cu/Fe atomic ratio (×100)	0	1	0	1	2	1
CO conversion rate (mol CO/h.g-at.Fe)	0.70	0.87	1.23	2.40	2.43	2.49
CO ₂ formation rate (mol CO/h.g-at.Fe)	0.02	0.06	0.10	0.30	0.32	0.30
Hydrocarbon formation rate (mol CO/h.g-at.Fe)	0.68	0.81	1.13	2.10	2.11	2.19
CO ₂ selectivity (%)	2.3	6.5	8.5	12.3	12.9	12.1
CH ₄ selectivity (%) ^a	4.8	10.2	1.8	1.8	2.0	2.5
C ₅₊ selectivity (%) ^a	81.9	62.1	87.5	87.6	86.7	85.2
<i>I</i> -C ₅ H ₁₀ / <i>n</i> -C ₅ H ₁₂ ratio	1.9	1.7	1.8	1.8	1.8	2.0
<i>I</i> -C ₁₀ H ₂₀ / <i>n</i> -C ₁₀ H ₂₂ ratio	0.4	0.4	1.7	1.8	1.7	1.7

^a CH₄ and C₅₊ selectivities are reported on a CO₂-free basis.

CO conversion rates increased with K (K/Fe=0.02) or Cu (Cu/Fe=0.01) addition, suggesting that the promotion of carburization and reduction rates by these species led to either a larger number of active sites or to sites with a higher intrinsic activity. These rates were higher on the sample containing both K and Cu ($\text{Fe}_2\text{O}_3\text{-Zn-K}_2\text{-Cu}_1$) than on Cu-promoted ($\text{Fe}_2\text{O}_3\text{-Zn-Cu}_1$), K-promoted ($\text{Fe}_2\text{O}_3\text{-Zn-K}_2$), or unpromoted ($\text{Fe}_2\text{O}_3\text{-Zn}$) catalysts. The effects of K and Cu on the doubly promoted sample are nearly additive, suggesting an almost independent effect of each promoter. The previously reported decrease in FTS rates with increasing K content on Fe-Si oxide precursors [18], was not observed in catalysts made from Fe-Zn precursors, possibly because of the higher surface of the precursors or the more dispersed nature of the promoter in the latter samples. For Fe-Zn oxide precursors, no detectable changes in FTS rates or selectivities were observed upon increasing the atomic K/Fe ratio above 0.02 (Table 2). Similarly, an increase in Cu/Fe atomic ratios from 0.01 to 0.02 did not influence reaction rates or product selectivities (Table 2). Thus, a Cu/Fe ratio of 0.01 and a K/Fe ratio of 0.02 led to optimum FTS catalytic properties. It appears that the surface density of promoters or the extent to which they contact the Fe oxide precursors does not continue to increase as the Cu or K contents increased above a threshold value. This threshold value is most rigorously expressed as a promoter surface density and it corresponds to $\sim 1 \text{ Cu/nm}^2$ and $\sim 2 \text{ K/nm}^2$.

Hydrocarbon formation rates (in mol CO converted/h.g-at. Fe) are shown in Figure 17 for the various promoted $\text{Fe}_2\text{O}_3\text{-ZnO}$ catalysts as a function of CO conversion. The effects of increasing CO conversion were similar on all catalysts, suggesting that these catalysts show similar kinetic dependences on reactant and product concentrations.

Figure 17. Hydrocarbon formation rates on $\text{Fe}_2\text{O}_3\text{-Zn}$ (●), $\text{Fe}_2\text{O}_3\text{-Zn-Cu}_1$ (▲), $\text{Fe}_2\text{O}_3\text{-Zn-K}_2$ (◆), and $\text{Fe}_2\text{O}_3\text{-Zn-K}_2\text{-Cu}_1$ (■) catalysts (493 K, 3.16 MPa, $\text{H}_2/\text{CO}=2$).

CO₂ selectivities are shown as a function of CO conversion in Figure 18 and compared at a similar CO conversion value (14-18%) in Table 4. CO₂ selectivities increased with increasing CO conversion on all four catalysts (Figure 18); they were higher on Fe₂O₃-ZnO promoted by both Cu and K than on unpromoted or singly promoted samples at all conversion levels. H₂O, which forms as a primary product during FTS reactions on Fe catalysts, reacts with CO to give CO₂ via secondary water gas shift reactions. The local slope of the curves in Figure 18 reflect the contributions from secondary reactions (predominately water gas shift), while CO₂ selectivities extrapolated to zero conversion reflect the relative rates at which chemisorbed oxygen, formed in CO activation steps, is removed by adsorbed CO (as CO₂) or by adsorbed hydrogen (as H₂O). The slopes of the CO₂ selectivity curves in Figure 18 are similar for K-promoted Fe₂O₃-Zn-Cu₁ and Fe₂O₃-Zn catalysts, consistent with similar secondary water gas shift rates. Fe₂O₃-Zn and Fe₂O₃-Zn-Cu₁ catalysts without K resemble each other in their secondary water gas shift rates, which are lower than those measured on K-containing samples. This lack of effect of Cu is unexpected, in view of the high water gas shift rates reported on Cu-based catalysts [39]. The presence of Cu predominately influences the intrinsic oxygen removal selectivity by promoting the removal of oxygen using CO. On the other hand, Fe₂O₃-Zn-K₂ and Fe₂O₃-Zn-K₂-Cu₁ showed significantly larger slopes than K-free samples, indicating that the presence of K increases secondary water gas shift rates, as also reported for Fe-Si oxide precursors [18], without influencing the primary oxygen removal selectivity.

Figure 18. CO₂ selectivities on Fe₂O₃-Zn (●), Fe₂O₃-Zn-Cu₁ (▲), Fe₂O₃-Zn-K₂ (◆), and Fe₂O₃-Zn-K₂-Cu₁ (■) catalysts (493 K, 3.16 MPa, H₂/CO=2).

The presence of K in $\text{Fe}_2\text{O}_3\text{-Zn}$ catalysts led to lower CH_4 selectivities (Table 4, Figure 19) and higher C_{5+} selectivities (Table 4, Figure 20), apparently by decreasing the availability of H^* atoms required for termination of growing chains via hydrogen addition reactions to form paraffins. In contrast, the addition of Cu to $\text{Fe}_2\text{O}_3\text{-Zn}$ increased CH_4 selectivities and decreased C_{5+} selectivities (Table 4, Figure 20). When Cu and K are both present, the tendency of Cu to decrease product molecular weight almost disappeared. Potassium also inhibits secondary reactions of α -olefins, such as isomerization to internal or branched olefins and hydrogenation to n -paraffins, by titrating acid sites or uncarbided sites on $\text{Fe}_2\text{O}_3\text{-Zn}$. The titration of these sites and the apparent decrease in the availability of adsorbed hydrogen also lead to lower rates of secondary hydrogenation reactions. *I*-Pentene/*n*-pentane ratios are shown in Figure 21 on various catalysts, and also compared in Table 4 at similar CO conversions. The olefin content in the K-promoted catalysts increased slightly with CO conversion. This is likely to reflect an inhibiting effect of H_2O or CO_2 on the termination of growing chains by hydrogen addition, as reported previously [16]. The intrinsic olefin/paraffin ratios (extrapolated to zero CO conversion) are actually higher on catalysts without K, but the tendency of K-free catalysts to hydrogenate olefins leads to a marked decrease in olefin content with increasing residence time. Similarly, *I*-decene/*n*-decane ratios (Figure 22, Table 4) are significantly higher in the presence of K and the effects of K are much stronger for the larger olefins, because of their greater propensity for secondary reactions.

Figure 19. CH_4 selectivities on $\text{Fe}_2\text{O}_3\text{-Zn}$ (●), $\text{Fe}_2\text{O}_3\text{-Zn-Cu}_1$ (▲), $\text{Fe}_2\text{O}_3\text{-Zn-K}_2$ (◆), and $\text{Fe}_2\text{O}_3\text{-Zn-K}_2\text{-Cu}_1$ (■) catalysts (493 K, 3.16 MPa, $\text{H}_2/\text{CO}=2$).

Figure 20. C₅⁺ selectivities on Fe₂O₃-Zn (●), Fe₂O₃-Zn-Cu₁ (▲), Fe₂O₃-Zn-K₂ (◆), and Fe₂O₃-Zn-K₂-Cu₁ (■) catalysts (493 K, 3.16 MPa, H₂/CO=2).

Figure 21. 1-C₅H₁₀/n-C₅H₁₂ ratios on Fe₂O₃-Zn (●), Fe₂O₃-Zn-Cu₁ (▲), Fe₂O₃-Zn-K₂ (◆), and Fe₂O₃-Zn-K₂-Cu₁ (■) catalysts (493 K, 3.16 MPa, H₂/CO=2).

Figure 22. $1\text{-C}_{10}\text{H}_{20}/n\text{-C}_{10}\text{H}_{22}$ ratios on $\text{Fe}_2\text{O}_3\text{-Zn}$ (●), $\text{Fe}_2\text{O}_3\text{-Zn-Cu}_1$ (▲), $\text{Fe}_2\text{O}_3\text{-Zn-K}_2$ (◆), and $\text{Fe}_2\text{O}_3\text{-Zn-K}_2\text{-Cu}_1$ (■) catalysts (493 K, 3.16 MPa, $\text{H}_2/\text{CO}=2$).

5. Design of high activity Fe Fischer-Tropsch Synthesis catalysts by promotion with Cu, Ru and by synthesis of high surface area Fe-Zn precursors

5.1. Introduction

Fe-based catalysts provide an attractive complement to Co-based catalysts for the Fischer-Tropsch synthesis (FTS). They lead to more olefinic products and to lower CH₄ selectivities than Co-based catalysts over a wide range of temperatures and H₂/CO ratios, including synthesis gas with low H₂/CO ratios derived from coal or biomass [1]. Cobalt catalysts are typically more active than Fe-based catalysts, but they require low reaction temperatures (470-490 K), because the selectivity to desired C₅₊ hydrocarbons and the quality of the diesel range products becomes unacceptably low at higher temperatures [40]. The lower apparent FTS rates on Fe-based catalysts reflect to some extent the lower dispersion of their active component. Thus, an increase in the surface area and in the density of active sites during synthesis and during the initial stages of use in synthesis gas may bring Fe-based catalysts into the range of productivity and reaction conditions typical of Co-based catalysts [41]. The resulting opportunities for using Fe-based catalysts at lower temperatures may also lead to even heavier products and to lower CO₂ selectivities. Such active Fe-based catalysts would also allow direct comparisons of FTS turnover rates on Fe and Co catalysts at similar conditions. Such comparisons require reliable measurements of the number of exposed active components in both catalysts. These measurements are available for Co catalysts, but not for Fe-based catalysts, which activate to form complex mixtures of oxide and carbide phases only during Fischer-Tropsch synthesis reactions.

Here, we report the design and synthesis of Fe-based catalysts with hydrocarbon synthesis productivities (per catalyst mass) similar to those on Co-based materials. We also report direct comparisons of turnover rates on these two types of catalysts. These comparisons exploit a method developed to titrate the number of CO binding sites on Fe catalysts after activation and FTS reaction. Our studies of the catalytic properties of Fe (Section 3) and Fe-Zn (Section 4) catalysts have shown that FTS rates increased with K or Cu addition, and that the rate was highest when both K and Cu were present [16]. These promotional effects reflect predominately the formation of Fe carbides with higher dispersion when K or Cu is present. Our initial attempt to improve the density of active sites in these materials and to decrease the CO₂ selectivity led us to replace Cu, the active component in the best available water-gas shift (WGS) catalysts [39], with Ru. Ru was chosen because it does not introduce undesired methanation side reactions and it is an active, but impractical, FTS catalyst [42], and a promoter for Co-based catalysts [43]. Ru increased FTS rates more effectively than Cu at similar atomic contents without detectable changes in chain growth selectivity. As in the case of Cu, Ru predominately increased the density of active sites by favoring the nucleation of smaller Fe carbide and Fe₃O₄ domains as Fe₂O₃ precursors convert to active catalysts during the initial stages of FTS reactions. This conclusion was confirmed by surface area, CO chemisorption, and isothermal transient experiments. These smaller crystallites, in turn, provided higher surface areas, shorter bulk diffusion distances, more complete carburization of Fe₂O₃ precursors, and higher steady-state FTS rates.

Higher FTS rates were also achieved by synthetic protocols leading to higher precursor surface areas. These led to a higher Fe_2O_3 dispersion, which was maintained during catalyst activation in synthesis gas, especially when decomposition and activation procedures were designed in order to minimize the subsequent sintering of these high surface area oxide precursors. FTS rates and selectivities were measured on these materials at operation conditions typical of Co catalysts ($\text{H}_2/\text{CO}=2$, 2.0 MPa, 473 K) on a high surface area Fe-Zn-K-Cu oxide catalyst and on a Co/ SiO_2 catalyst. The obtained results show that turnover rates are higher on exposed Co surface atoms than on Fe-based active sites. Fe-based catalysts designed with a high density of CO binding sites, however, can lead to similar and even higher hydrocarbon synthesis productivities and to lower CH_4 selectivities than Co-based FTS catalysts.

5.2. Comparison of the Reduction and Carburization Behavior of Fe-Zn-K oxides Promoted with Ru or Cu

Figure 23. Oxygen removal rates for Fe-Zn-K-Cu(Ru) oxides in H_2 . (a) Fe-Zn-K₂, (b) Fe-Zn-K₂-Cu₁, and (c) Fe-Zn-K₂-Ru₁. (0.2 g sample; K/Fe=0.02, Cu(Ru)/Fe=0.01; 0.167 K/s ramping rate; 20% H_2/Ar , 0.268 mol/h flow rate).

Figure 23 shows oxygen removal rates for Fe-Zn-K-Cu and Fe-Zn-K-Ru oxides as a function of temperature during exposure to H_2 . The amounts of oxygen removed in each of the two major reduction peaks indicate that the reduction of Fe-Zn-K-Cu(Ru) oxides

follows the same sequential reduction steps observed for Fe_2O_3 discussed in Section 4. Fe_2O_3 reduces to Fe_3O_4 and then to Fe in two steps with distinct kinetics. The addition of Cu to Fe-Zn-K oxides led to incipient reduction at ~ 130 K lower temperatures than on Cu-free samples (Figures 23a and 23b), as a result of H_2 dissociation sites formed by reduction of CuO to Cu metal at low temperatures. Ru had similar but stronger effects on the temperature required for reduction of Fe_2O_3 to Fe_3O_4 and of Fe_3O_4 to Fe (by an additional 50 K and 100 K, respectively). It appears that Ru, because of its higher metal dispersion, lower reduction temperature, or higher H_2 dissociation turnover rate, leads to hydrogen dissociation at lower temperatures than for oxide precursors with similar atomic Cu content.

Figure 24. Oxygen removal and carbon introduction rates for Fe-Zn-K-Cu(Ru) samples in CO. (a) Fe-Zn-K₂, (b) Fe-Zn-K₂-Cu₁, and (c) Fe-Zn-K₂-Ru₁. (0.05 g sample; K/Fe=0.02, Cu(Ru)/Fe=0.01; 0.167 K/s ramping rate; 20% CO/Ar, 0.268 mol/h flow rate).

Figure 24 shows oxygen removal and carbon introduction rates for Fe-Zn-K-Cu and Fe-Zn-K-Ru oxides as a function of temperature using CO as the reducing and carburizing reagent. Fe-Zn-K-Cu(Ru) oxides convert via reduction/carburization steps identical to those for pure Fe_2O_3 (Section 4). Fe_2O_3 reacts with CO to form Fe_3O_4 and the latter simultaneously reduces and carburizes to form a mixture of $\text{Fe}_{2.5}\text{C}$ and Fe_3C , confirmed by X-ray diffraction and denoted here as FeC_x (Section 4). The temperature required for these reduction-carburization processes is lowest for Fe-Zn-K₂-Ru₁ and highest for the sample without either Cu or Ru (Fe-Zn-K₂). Ru-promoted samples reduced and carburized at a temperature ~ 30 K lower than the Cu-containing samples. The promoting effects of Ru and Cu on the reduction and carburization of Fe-Zn oxide precursors by CO were weaker than their respective effects when H_2 was used as the reductant, but Cu, and especially Ru, clearly increased the rate of oxygen removal using CO as the reductant. The effects of Ru and Cu on the rate of reduction and carburization of Fe-Zn oxide precursors suggest that these components increase the initial rate of nucleation of reduced Fe-containing phases (Fe_3O_4 , FeC_x). The resulting larger number of nuclei then lead to a

better dispersion of these reduced phases, as shown earlier (Section 3), and to a larger number of active sites for Fischer-Tropsch synthesis reactions. This expectation was confirmed by the catalytic measurements reported in the next section.

5.3. *Effect of Ru and Cu on Fischer-Tropsch Synthesis rate and selectivity*

Fischer-Tropsch synthesis rates were measured on Fe-Zn-K₂, Fe-Zn-K₂-Cu₁, and Fe-Zn-K₂-Ru₁ samples at 508 K and 2.14 MPa. Measurements were conducted at different CO space velocities; steady-state hydrocarbon formation rates (mol CO/h.g-at.Fe) are shown as a function of the resulting extent of CO conversion in Figure 25a. These rates were higher on the Ru-promoted sample (Fe-Zn-K₂-Ru₁) than on Cu-promoted (Fe-Zn-K₂-Cu₁) or unpromoted (Fe-Zn-K₂) catalysts. The effects of increasing conversion on FTS rates were similar on all samples, suggesting similar kinetic dependencies on reactant and product concentrations on all catalysts. Ru and Cu appear to increase the number of active sites available on catalysts derived from Fe-Zn oxide precursors, without any detectable changes in turnover rates, in the kinetics of chain growth or CO hydrogenation on active sites, or in the pathways available for these reactions. This is consistent with the nearly identical selectivities to C₅₊ (Figure 25c) and CH₄ (compared in Table 5 at similar CO conversions), and with the similar α -olefin/*n*-paraffin ratios (Figure 25d) on all catalysts at all conversion levels.

CO₂ selectivities increased with CO conversion on all three catalysts (Figure 25b). They were higher on Cu- or Ru-promoted Fe-Zn-K oxides than on unpromoted catalysts at all conversion levels. The slopes of the CO₂ selectivity-CO conversion curves in Figure 25b are similar on all three catalysts, suggesting that the rate of secondary water-gas shift reactions are not influenced by these promoters, even though high water-gas shift rates have been reported on Cu-containing catalysts [39]. The extrapolated y-intercepts in Figure 25b reflect the relative rates of removal of chemisorbed oxygen atoms, formed in CO dissociation steps, using either CO or hydrogen. Cu and Ru increase slightly the value of this intercept in Figure 25b, suggesting an increase in the probability of oxygen removal via reactions with CO when these promoters are present. Another possible explanation for these higher intercepts is the presence of intrapellet H₂O concentration gradients caused by diffusional restrictions, which can become more severe within liquid-filled pores as volumetric productivities become higher in the presence of Cu or Ru promoters.

The catalytic properties of Fe-Zn-K₂, Fe-Zn-K₂-Cu₁, and Fe-Zn-K₂-Ru₁ are compared in Table 5 at similar CO conversions. The addition of Cu or Ru to Fe-Zn oxide precursors led to two-fold and four-fold increases in hydrocarbon synthesis rates, respectively. These promotion effects cannot be explained by the FTS activity of the Ru promoter, which, even if atomically dispersed, would account for only about 20% of the rate increase observed upon Ru addition, based on reported FTS turnover rates on Ru [19].

Figure 25. Steady-state FTS rates and selectivities on promoted Fe oxide catalysts as a function of CO conversion ($H_2/CO=2$, 508 K and 2.14 MPa). (a) Hydrocarbon formation rate, (b) CO₂ selectivity, (c) C₅+ selectivity, and (d) 1-C₅H₁₀/n-C₅H₁₂ ratio. (■) Fe-Zn-K₂, (●) Fe-Zn-K₂-Cu₁, and (◆) Fe-Zn-K₂-Ru₁.

C₅₊ formation rates increased proportionately with the observed increase in hydrocarbon synthesis rates, leading to nearly identical C₅₊ selectivities on all catalysts. The slightly lighter products formed on samples promoted with Cu or Ru reflects the lower surface density of the potassium promoter at the higher surface areas prevalent in metal-promoted samples, as discussed below. Ru, and to a lesser extent Cu, appear to increase the number of FTS active sites formed during the activation of Fe-Zn oxide precursors. This proposal is confirmed below by measurements of the structural evolution of the active phases during reaction and by surface area and CO chemisorption measurements after catalyst activation and Fischer-Tropsch synthesis.

Table 5. Steady-state Fischer-Tropsch synthesis rates and selectivities on Fe-Zn-K₂, Fe-Zn-K₂-Cu₁, and Fe-Zn-K₂-Ru₁ samples (atomic ratios: Zn/Fe=0.1, K/Fe=0.02, Cu(Ru)/Fe=0.01; H₂/CO=2, 508 K, 2.14 MPa, CO conversion is 13-16%).

Sample	Fe-Zn-K ₂	Fe-Zn-K ₂ -Cu ₁	Fe-Zn-K ₂ -Ru ₁
CO conversion rate (mol CO/h.g-at. Fe)	1.7	3.5	7.2
CO ₂ formation rate (mol CO/h.g-at. Fe)	0.2	0.7	1.1
Hydrocarbon formation rate (mol CO/h.g-at. Fe)	1.5	2.8	6.0
CO ₂ selectivity (%)	11.5	20.2	16.8
CH ₄ selectivity (%) ^a	2.0	2.4	2.8
C ₅₊ selectivity (%) ^a	88.2	85.3	85.0
<i>I</i> -C ₅ H ₁₀ / <i>n</i> -C ₅ H ₁₂ ratio	2.3	2.5	2.5

^aCH₄ and C₅₊ selectivities are reported on a CO₂-free basis.

5.4. Surface areas and CO chemisorption site densities on fresh and activated Fe-Zn-K-Cu(Ru) oxides

Table 6 shows BET surface areas and CO chemisorption uptakes (measured as illustrated in Section 3.9) on Fe-Zn-K₂, Fe-Zn-K₂-Cu₁, and Fe-Zn-K₂-Ru₁ oxide precursors after FTS reactions for 1 h at the conditions indicated. BET surface areas are also reported for the oxide precursors after thermal treatment in air at 673 K for 4 h, but before FTS reactions. Before reaction, BET surface areas were not affected by the presence of Cu or Ru promoters. After FTS reactions for 1 h, surface areas were higher on the metal-promoted samples than on unpromoted samples, suggesting that smaller Fe₃O₄ and FeC_x crystallites form when Cu or Ru are present during *in situ* activation of Fe-Zn oxide precursors.

Table 6. BET surface areas and CO chemisorption uptakes on Fe-Zn-K₂, Fe-Zn-K₂-Cu₁, and Fe-Zn-K₂-Ru₁ samples after FTS reactions (H₂/CO=2, 523 K, 1 h); Fe carbide concentrations were obtained from *in situ* XAS measurements; CH₄ formation rates were obtained from isothermal transient experiments.

Sample	Fe-Zn-K ₂	Fe-Zn-K ₂ - Cu ₁	Fe-Zn-K ₂ - Ru ₁
Surface area before FTS (m ² /g)	56	65	63
Surface area after FTS ^a (m ² /g)	23	31	39
Amount of CO _x desorbed before CO chemisorption (mmol/g-at. Fe)	11.3	65.3	68.4
Amount of CO _x desorbed after CO chemisorption (mmol/g-at. Fe)	31.6	109.9	124.5
Amount of CO chemisorbed (mmol CO/g-at. Fe)	20.3	44.6	58.1
FeC _x concentration ^b (atom %)	11.8	23.6	57.1
CH ₄ formation rate ^c (mmol/s.g-at. Fe)	0.173	0.262	0.372

^aSurface areas measured after exposure to synthesis gas at 523 K for 1 h (0.2 g sample, K/Fe=0.02, Cu/Fe=0.01, H₂/CO=2, synthesis gas flow rate=64.3 mol/h.g-at. Fe).

^bFeC_x concentration measured after exposure to synthesis gas at 523 K for 5 h (1 mg precipitated Fe₂O₃, K/Fe=0.02, Cu/Fe=0.01, H₂/CO=2, synthesis gas flow rate=107 mol/h g-at. Fe).

^cCH₄ formation rates measured after exposure to synthesis gas at 523 K for 1 h (0.2 g sample, K/Fe=0.02, Cu/Fe=0.01, H₂/CO=2, synthesis gas flow rate=64.3 mol/h.g-at. Fe).

CO chemisorption uptakes on activated samples were significantly higher when Cu or Ru were present, suggesting the presence of a larger number of CO adsorption sites when Fe-Zn oxide precursors are activated in the presence of Cu or Ru. Chemisorption uptakes were higher on the Ru-promoted sample than on the Cu-promoted sample, a trend also observed for hydrocarbon synthesis rates. This apparent correlation between FTS rates and CO chemisorption uptakes was also observed on Zn-free Fe-K-Cu samples (Section 3). It is consistent with Cu and Ru leading to the formation of smaller Fe carbide crystallites, which in turn provide a higher density of sites for CO chemisorption and for FTS reaction turnovers. Thus, it appears that these reduction-carburization promoters increase the rate of catalyst activation by providing a large number of nucleation sites, which favor the formation of smaller FeC_x and Fe₃O₄ crystallites. These smaller crystallites, and the faster carburization kinetics introduced by Cu and Ru, were probed directly during activation of Fe-Zn oxide precursors using *in situ* X-ray absorption spectroscopy, as described in the next section.

5.5. Structural characterization of Fe-Zn-K-Cu(Ru) catalysts during Fischer-Tropsch Synthesis using X-ray absorption spectroscopy

In situ Fe K-edge X-ray absorption spectroscopy was used to monitor the structural evolution of Fe-Zn oxides during activation and FTS reactions and the effects of Cu and Ru on the kinetics of formation and on the relative abundance of species formed as Fe-Zn oxide precursors undergo activation during contact with synthesis gas. Fe_2O_3 , Fe_3O_4 , and FeC_x were identified by principal component analysis and the sample spectra were described as linear combinations of these standard compounds as a function of time in contact with synthesis gas. FeC_x concentrations are reported as Fe atomic fractions as a function of contact time in Figure 26. The reduction and carburization rates and the extent of carburization of these materials are smaller than for the Zn-free samples reported in Section 3, because Zn species, in the form of ZnFe_2O_4 , inhibit the rate of reduction/carburization processes (Section 4). The structure evolves, however, in a manner similar to that previously found for Zn-free samples - via the initial formation of Fe_3O_4 and the rapid subsequent transformation of this phase into FeC_x . Since the details of such transformations are very similar for Fe and Fe-Zn oxide precursors, we restrict our discussion here to the extent and kinetics of FeC_x formation and to the effect of Cu and Ru on these properties for Fe-Zn oxide precursors.

Figure 26. The evolution of Fe carbides during *in situ* XAS measurement of Fe-Zn-K-Cu(Ru) samples in synthesis gas. (a) Fe-Zn-K₂, (b) Fe-Zn-K₂-Cu₁, and (c) Fe-Zn-K₂-Ru₁. (1 mg sample, K/Fe=0.02, Cu(Ru)/Fe=0.01, H₂/CO=2, synthesis gas flow rate=107 mol/h.g-at. Fe).

Figure 26 shows that Cu, and especially Ru, increased carburization rates and the steady-state extent of carburization of Fe-Zn oxide precursors promoted also with K. The faster carburization kinetics of oxides promoted with Ru or Cu using synthesis gas is similar to their promotion effect reported above using either H₂ or CO as the reducing agents. As shown in Figure 26, the extent of carburization is also higher on samples promoted with Ru or Cu than on the Fe-Zn-K sample. The FeC_x content, however, reached a nearly constant value after ~8 h on stream at the conditions of this study (Figure 26). Thus, while faster carburization may lead to the more rapid attainment of steady-state FTS reaction rates, it should not lead to higher steady-state FTS reaction rates, which are measured after contact with synthesis gas for more than 24 h. Also, it is not obvious how the greater extent of carburization achieved when Cu or Ru are present would lead to higher steady-state FTS rates, because previous studies using Fe₂O₃ precursors have shown that the carburization of one or two near-surface layers is sufficient to attain steady-state FTS reaction rates. We conclude that the extent of carburization is controlled by the diffusion path for the removal of lattice oxygen from the core of Fe oxide precursors. Thus, the shorter diffusion path within the smaller crystallites formed during activation on promoted samples is responsible for the greater extent of carburization on the promoted samples. In this manner, both the higher FTS rates and the faster and more extensive carburization find a common cause in the role of promoters in nucleating Fe active phase as smaller crystallites. No causal relationship between the extent of carburization and the observed FTS reaction rates is warranted by these observations.

5.6. *Isothermal transient analysis of reduction, carburization, and Fischer-Tropsch Synthesis products during activation of Fe-Zn-K-Cu(Ru) catalysts*

Fischer-Tropsch synthesis rates were measured during exposure to synthesis gas at the same conditions as those used to measure X-ray absorption spectra of these samples (H₂/CO=2, 523 K) in order to relate the observed structural evolution to the rate of hydrocarbon formation as Fe oxide catalyst precursors activate during FTS. CH₄ formation rates on Fe-Zn-K oxide precursors promoted with Cu or Ru are shown in Figure 27 as a function of time. For unpromoted Fe-Zn-K oxides, a short induction period was observed upon initial contact with synthesis gas. CH₄ was immediately detected, however, on Fe-Zn oxides promoted with Cu or Ru. CH₄ formation rates during initial contact with synthesis gas and at steady state were higher on promoted catalysts. The initial increase in CH₄ formation rates is accompanied by the formation of an excess amount of CO₂ and H₂O, indicative of the removal of lattice oxygen during the initial reduction and carburization of the oxide precursors. These reduction-carburization processes are faster on Ru-containing samples than on Cu-containing or unpromoted Fe-Zn-K samples. Steady-state FTS rates were attained after ~1 h in contact with synthesis gas, even though X-ray absorption spectra detected a continuing increase in FeC_x content up to ~8 h. These data confirm the previous proposal that FTS reactions are influenced only by the density of active carbide sites in near-surface layers, irrespective of the presence of a remaining Fe oxide core. These data are also consistent with FTS data obtained at higher pressures and reported above, and with a role of Cu or Ru in nucleating smaller and more easily carburized structures from Fe-Zn-K oxide precursors.

On samples containing Cu or Ru (Table 6), FTS rates increased proportionally with the observed increase in FeC_x content and in CO chemisorption uptakes. All these results clearly show that Cu and Ru favor the formation of a more dispersed active phase, and that chemical promotion effects, such as an increase in the turnover rate of FeC_x sites, are unnecessary in order to account for the observed increase in FTS rates when Cu or Ru are present during the activation of Fe-Zn oxide precursors. These conclusions, taken together with the previous observation that higher surface area precursors prepared by incorporating ZnO during the precipitation of Fe_2O_3 also led to higher FTS reaction rates [16], led us to attempt the synthesis of more highly dispersed active carbide phases by using Fe oxide precursors with higher surface areas.

Figure 27. CH_4 formation rate as a function of reaction time in contact with synthesis gas ($\text{H}_2/\text{CO}=2$, 523 K, synthesis gas flow rate=107 mol/h.g-at.Fe). (a) Fe-Zn-K₂, (b) Fe-Zn-K₂-Cu₁, and (c) Fe-Zn-K₂-Ru₁ sample.

5.7. Synthesis of Fe-Zn-K-Cu oxide precursors with high surface area

Our efforts to improve the dispersion and site density of the FeC_x structures formed during reaction included the use of specific synthetic protocols designed to increase the surface area of Fe-Zn oxide precursors and to minimize the sintering that occurs during drying and impregnation with Cu(Ru) and K. In this section, we examine the promoter concentrations required in order to optimize catalysts prepared from precursors with varying surface area. We also show that the surface density of the Cu and K promoters ($\sim 2 \text{ K/nm}^2$ and 1 Cu/nm^2), and not their atomic content, are the relevant controlling variables in determining the dispersion and catalytic properties of FeC_x structures.

Several factors, such as the drying processes after precipitation or impregnation and the temperature and time of thermal treatments designed to decompose precursors, influence the surface area of Fe-Zn oxide precursors. These factors were systematically examined in order to increase catalyst surface areas and FTS reaction rates. The effect of precipitation pH was examined previously; it was found that a pH of 7.0 held constant during precipitation, led to the highest precursor surface areas [44]. The effect of Zn/Fe ratio on the performance of Fe-Zn-K catalysts for FTS reactions was also previously examined and a Zn/Fe atomic ratio of 0.1 was found to give highest FTS reaction rates (Section 4). Sintering of porous materials often occurs as a result of pore pinching during the final stages of drying, even at low temperatures. This process is particularly severe with water, because of its high surface tension ($\gamma=72$ mN/m at 298 K). Alcohols have lower surface tensions (e.g. $\gamma=22$ mN/m for ethanol and isopropanol at 298 K); they also act as surface-active agents that decrease the surface tension of aqueous solutions [35]. Therefore, the water contained within the pores in Fe-Zn oxide precipitates was replaced before drying by extensive washing with either ethanol or isopropanol in an attempt to inhibit sintering of Fe-Zn oxide precursors during drying.

Figure 28. BET surface areas of Fe-Zn and Fe-Zn-K₂-Ru₁ samples dried with various intrapore liquids as a function of thermal treatment temperature. (a) Fe-Zn precursor washed by intrapore water (■), (b) Fe-Zn precursor washed by intrapore ethanol (●), (c) Fe-Zn precursor washed by intrapore isopropanol (+), (d) Fe-Zn precursor washed by ethanol and subsequently promoted with K and Ru (♦) (K/Fe=0.02, Ru/Fe=0.01). (All the samples were treated in dry air at the stated temperature for 4 h).

Figure 28 shows the surface area of Fe-Zn oxide precursors with different intrapore liquids after thermal treatment at various temperatures (Figure 28a-c). After drying at 398 K for 12 h, precipitates washed with ethanol or isopropanol showed higher Fe-Zn oxyhydroxide surface areas than precipitates dried without replacing intrapore water with alcohols (215 vs. 148 m²/g). The similar precursor surface areas obtained with isopropanol and ethanol are consistent with the similar surface tension of these two liquids. All other precipitation variables were kept constant; therefore, it appears that the drying step and the surface tension of the intrapore liquids during drying strongly influence the pore structure and the surface area of the Fe-Zn oxide precursors. Our data show that a high space velocity of dry air (~2000 cm³/h.g-cat.) is also required in order to minimize sintering during the decomposition of these oxyhydroxide precursors. The replacement of H₂O with lower surface tension liquids during drying and the rapid removal of H₂O as it forms during oxyhydroxide decomposition at higher temperatures are critical in preserving the initial surface area of these precipitated precursors.

The temperature and time of the final thermal treatment in air also influenced Fe-Zn oxide surface areas. After drying oxyhydroxide precipitates with different intrapore liquids at 398 K for 12 h, they were treated in flowing dry air at various temperatures for 4 h in order to identify optimum treatment protocols. All samples showed the expected decrease in surface area with increasing treatment temperature, but the higher surface area samples obtained by drying alcohol-containing precipitates were more sensitive to this treatment temperature. X-ray diffraction confirmed that Fe-Zn hydroxides formed poorly crystalline Fe₂O₃ at ~543 K. Zn, possibly as the ZnFe₂O₄ phase detected in samples with higher Zn/Fe ratio (>0.2) and treated at higher temperatures (~673 K), was well dispersed and not detected in these alcohol-washed samples. It appears that thermal treatment at 543 K provides a compromise between structural purity and a high surface area in Fe₂O₃, and that the surface area of the resulting oxide is highest when intrapore water is replaced with lower surface tension liquids, such as alcohols.

The effects of impregnation with K and Cu promoters on surface areas were also investigated. Fe-Zn oxyhydroxide precursors were impregnated with K carbonate (K/Fe=0.02) and dried at 393 K for 12 h. Ru (Ru/Fe=0.01) was then added as Ru nitrosyl nitrate using similar impregnation procedures. The addition of K to Fe-Zn hydroxide precursors decreased its surface area (220 vs. 192 m²/g), apparently because of pore collapse caused by the removal of high surface tension intrapore liquids. Similarly, the subsequent impregnation of the Fe-Zn-K with Ru led to an additional decrease in its surface area. Each impregnation and subsequent drying decreased the surface area by 10-20%. Ru-promoted Fe-Zn-K hydroxides were then treated at different temperatures in order to examine the effect of treatment temperature on surface area (Figure 28d). The effects of temperature on the surface area of Fe-Zn-K-Ru oxides were similar to those found in Fe-Zn oxides. The surface area of Ru-promoted Fe-Zn-K oxides decreased from 142 to 96 m²/g as thermal treatment temperatures increased from 523 to 623 K.

Based on these surface areas for Fe-Zn hydroxides and Fe-Zn-K-Ru oxide precursors prepared by different methods, we selected a procedure for maximizing the surface area of Fe-Zn-K-Cu samples. Fe-Zn hydroxide precursors were first prepared by co-

precipitation at a constant pH of 7.0 and the precipitates were thoroughly washed with ethanol in order to replace intrapore water. Fe-Zn hydroxide precursors were then treated at 543 K for 4 h in flowing dry air (2000 cm³/h.g-cat). The resulting Fe-Zn oxide precursors were impregnated with K and Cu using incipient wetness impregnation method and aqueous solutions of Cu nitrate and K carbonate. The amounts of K (K/Fe=0.04) and Cu (Cu/Fe=0.02) were chosen so as to maintain the K and Cu surface densities at the levels previously shown to lead to maximum FTS reaction rates on conventionally prepared samples (~2 K-atom/nm²; 1 Cu-atom/nm²). The surface area of the resulting Fe-Zn-K₄-Cu₂ oxides was 120 m²/g, almost twice that of the Fe-Zn-K₂-Cu₁ oxide samples. As a result, the K and Cu content were chosen to be about twice as high as those in the conventionally prepared Fe-Zn-K₂-Cu₁ sample. A Fe-Zn-K₂-Cu₁ sample prepared from high surface area Fe-Zn oxide precursors led to lower FTS rates and to significantly lighter products than a sample with the higher promoter concentrations (Fe-Zn-K₄-Cu₂), suggesting the presence of sub-optimum levels of K and Cu and confirming the relevant role of atomic surface density as the defining variable in the design of these promoted catalytic materials.

5.8. *Site density of active species and promoters and effects on the Fischer-Tropsch Synthesis*

The relevance of improvements in surface area to the catalytic performance of these materials in FTS reactions was confirmed by the FTS rate and selectivity measurements on a high surface area Fe-Zn-K₄-Cu₂ oxide (120 m²/g) and on a lower surface area Fe-Zn-K₂-Cu₁ oxide prepared *via* conventional methods (65 m²/g). The amounts of K and Cu in the Fe-Zn-K₄-Cu₂ sample were chosen in order to maintain the same surface density of promoters as in the Fe-Zn-K₂-Cu₁ sample prepared from Fe-Zn oxide precursors with lower surface area. Steady-state FTS rates and selectivities at 508 K and 2.14 MPa are shown as a function of CO conversion in Figure 29. Hydrocarbon synthesis rates are about two-fold higher on Fe-Zn-K₄-Cu₂ than on Fe-Zn-K₂-Cu₁, a difference that parallels the difference in surface area for their respective Fe-Zn oxide precursors. The similarities between these two samples in CO₂ and C₅₊ selectivities, in α -olefin/*n*-paraffin ratios, and in their kinetic response of FTS rates to changes in conversion, suggest that the synthetic protocols used to increase the precursor surface areas led to a larger number of active sites in working catalysts, without detectable changes in chain growth pathways.

Figure 30 shows FeC_x concentrations obtained from XAS measurements of the structural evolution of these oxide precursors during FTS reactions. Figure 31 shows the corresponding CH₄ formation rates on these two samples at the same conditions used for the X-ray absorption experiments. Both the extent of carbide formation and the steady-state CH₄ formation rate are significantly higher on Fe-Zn-K₄-Cu₂ than on Fe-Zn-K₂-Cu₁. The consistent correlation between the Fe carbide concentration and FTS rates is again not causal, but it confirms that promoters (Ru, Cu, K) and higher surface area precursors increase the density of active sites in the Fe carbide structures prevalent during steady-state Fischer-Tropsch synthesis. Accordingly, we examined next whether further increases in the surface density of these promoters leads to additional improvements in active site density and in FTS rates.

Figure 29. Comparison of the FTS activity of (●) Fe-Zn-K₂-Cu₁, and (▲) Fe-Zn-K₄-Cu₂ as a function of CO conversion at steady-state reaction conditions (H₂/CO=2, 508 K and 2.14 MPa). (a) Hydrocarbon formation rate, (b) CO₂ selectivity, (c) C₅+ selectivity, and (d) 1-C₅H₁₀/n-C₅H₁₂ ratio.

Figure 30. FeC_x concentrations as a function of time on (a) $\text{Fe-Zn-K}_2\text{-Cu}_1$ and (b) $\text{Fe-Zn-K}_4\text{-Cu}_2$ samples as a function of reaction time during *in situ* X-ray absorption measurements in synthesis gas (1 mg precipitated sample, $\text{H}_2/\text{CO}=2$, synthesis gas flow rate=107 mol/h.g-at. Fe).

Figure 31. CH_4 formation rates as a function of time in contact with synthesis gas at the conditions of X-ray absorption measurements shown in Figure 8 ($\text{H}_2/\text{CO}=2$, 523 K, synthesis gas flow rate=107 mol/h.g-at. Fe). (a) $\text{Fe-Zn-K}_2\text{-Cu}_1$ sample, (b) $\text{Fe-Zn-K}_4\text{-Cu}_2$ sample.

We prepared a Fe-Zn-K-Cu sample using the same Fe-Zn oxide precursor and treated the sample at the same conditions as the Fe-Zn-K₂-Cu₁ sample but added a higher K concentration (Fe-Zn-K₄-Cu₁).

Table 7. Steady-state FTS rates and selectivities ($H_2/CO=2$, 508 K, 2.14 MPa, CO conversion is 13-16%), and the characterization results for Fe-Zn-K₂-Cu₁, Fe-Zn-K₄-Cu₁ and Fe-Zn-K₄-Cu₂ samples after FTS reactions.

Sample	Fe-Zn-K ₂ -Cu ₁	Fe-Zn-K ₄ -Cu ₁	Fe-Zn-K ₄ -Cu ₂
CO conversion rate (mol CO/h.g-at. Fe)	3.5	3.6	6.8
CO ₂ formation rate (mol CO/h.g-at. Fe)	0.7	0.8	1.4
Hydrocarbon formation rate (mol CO/h.g-at. Fe)	2.8	2.8	5.4
CO ₂ selectivity (%)	20.2	22.4	20.5
CH ₄ selectivity (%) ^a	2.4	2.4	3.8
C ₅₊ selectivity (%) ^a	85.3	85.5	80.8
<i>l</i> -C ₅ H ₁₀ / <i>n</i> -C ₅ H ₁₂ ratio	2.5	2.5	2.7
Surface area before FTS (m ² /g)	65	58	120
Surface area after FTS ^b (m ² /g)	31	26	43
Amount of CO _x desorbed before CO chemisorption (mmol/g-at. Fe)	65.3	72.0	75.2
Amount of CO _x desorbed after CO chemisorption (mmol/g-at. Fe)	109.9	112.3	141.1
Amount of CO chemisorbed (mmol CO/g-at. Fe)	44.6	40.3	65.9
FeC _x concentration ^c (atom %)	23.6	-	69.2
CH ₄ formation rate ^d (mmol/s.g-at. Fe)	0.262	0.289	0.527

^aCH₄ and C₅₊ selectivities are reported on a CO₂-free basis.

^bSurface areas measured after exposure to synthesis gas at 523 K for 1 h (0.2 g sample, K/Fe=0.02, Cu/Fe=0.01, $H_2/CO=2$, synthesis gas flow rate=64.3 mol/h g-at. Fe).

^cFeC_x concentration measured after exposure to synthesis gas at 523 K for 5 h (1 mg precipitated Fe₂O₃, K/Fe=0.02, Cu/Fe=0.01, $H_2/CO=2$, synthesis gas flow rate=107 mol/h g-at. Fe).

^dCH₄ formation rates measured after exposure to synthesis gas at 523 K for 1 h (0.2 g sample, K/Fe=0.02, Cu/Fe=0.01, $H_2/CO=2$, synthesis gas flow rate=64.3 mol/h g-at. Fe).

Table 7 compares FTS performance, surface area, CO chemisorption uptake, and the extent of carburization for Fe-Zn-K₂-Cu₁, Fe-Zn-K₄-Cu₁ and Fe-Zn-K₄-Cu₂ catalysts. Fe-Zn-K₂-Cu₁ and Fe-Zn-K₄-Cu₁ samples have similar surface areas, but different potassium contents and surface densities (2 vs. 4 K/nm²); yet, similar FTS reaction rates, CO chemisorption uptakes, and extents of carburization were obtained. This suggests that the higher K surface density did not lead to a further increase in the number of active sites, possibly because excess potassium leads to larger promoter domains without a significantly better contact between the promoter and the Fe oxide precursors or a higher actual surface density of potassium species. We have observed that increasing Cu or K concentrations beyond those required to achieve surface densities of 1 and 2 atom/nm², respectively, did not increase FTS reaction rates on conventionally prepared samples. Fe-Zn-K₂-Cu₁ and Fe-Zn-K₄-Cu₂ samples have different BET surface areas but similar apparent surface densities of K and Cu on the available surface area. The Fe-Zn-K₄-Cu₂ sample with the higher surface area shows higher FTS rates and a higher density of CO binding sites, indicating that higher precursor surface areas lead to proportionately higher FTS rates and active site densities, as long as the promoter surface densities are kept above a threshold level. These results suggest that promoter concentrations are more appropriately defined in terms of surface density in designing catalysts with similar and optimum promoter contents as the surface areas of Fe oxide precursors are changed by modifying precipitation, drying, and promoter impregnation protocols. The parallel increases in FTS rates, surface area, CO adsorption site availability, and steady-state concentration of Fe carbides suggest that higher FTS activity can be achieved by the design and appropriate promotion of high surface area oxide precursors.

5.9. Fischer-Tropsch Synthesis Rates and Selectivities on Fe-based catalysts – A comparison

The apparent low Fischer-Tropsch synthesis rates on Fe-based catalysts at reaction conditions typically used for Co-based catalysts (473 K-488 K) has led to their predominant use at higher temperatures (500 K-543 K). Here, we compare FTS reaction rates and selectivities on a Fe-Zn-K₄-Cu₂ catalyst with those on previously reported Fe-based catalysts.

The Fe-Zn-K₄-Cu₂ sample is compared with previously reported Fe-based catalysts in Table 8 for nearly stoichiometric reactants (H₂/CO=1.7-2.0) and at relatively high CO conversions (~50%). The results from the low-surface area Fe-Zn-K₂-Cu₁ sample are representative of the catalyst reported in reference [16]. The CO conversion rate and the hydrocarbon synthesis productivity on Fe-Zn-K₄-Cu₂ are about twice that of the Ruhrchemie AG catalyst (Fe-SiO₂-K_{5.9}-Cu_{4.4}) [45], and nearly three times higher than that of the Fe-Zn-K₂-Cu₁ catalyst, even though our Fe-Zn-K₄-Cu₂ catalyst was tested at lower temperatures (508 K vs. 523-543 K). Fe-Zn-K₄-Cu₂ also compares well with a Fe-Si_{4.6}-K_{1.4} catalyst tested at 543 K [18,46]. CO₂ selectivities are lower on Fe-Zn-K₄-Cu₂ than on the other catalysts, predominately because of the lower reaction temperatures made possible by its high surface area and FTS activity. The proper design of synthesis, promotion, and activation protocols that increase the density of FTS active sites have led

to additional improvements in hydrocarbon synthesis productivities, even after several decades of active research on Fe-based FTS catalysts.

Table 4. Steady-state FTS performance of various Fe-based catalysts using natural gas-derived synthesis gas ($H_2/CO=1.7-2.0$)

Catalyst	Fe-Zn-K ₄ - Cu ₂	Fe-Zn-K ₂ - Cu ₁	Fe-Si _{4.6} - K _{1.4} [18,46]	Fe-SiO ₂ -K _{5.9} - Cu _{4.4} [Ruhchemie LP33/81] [45]
Reactor Type	Fixed-Bed	Slurry	Slurry	Spinning Basket
Temperature (K)	508	543	543	523
Pressure (MPa)	2.14	0.50	1.31	2.40
H ₂ /CO ratio	2.0	2.0	1.7	2.0
CO space velocity (NL/h.g-cat)	3.4	1.4	5.7	2.4*
CO conversion (%)	50.8	55.5	50.0*	52.7
CO rate (mol CO/h.g-cat)	0.08	0.03	0.12*	0.05*
Hydrocarbon productivity (g/h.kg-cat)	765	258	1008*	404
CO ₂ selectivity (%)	31.7	48.6	40.0*	42.3*

*- Values calculated based on reported data or graphs

6. Comparison of the performance of a Fe-Zn-K-Cu and Co/SiO₂ catalysts at Co conditions

The high surface area Fe-Zn-K₄-Cu₂ sample discussed in the previous section was also compared with a Co/SiO₂ catalyst at conditions typical of Co-based FTS catalysts (Table 5). Fe-based catalysts typically require higher temperatures, while Co-based catalysts must be operated within a very narrow range of temperature (473-500 K), pressure (~2 MPa), and synthesis gas stoichiometry (H₂/CO~2), because of their predominant methanation activity at higher temperatures, lower pressures, or higher H₂/CO ratios.

The Co/SiO₂ catalyst (21.9 wt.% Co) used for comparison purposes, was prepared by incipient wetness impregnation of SiO₂ (Grace-Davison; grade 62) with a solution of cobalt nitrate (Aldrich, 98%, 2.5 M), dried in ambient air at 333 K, and treated in H₂ using previously reported procedures [13]. This sample showed a Co dispersion of 4.6% using H₂ chemisorption methods. Its FTS turnover rate at standard conditions (473 K, 2.0 MPa) was 46-73 h⁻¹. This performance places it among the Co-based catalysts with the highest reported turnover rates at these reaction conditions [14].

The hydrocarbon synthesis productivity, CH₄ selectivity, C₅₊ selectivity, and *l*-pentene/*n*-pentane and *l*-decene/*n*-decane ratios are shown as a function of CO conversion on Fe-Zn-K₄-Cu₂ and Co/SiO₂ in Figures 32a-e. Table 9 provides a summary of these comparisons at similar CO conversions (18-21%). Hydrocarbon synthesis productivities are very similar on these two catalysts (Table 9, Figure 32a). Hydrocarbon synthesis turnover rates estimated from the number of sites available on Co/SiO₂ (using H₂ chemisorption before reaction) and on Fe-Zn-K₄-Cu₂ (using CO chemisorption after reaction) are higher on the former catalyst [Co; 60.9 h⁻¹; Fe; 19.8 h⁻¹] (Table 9). FTS rates increased slightly with CO conversion on Co catalysts, because of a promoting effect of the water formed in FTS reactions [14]. CH₄ selectivities (Figure 32b) were lower on Fe than on Co catalysts, but C₅₊ selectivities (Figure 32c) were very similar on the two catalysts, because of higher C₂-C₄ olefin selectivities on Fe (Fe: 6.4%; Co: 4.4%). The *l*-pentene/*n*-pentane ratios are similar on the two catalysts (Figure 32d and Table 9). Larger hydrocarbons are essentially paraffinic on Co catalysts, because of extensive readsorption and chain initiation by larger α -olefins formed in primary chain termination steps, as shown by the lower *l*-decene/*n*-decane ratios on Co than on Fe catalysts (Figure 32e, Table 9).

In summary, hydrocarbon synthesis rates (per g) on Fe-Zn-K₄-Cu₂ catalysts prepared via the synthesis, promotion, and activation protocols reported here are nearly identical to those observed on Co/SiO₂ catalysts representative of the state-of-the-art. The lower apparent turnover rates on Fe-based catalysts are compensated by a larger density of active sites per gram of catalyst to yield similar hydrocarbon synthesis rates per gram of catalyst. The higher bed density of Fe oxide precursors relative to Co/SiO₂ leads to much higher volumetric productivities on Fe-Zn-K₄-Cu₂ (0.188 g-hydrocarbons/cm³-catalyst.h) than on Co/SiO₂ (0.061 g-hydrocarbons/cm³-catalyst.h), an advantage that can be used to decrease the reactor volumes required in packed bed or bubble column reactors. These Fe-based catalysts, with their lower CH₄ selectivities and more olefinic products, provide

attractive alternatives to Co-based catalysts. These Fe-based catalysts also show a much weaker dependence of selectivity on temperature, pressure, and synthesis gas ratio than Co catalysts. Their higher CO₂ selectivity, even at low temperatures, continues to inhibit their use in the conversion of natural gas-derived synthesis gas. Additional decreases in CO₂ selectivities on Fe catalysts will require even lower reaction temperatures or the internal recycle of some CO₂ to the inlet of FTS reactors or synthesis gas generation units.

Figure 32. Comparison of the performance of the Fe-Zn-K₄-Cu₂ (●), and 21.9 wt.% Co/SiO₂ (■) catalysts for the FTS reactions (473 K and 2.14 MPa, H₂/CO=2). (a) Hydrocarbon productivity, (b) CH₄ selectivity, (c) C₅+ selectivity, (d) *l*-C₅H₁₀/*n*-C₅H₁₂ ratio, and (e) *l*-C₁₀H₂₀/*n*-C₁₀/H₂₂ ratio.

Table 9. A comparison of the Steady-state FTS performances between Fe and Co catalysts (473 K, 2.0 MPa, H₂/CO=2) at CO conversion range of 18~21% (atomic ratios: Zn/Fe=0.1, K/Fe=0.04, Cu/Fe=0.02; 21.9 wt.% Co/SiO₂).

Catalyst	Fe-Zn-K ₄ -Cu ₂	Co/SiO ₂
Total available metal sites for FTS ($\times 10^{-4}$ mol/g-cat.)	7.4	1.7
Hydrocarbon synthesis turnover rate (h ⁻¹)	16.7	59.6
Hydrocarbon synthesis productivity (g/h.kg-cat)	171	143
Hydrocarbon synthesis volumetric productivity (g-hydrocarbons/cm ³ -catalyst.h)	0.188	0.061
CO ₂ selectivity (%)	15.8	0.3
CH ₄ (%) ^a	2.0	6.8
C ₂ -C ₄ (%) ^a	8.9	6.4
C ₅₊ (%) ^a	89.1	86.8
<i>I</i> -C ₅ H ₁₀ /n-C ₅ H ₁₂ ratio	2.1	2.0
<i>I</i> -C ₁₀ H ₂₀ /n-C ₁₀ H ₂₂ ratio	1.6	0.3

^a CH₄ and C₅₊ selectivities are reported on a CO₂-free basis.

7. Structural analysis of unpromoted Fe-based FTS catalysts using X-ray absorption and Mössbauer emission spectroscopy

7.1. Introduction

The activation of Fe-based precursors in synthesis gas is a complex process, which is difficult to follow as it occurs. The effects of the structural changes that occur during activation on the catalytic behavior of these materials remain unclear. For example, as the partial pressure of hydrogen increases relative to that of CO during activation, at otherwise similar conditions, the ultimate steady-state FTS rates decrease [47]. Promoters, such as Cu and K, shorten the time required for the conversion of Fe oxide precursors into active catalysts. After the initial activation, the structure of Fe-based FTS catalysts continues to evolve with increasing time-on-stream [48].

X-ray absorption near-edge spectroscopy (XANES) and extended X-ray absorption fine structure (EXAFS) methods provide unique information about the oxidation state and local environment of each absorber element in complex multi-component materials. In this study, these techniques were used in order to determine the structure of Fe catalysts after they catalyze FTS reactions for various periods of time. In the studies reported here, which were conducted in collaboration with the University of Kentucky, an unpromoted precipitated iron catalyst was used in order to avoid the complexity introduced by chemical and structural promoters. The X-ray absorption results were compared with previous Mössbauer spectroscopy data [48,49] on similar Fe catalysts and the results of these two structural characterization techniques are taken together with their catalytic properties at a given time-on-stream in order to infer the nature of the active species and the chemical and structural changes that accompany deactivation during FTS reactions.

7.2. Catalyst preparation

One sample of the unpromoted Fe oxide precursor (Sample 0) and samples of this precursor after activation (Sample 1) and after use for various lengths of time (Samples 3, 5, 7, 10, 13, 19 and 20) were examined. The Fe oxide precursor was prepared by precipitation from an aqueous solution of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Johnson Matthey Co., >98% metals basis, 1 M; $2.6 \text{ cm}^3/\text{s}$) using concentrated NH_4OH (VWR, reagent grade, 28-30 wt.%; $1.2 \text{ cm}^3/\text{s}$). The pH of the slurry was kept constant at 9.3 and the residence time in the reactor was 300 s. This resulted in a total slurry volume of 34.4 l. After initial filtration, the precipitates were washed by re-slurring twice with 34.4 l of deionized water with intervening filtration using rotary drum filters. The washed precipitates were dried in air at 373 K overnight. The dried materials were ground using a mortar and pestle in order to obtain particles with $\sim 0.15 \text{ mm}$ diameter and then treated in stagnant dry air at 623 K for 4 h.

7.3. Activation and FTS reactions

All FTS experiments were carried out in a 1-liter continuous stirred tank reactor (CSTR). The catalyst precursor (64.44 g) was suspended in C-30 oil (Ethylflow, decene trimers;

Ethyl Corp., 290 g) and pretreated with CO at 543 K and 1.22 MPa for 24 h. The CO flow (58.7 sl/h. g-Fe) was started at ambient conditions (298 K and 0.1 MPa), the pressure was raised to 1.22 MPa, and the temperature of the reactor was then increased to 543 K at 0.033 K/s and maintained at this temperature for 24 h. After this activation treatment, the reactor was brought to reaction conditions (543 K; 1.22 MPa; H₂/CO=0.68; 3.1 sl(CO+H₂)/h. g-Fe) by introducing H₂ into the CO stream over a period of ~3 h.

Reaction products were analyzed using gas chromatography. Gas products were analyzed using a Hewlett-Packard Quad-Series Refinery Gas Analyzer (QRGA). The analysis of the aqueous phase collected after the reactor was carried out using a Hewlett-Packard 5790 gas chromatograph equipped with a thermal conductivity detector and a Porapak Q-column. Oil and wax were combined and analyzed with a Hewlett-Packard 5890 gas chromatograph equipped with a flame ionization detector and a 60 m DB-5 column. The wax products were analyzed using a Hewlett-Packard 5890 high temperature gas chromatograph using flame ionization detection and a 30 m alumina clad HT-5 column.

Catalyst samples were extracted from the autoclave during reaction using a dip tube blanketed with an inert gas. All subsequent handling of the used catalysts was carried out under inert gas within a glove box. A total of 20 samples were withdrawn from the reactor during the 452 h experiment. The conversions have not been corrected for the decline in the amount of catalyst withdrawn from the reactor. Based upon the initial solid content of the slurry, the initial slurry volume, and the amount of sample removed from the reactor, catalyst removal would account less than a 15% decrease in CO conversion by the end of the experiment.

7.4. *Mössbauer emission spectroscopy measurements*

The Mössbauer experiments used a constant acceleration spectrometer. The radioactive source consisting of 50 mCi of ⁵⁷Co in a Rh matrix. Samples 1, 3, 10 and 20 in powdered form were loaded into Plexiglass compression holders presenting a thin sample to the beam. Spectra collected from Samples 1, 3 and 10 were analyzed by least squares fitting the data to a summation of five sextets, while the spectrum collected from Sample 20 was fitted to the sum of two sextets. Hyperfine parameters extracted from the fits were used to estimate the composition of the samples. The two sextets having the highest hyperfine magnetic field were found to correspond to Fe at the tetrahedral and the octahedral sites of Fe₃O₄. The remaining three sextets were found to correspond to Fe centers located at the three crystallographic sites in the Hägg carbide (Fe₅C₂).

7.5. *Mössbauer structural analysis*

Table 10 shows the catalyst composition and the relative areal fraction of their sextets obtained from the Mössbauer spectra as a function of time-on-stream. It is worth noting here that these areal fractions measured at room temperature were not corrected by using the recoil-free fraction ratio of the different Fe sites. Therefore, the fractional composition of the samples might be slightly different from the areal fractions. The Fe₅C₂ phase was established from the measured hyperfine parameters, although the measured

atomic ratio, Fe(I):Fe(II):Fe(III), did not conform to the expected ratio of 2:2:1. In large-crystal Fe carbide samples, the ratio frequently differs from 2:2:1 because of the variable concentration of carbidic carbon. Here, however, the deviation is stronger and indicates that crystallization is incomplete. In spite of this, Fe₅C₂ is the only iron carbide that can be discerned from the Mössbauer measurements. The Mössbauer data (Table 10) show that the extent of carburization was nearly complete after the 24 h activation period in contact with flowing CO, and then decreased with time-on-stream. After 452 h, only Fe₃O₄ was detected.

Table 10. Mössbauer structural analysis results

	Sample			
	1	3	10	20
FTS reaction time (h)	0	23	168	452
Fe ₅ C ₂ (at.%)	94	83	42	0
Fe ₃ O ₄ (at.%)	6	17	58	100

7.6. Fe K-edge XANES

Figure 33 shows X-ray absorption near-edge spectra (XANES) for Samples 0, 5, 7, 13 and 19. All spectra show weak pre-edge peaks, indicating the presence of some residual Fe oxides. The absorption edge energy, defined at the first inflection point in the absorption edge, shifts to lower energies for Samples 5 and 7, suggesting the formation of Fe species with lower oxidation states than in Fe₃O₄. The absorption edge energy shifts back to higher values for Samples 13 and 19. The higher absorption edge energies on the catalyst precursor (Sample 0) and in Samples 13 and 19 and the more intense pre-edge features and first maximum in the absorbance spectrum, in the near-edge region indicate the more prevalent presence of Fe oxides in these samples compared to the other used samples.

Principal component analysis (PCA) indicated the presence of two species, identified as Fe₃O₄ and FeC_x in Samples 5-19. The near-edge spectra for these samples can be described as a combination of the standard spectra for Fe₃O₄ and FeC_x; the relative amounts of these two phases can be obtained using least square error minimization techniques [26]. Fe₂O₃, FeO and Fe were excluded from the fittings because they were rejected by PCA and because their presence failed to improve fits.

The XAS spectra of the catalyst precursor before activation cannot be fitted to combinations of Fe₂O₃ and Fe₃O₄ spectra. The EXAFS of this sample (Sample 0)

suggests the presence of $\text{FeO}(\text{OH})$, apparently as a result of the incomplete crystallization of the oxides during calcination at relatively low temperatures. These temperatures (623 K) are generally sufficient to decompose $\text{FeO}(\text{OH})$, but the short treatment time and the stagnant nature of the ambient air within and above the sample bed appeared to inhibit water removal and dehydration, and led to amorphous Fe oxides. Therefore, Sample 0 contained hydrated Fe oxides, which did not crystallize fully during synthesis. X-ray diffraction (XRD) and Mössbauer analyses of other samples that received a similar activation did not detect crystalline Fe compounds in these samples.

Figure 33. Normalized Fe K-edge XANES for (A) Sample 0, (B) Sample 5, (C) Sample 7, (D) Sample 13 and (E) Sample 19.

Table 11 shows the relative abundances of standard compound structures corresponding to the best fits of the experimental spectra for each sample. Figure 34 presents a typical fit to the spectrum for Sample 5. All the fits were excellent. The results from linear combination fits show a monotonic decrease in the relative abundance of Fe carbides with increasing time-on-stream (Samples 5, 7 and 13). After FTS reactions for 432 h, the only detectable phase was Fe_3O_4 (Sample 19), as also found by Mössbauer emission spectroscopy.

7.7. Fe K-edge fine structure

Figure 35 shows the Fourier transforms of the Fe K-edge EXAFS for each sample and for the standard Fe compounds. The radial structure function for the catalyst precursor (Sample 0) is poorly resolved, indicating a disordered or non-uniform geometry around Fe absorbers. The radial structure functions for Samples 5 and 7 appear to reflect the combined contributions of Fe_3O_4 and FeC_x . The relative contributions of these two structures suggest that Sample 5 has a higher Fe carbide fraction than Sample 7. After

264 h on-stream, the catalyst (Sample 13) shows a fine structure similar to that of pure Fe_3O_4 ; after 432 h, the fine structure features in Sample 19 are identical to those in pure Fe_3O_4 . The evolution of the radial structure function with increasing time-on-stream is consistent with the changes in structure detected from the linear combination analysis of the near-edge spectra.

Table 11. Linear combination of standard spectra fits to the sample XANES

	Sample				
	0	5	7	13	19
FTS reaction time (h)	-	71	121	264	432
FeC_x (at.%)	0	52	35	2	0
Fe_3O_4 (at.%)	-	48	65	98	100

Figure 34. Experimental and the linear combination XANES fit for Sample 5.

7.8. Comparison of the results from Mössbauer emission and X-ray absorption spectroscopy

The quantitative phase compositions obtained from Mössbauer emission and X-ray absorption spectroscopies differ (Figure 36). The compositional trends obtained by the two techniques, however, are very similar. Both techniques show that the carbide phase is more prevalent in the earlier stages of contact with synthesis gas and that the Fe carbide content decreases with increasing reaction time. After about 400 h, the only detectable phase is Fe_3O_4 . Both techniques indicate that the decrease in the amount of Fe carbide parallels the observed decrease in catalytic activity (Figure 36). Two possible explanations can be proposed for the quantitative differences in the carbide fractions obtained from the two spectroscopic techniques. The first is that the samples used for X-ray absorption spectroscopic measurements were stored for ~2 years. The samples were

stored in the wax FTS product and under an inert gas blanket, but it is possible that some of the carbides were oxidized during storage, leading to the lower carbide fraction detected by XAS. Another possibility is that the Mössbauer technique overestimated the amount of the carbide phase present in the samples. The measured fractions of the oxide and the carbide were calculated from the areas of their sub-spectra divided by the area of the main spectrum, which included all sub-spectra. Corrections were not made for the fraction of the solid sampled by the Mössbauer technique, because such corrections require literature data for the recoil-free fraction of the oxide and carbide phases. Literature values are available for large crystals of these phases, but the small crystals present in FTS catalyst samples make such corrections non-rigorous.

Figure 35. Fe K-edge EXAFS for (A) Sample 0, (B) Sample 5, (C) Sample 7, (D) Sample 13, (E) Sample 19, and standard compounds Fe_2O_3 (triangle), Fe_3O_4 (plus), FeC_x (dot).

7.9. Discussion

Integral FTS rates decreased by almost a factor of 10 leading to a decrease in CO conversion from 86 to 12% after 452 h on-stream (Figure 36). Clearly, the high conversions in the early stages of the reaction lead to much higher $\text{H}_2\text{O}/\text{H}_2$ and CO_2/CO ratios than those present at the low conversions prevalent at later reaction times. Thus, the oxidizing potentials of the reactant-product mixtures in the gas phase and in the liquid

phases in equilibrium with this gas phase are significantly higher during the early stages of the experiment. Yet Fe carbides were the predominant Fe species at these conditions, although they decreased in relative abundance as the reaction proceeded for longer periods of time. In spite of the fact that CO₂ can lead to the oxidation of Fe carbides, the presence of added CO₂ (CO₂/CO=0.3) in the feed gas did not influence CO conversion rates or apparently alter the structure of the catalytic phases. Thus, CO₂ was essentially inert at our reaction conditions. The addition of water at H₂O/CO ratios up to 0.3 also did not influence the rate of hydrocarbon formation, but increased the rate of water gas shift [50]. However, the lack of impact of added CO₂ and H₂O was studied only for an iron catalyst containing silica (4.4 at.% Si to 100 at.% Fe) and potassium (1.0 at.% K to 100 at.% Fe). Thus, the extrapolation of these results to the unpromoted catalyst used in this study may not be appropriate.

Figure 36. FTS rates measured from the CSTR (543 K; 1.22 MPa; H₂/CO=0.68; 3.1 litres (CO+H₂)/h g Fe), and the Fe carbide concentrations obtained from the Mössbauer and the XAS measurements as a function of reaction time.

It appears that individual iron particles undergo re-oxidation rather uniformly. If only the surfaces of each catalyst particle were rapidly oxidized during deactivation, and this initial process were followed by the slower oxidation of the bulk carbide phase, the CO conversion would decline much more rapidly than the concentration of the active Fe carbide phase. The experimental evidence indicates that both decline to a similar extent as deactivation occurs. Thus, it appears that catalyst particles start to re-oxidize via the nucleation of an oxide phase either at the surface or within their core, and ultimately re-oxidize completely, while other particles remain essentially as iron carbide. One possible explanation for this unusual behavior would be a distribution of carbide crystallites and a size-dependent thermodynamic propensity to re-oxidize, but data supporting such effects are not available and such particle size dependence would be unexpected for the large crystallites of Fe phases detected by X-ray diffraction. In any event, the bulk phase composition and specifically the relative abundance of Fe carbides in the unpromoted

iron catalyst directly influence CO conversion rates (Figure 36). This is most readily explained if the catalyst system is composed of a mixture of catalyst particles whose surface resembles either iron oxide or iron carbide phases, and whose distribution favors less active Fe oxides over more active Fe carbides as the catalyst deactivates.

A tenuous balance among several concurrent processes determines the surface and bulk composition of a catalyst during steady-state FTS. First, there must be a balance between the amount of CO that is converted to products in the Fischer-Tropsch and the water-gas shift reactions, and the amount of CO that is dissociated on the catalyst surface in a form that maintains the carbide phase. Any imbalance between these rates would lead to the net introduction or removal of carbon or oxygen atoms into the inorganic structure, and to the interconversion of Fe oxides and Fe carbides. If the removal of the carbon and oxygen atoms using hydrogen or CO becomes imbalanced, the surface chemical potential of either carbon or oxygen becomes higher than in the contacting gas phase. This can lead to the formation of bulk structures in thermodynamic equilibrium with the steady-state surface chemical potential. On unpromoted iron catalysts, it appears that deactivation leads to the preferential inhibition of oxygen removal pathways over those leading to the removal of carbon to form CH_x species and ultimately hydrocarbons. The concomitant depletion of the surface carbon pool leads to the nucleation of Fe_3O_4 patches, which dissociate CO and catalyze FTS with very low reaction rates. If only the surface were oxidized, to resemble Fe_3O_4 , however, the catalytic activity would change much more rapidly than the Fe oxide content in the catalysts and the catalyst would recarburize in the presence of the carburizing synthesis gas mixture present at low conversions. The catalytic activity declines at about the same rate as the bulk carbide phase. This eliminates the possibility of just surface oxidation causing the compositional changes defined by the Mössbauer and the X-ray absorption spectroscopy measurements and influencing FTS reaction rates.

In the case of the unpromoted Fe catalysts of this study, the re-oxidation may be caused, or at least initiated, by changes in the relative rates of oxygen formation in CO activation steps and of oxygen removal by reaction with hydrogen or CO to form water and CO_2 , respectively. Such changes occur concurrently with the observed decrease in the rate of the reaction, apparently because of the common need for H_2 activation steps for both monomer formation and for oxygen removal in FTS reaction catalyzed by Fe carbide particles. Thus, re-oxidation reflects changes in the surface chemical potential of C^* , O^* , and H^* adsorbed species, instead of corresponding changes in chemical potential within the contacting gas phase. In turn, this suggests that the removal of oxidizing species, such as adsorbed H_2O^* , OH^* , or O^* , occurs via steps that are not quasi-equilibrated during FT synthesis, and that their surface concentrations can significantly exceed those that would be in equilibrium with the contacting gas phase. The non-equilibrated nature of water desorption steps has been recently demonstrated during FTS reactions on Co catalysts by the very low HD and D_2 concentrations among hydrogen molecules and by the low D-content in the hydrocarbon formed from $\text{CO}/\text{H}_2/\text{D}_2\text{O}$ reactant mixtures as discussed in Section 5 in the discussion on Co-FTS catalysts.

The data in Figure 36 suggest a direct relationship between the FTS rates and the concentration of Fe carbides during reaction. It appears that catalytically active species reside on carbided surfaces. We have shown in Section 4 and 5 that Fe_3O_4 crystallites become almost immediately active in FTS reactions after exposure to synthesis gas and that only the incipient conversion of near surface oxide layers to Fe carbides is required for steady-state FTS rates. Thus, the observed deactivation with time-on-stream is unlikely to reflect merely the bulk re-oxidation of a particle core to Fe_3O_4 , because such particles would immediately re-activate to give high FTS reaction rates, as they initially do when Fe oxides precursors are activated in synthesis gas. Instead, it appears that the observed oxidation and deactivation of Fe carbides are concurrent processes caused by changes in the carbide surface, which render the oxidation potential of adsorbed species high enough to form Fe_3O_4 surfaces. These surfaces exhibit a structure or composition that prevents their re-carburization at FTS reaction conditions, even at the low conversion levels and reducing conditions prevalent as conversion decreases during catalyst deactivation.

7.10. Conclusions

Mössbauer and XAS measurements of the phase composition of unpromoted Fe catalysts sampled at various periods of FTS reactions showed a consistent decrease in the Fe carbide concentration with time-on-stream. The CO conversion decreased by a factor of 10 during the structural evolution of the catalysts from initial nearly pure Fe carbides after activation in CO, to their gradual oxidation with increasing reaction time, and their ultimate transformation to pure Fe_3O_4 after 450 h on-stream. It appears that the observed oxidation and deactivation of Fe carbides are concurrent processes caused by changes of chemical potential of adsorbed species at the carbide surface, which render higher concentrations of oxidizing species on the surface than in the contacting gas phase. These conditions, in turn, lead to the oxidation of Fe carbides even in the reducing environments prevalent as conversion decreases during catalyst deactivation.

8. Pathways for CO₂ Formation and Conversion during FTS reactions on Iron-Based Catalysts

8.1. Introduction

The removal of chemisorbed oxygen atoms (O*) formed in the CO dissociation steps required for monomer formation during FTS can occur *via* reactions of O* with co-adsorbed hydrogen (H*) or carbon monoxide (CO*). These reactions lead to the formation of H₂O and CO₂, respectively, as the oxygen carrier. In this manner, H₂O and CO₂ both form as primary FTS products. CO₂ and H₂O can also form *via* secondary reactions, but thermodynamic constraints lead to the net formation of CO₂ and the net depletion of H₂O at typical FTS reaction conditions. This occurs with the overall stoichiometry of the water-gas shift (WGS) reactions on Fe-based FTS catalysts [51-53]. Fe, Zn and Cu oxides can also provide active sites for these CO₂-forming reactions [52-54], which are useful for coal-derived synthesis gas streams (H₂/CO ~ 0.7), because oxygen rejection by excess CO reactants allows more efficient use of these CO-rich streams. For synthesis gas streams derived from natural gas, CO₂ formation leads to high H₂/CO ratios along the reactor bed and to lower olefin and C₅₊ selectivities. The control of oxygen removal *via* both primary removal and secondary oxygen removal pathways remains a critical issue in the design and use of Fe-based catalysts for FTS reactions.

The mechanism of CO₂ formation and the role of CO₂ in chain growth remain controversial. Some studies propose that FTS and WGS reactions proceed on different sites [20,54,55] with carbide sites involved in FTS and Fe₃O₄ as the active phase for WGS reactions involving surface formate (HCOO*) intermediates [45]. The rapid dynamic interconversion between FeC_x and Fe₃O₄ during FTS discussed in Section 3 makes the site assignments for these two reactions difficult to support with definitive experimental evidence. Most studies, however, do not consider primary CO₂ formation routes at all during FTS. The non-zero CO₂ selectivity observed at low CO conversions and low H₂O concentrations, and the expected presence of O* and CO* during FTS, show that CO₂ can also form as a primary product. Yet another CO₂ formation route involves the synthesis and decomposition of organic acids [56-58]. CO₂ can form *via* decarboxylation of organic acids formed from FTS alcohol products. The addition of ¹⁴CH₃OH [56] or 1-pentanol [¹⁻¹⁴C] [57] to H₂/¹²CO led to higher ¹⁴C contents in CO₂ than in CO, suggesting an intermediate role of alcohols in CO₂ formation. The absence of ¹⁴C in C₁-C₄ products during the addition of *l*-¹⁴C suggests that CO₂ is not formed *via* direct alcohol decomposition, but rather *via* oxidation of alcohol to carboxylic acids followed by subsequent decarboxylation to form CO₂ and an olefin [57].

Another important aspect of CO₂ chemistry during FTS is its potential role in monomer formation and chain initiation. The addition of ¹⁴CO₂ (1.4% mol) to H₂/¹²CO (1:1) did not lead to detectable ¹⁴C contents on fused Fe catalysts (501 K, 0.1 MPa, H₂/CO=1) [58]. More recent studies by Xu *et al.* [59,60], however, detected almost identical radioactivity per mole in CO₂ and in hydrocarbons on a Fe-Si-K catalyst (543 K, 0.8 MPa, H₂/CO=0.7), suggesting that each hydrocarbon molecule contained one ¹⁴C from ¹⁴CO₂. These latter results are surprising in view of the isotopic and chemical equilibration

detected between CO and CO₂ in the effluent stream, which would render the chemical source of the carbon atoms indeterminate.

In this section, we describe the role of CuO and K₂CO₃ promoters on primary and secondary CO₂ formation pathways during FTS and probe the relative rates of primary oxygen removal *via* reaction with adsorbed hydrogen (to form H₂O) or with adsorbed CO (to form CO₂). ¹³CO₂ addition studies at conditions far from water-gas shift equilibrium are used to show that CO₂ is essentially inert in chain growth or initiation reactions and that its chemical conversion to hydrocarbons occurs *via* surface or gas phase CO intermediates. Finally, a reversible reaction kinetic analysis approach is developed in order to describe the effects of CO₂ recycle on CO₂ selectivity. As suggested previously [16], the presence of CO₂ inhibits the net rate of WGS during Fischer-Tropsch synthesis on Fe-based catalysts. The addition or recycle of CO₂ decreases the net rate of CO₂ formation and increases the fraction of the oxygen atoms in CO removed as H₂O, an important practical issue in the use of Fe-based catalysts for H₂/CO mixtures derived from natural gas.

8.2. *Experimental Methods*

¹²CO₂ and ¹³CO₂ addition experiments were carried out on the low surface area Fe-Zn-K₂-Cu₁ catalyst and the high surface area Fe-Zn-K₄-Cu₂ catalyst respectively. An equimolar ¹²CO₂/Ar mixture (Linde, Air Products Co.) was used in ¹²CO₂ addition experiments carried out to simulate recycle conditions. The pressure of ¹²CO₂ was varied while maintaining a constant synthesis gas pressure. ¹³CO₂ addition experiments were carried out in order to probe the role of CO₂ in chain initiation and growth by adding 0.1 MPa ¹³CO₂ (Cambridge Isotope Laboratories Inc., 99% isotopic purity) at 508 K, 0.8 MPa synthesis gas pressure, and a H₂/CO ratio of 2.0. The ¹³C content in the products of ¹³CO₂/¹²CO/H₂ mixtures was measured using a mass selective detector (Hewlett Packard, Model 5890; Series II/5791A) and separating the products with a HP-1 capillary column (cross-linked methyl silicone, 50 m × 0.32 mm × 1.05 μm). The ¹³C contents in reactants and products were measured from mass ion intensities using deconvolution techniques that account for natural abundance and mass fragmentation patterns [61].

8.3. *Role of CuO and K₂CO₃ promoters on CO₂ formation pathways*

CO₂ selectivities on Fe-Zn, Fe-Zn-Cu₁, Fe-Zn-K₂ and Fe-Zn-K₂-Cu₁ are shown as a function of CO conversion for stoichiometric synthesis gas (H₂/CO=2) at 508 K and 2.14 MPa in Figure 37a and at 543 K and 0.5 MPa in Figure 37b. These data were obtained by changing the CO space velocity at constant temperature and H₂ and CO partial pressures. CO₂ selectivities increased with decreasing space velocity (and increasing reactor residence time and CO conversion) on all catalysts. This increase in CO₂ selectivity reflects the formation of CO₂ by reactions of water with CO-derived intermediates in secondary reactions with the stoichiometry of the water-gas shift reaction. In these reactions, H₂O formed in primary oxygen removal steps readsorbs on sites where it can dissociate and its extent of readsorption and reaction increases, as the concentration of water increases with increasing CO conversion and decreasing space velocity. The

dependence of CO₂ selectivity on reactor residence time weakens at higher CO conversion levels, as CO₂-forming reactions approach equilibrium on all catalysts.

Figure 37. CO₂ selectivity as a function of CO conversion on the different Fe catalysts at (a) 508 K, 2.14 MPa, H₂/CO=2, and (b) 543 K, 0.5 MPa, H₂/CO=2. (▲): Fe-Zn, (◆): Fe-Zn-Cu₁, (■): Fe-Zn-K₂, and (●): Fe-Zn-K₂-Cu₁.

Figure 38. Oxygen selectivity to H₂O as a function of CO conversion on the different Fe catalysts at (a) 508 K, 2.14 MPa, H₂/CO=2, and (b) 543 K, 0.5 MPa, H₂/CO=2. (▲): Fe-Zn, (◆): Fe-Zn-Cu₁, (■): Fe-Zn-K₂, and (●): Fe-Zn-K₂-Cu₁. Dashed line: Oxygen selectivity to H₂O at WGS equilibrium.

CO₂ selectivities are higher on promoted Fe catalysts than on unpromoted samples at all CO conversion levels. The slope of these CO₂ selectivity curves at different points (Figure 37) (or more rigorously the slopes of the CO₂ formation rates shown later) gives a measure of the rate of secondary CO₂-forming reactions. These slopes are very similar for Fe-Zn-K₂ and Fe-Zn-K₂-Cu₁ catalysts at 508 K (Figure 37a). Similarly, Fe-Zn and Fe-Zn-Cu₁ catalysts also show nearly identical slopes, indicating that the addition of Cu to Fe-Zn-K₂ or Fe-Zn does not increase the rate of WGS reactions. Figures 38a and 38b show the oxygen selectivities to H₂O on all four catalysts at the two reaction conditions of this

study. This oxygen selectivity is defined as the percentage of the oxygen in the converted CO that appears as a given product, in the case of Figure 38 as H₂O. The oxygen selectivity to H₂O decreases with increasing CO conversion as water readsorbs and finds additional opportunities to react and approach equilibrium, which favors CO₂ as the oxygen removal carrier at these reaction conditions. These H₂O selectivities extrapolate to high values as CO conversion decreases, consistent with a high primary selectivity for oxygen removal as water. The readsorption of water and its subsequent probability of reaction with CO-derived intermediates to form CO₂, leads to a decrease in the H₂O selectivity with increasing CO conversion (Figure 38).

The CO₂ selectivities extrapolated to low CO conversion levels are non-zero, consistent with these primary pathways for oxygen removal as both CO₂ and H₂O. Cu increases this primary selectivity to CO₂ and thus the propensity for O* removal as CO₂ on Fe-Zn catalysts. In contrast, K increases the rate of the secondary WGS reaction without influencing primary CO₂ selectivities (Figures 37 and 38). It appears that K promotion does not influence the relative abundance of CO* and H* species available for oxygen removal, even though previous studies have suggested that K effects on hydrocarbon selectivity and FTS rates reflect an increase in the binding energy of adsorbed CO relative to that of hydrogen [4,16]. The higher CO₂ selectivity on Cu-containing catalysts suggests that Cu increases the availability of CO* for O* removal in primary pathways, but that Cu does not increase the rate of secondary CO₂-forming reactions (see slopes in Figure 37), even though previous reports have attributed higher CO₂ selectivities on Cu-promoted samples to Cu-catalyzed WGS reactions [62]. The primary CO₂ selectivity is lower at 508 K and 2.14 MPa (Figure 37a) than at 543 K and 0.5 MPa (Figure 37b) on all catalysts, suggesting that O* removal as H₂O has a lower activation energy than parallel pathways leading to CO₂.

The slope of the CO₂ selectivity data in Figure 37 may also include other secondary routes for the formation of CO₂, such as the conversion of alcohol primary products to acids and their subsequent decarboxylation [57,59]. These pathways are unlikely to contribute appreciably to CO₂ at the conditions of our experiments (508-543 K, 0.5-2.14 MPa, and H₂/CO=2), because alcohol selectivities, and their observed changes with space velocity, are much smaller than the changes in CO₂ selectivity shown in Figure 37 and than the changes in alcohol selectivities reported previously at lower H₂/CO ratios (0.7) [18,20]. Water-gas shift reactions, possibly on sites that also catalyze CO dissociation and chain growth as part of FTS catalytic sequences, appear to provide the predominant secondary route for CO₂ formation at the conditions of our experiments.

8.4. *Effects of CO₂ addition to synthesis gas on Fe-based catalysts*

Water-gas shift reactions approach equilibrium with increasing residence time and temperature during FTS (Figure 37). This approach to equilibrium and its kinetic consequences can be rigorously described by a parameter η , given by the concentration ratio in equation (1) divided by the equilibrium constant at the reaction temperature:

$$\eta = \frac{1}{K_{WGS}} \left(\frac{P_{CO_2} P_{H_2}}{P_{CO} P_{H_2O}} \right) \quad (1)$$

In Equation (1), P_j is the partial pressure of species j and K_{WGS} is the WGS equilibrium constant. The value of η ranges from 0 to 1 as chemical reactions approach equilibrium. Figures 39a and 39b show this value for the two experimental conditions used to obtain the data in Figures 37a and 37b. These values suggest that reverse WGS reaction rates are significant. Therefore, the addition of CO_2 to synthesis gas feeds can lead to lower net rates of CO_2 formation and of O^* removal as CO_2 during FTS.

Figure 39. The approach to equilibrium parameter (η) for water-gas shift reaction as a function of the amount of CO_2 added on the Fe-Zn- K_2 - Cu_1 catalyst; (a) 508 K, 2.14 MPa, $H_2/CO=2$, and (b) 543 K, 0.5 MPa, $H_2/CO=2$.

The kinetic consequences of this approach to equilibrium and of the addition of CO_2 can be described by considering how forward rates $r_{f,i}$, and reverse rates $r_{r,i}$, of each elementary step i in the WGS reaction:

depend on the affinity of that step (A_i), as given by the De Donder equation [63] of non-equilibrium thermodynamic treatments of chemical kinetics:

$$\frac{r_{f,i}}{r_{r,i}} = \exp\left(\frac{A_i}{RT}\right) \quad (2)$$

The affinity is the negative of the Gibbs free energy of step i :

$$A_i = -\Delta G_i \quad (3)$$

and it is related to standard affinity for that step A_i^o by:

$$A_i = A_i^o + RT \ln\left(\frac{P_{CO_2} P_{H_2}}{P_{CO} P_{H_2O}}\right) \quad (4)$$

The net rate of the overall reaction is then given by:

$$r = r_f - r_b = r_f \left(1 - \exp \left(\frac{-A}{\sigma RT} \right) \right) \quad (5)$$

in which, σ is the average stoichiometric number for the catalytic sequence. This number is unity for overall reactions, such as WGS, in which every elementary steps occurs only once in the complete catalytic sequence [64]. Equation (5) then becomes:

$$r = r_f - r_r = r_f \left(1 - \exp \left(\frac{-A}{RT} \right) \right) \quad (6)$$

The affinity of the overall reaction (A) depends on the standard reaction affinity A° and on the partial pressures of reactants and products:

$$A = A^\circ + RT \ln \left(\frac{P_{CO_2} P_{H_2}}{P_{CO} P_{H_2O}} \right) \quad (7)$$

The standard affinity A° equals the negative of the standard Gibbs free energies for the reaction and it is related to the equilibrium constant:

$$A^\circ = -\Delta G^\circ = RT \ln K_{WGS} \quad (8)$$

Combining Equations (5) and (6), we obtain:

$$A = RT \ln \frac{1}{K_{WGS}} \left(\frac{P_{CO_2} P_{H_2}}{P_{CO} P_{H_2O}} \right) \quad (9)$$

and then from Equations (1), (6) and (9) we obtain an expression for the net rate of a chemical reaction as it approaches equilibrium in terms of the parameter η that measures the extent of this approach to equilibrium:

$$r = r_f \left(1 - \frac{1}{K_{WGS}} \left(\frac{P_{CO_2} P_{H_2}}{P_{CO} P_{H_2O}} \right) \right) = r_f (1 - \eta) \quad (10)$$

The forward WGS rate can then be calculated from the measured net rate of CO_2 formation divided by $(1-\eta)$, where the latter is evaluated at the average partial pressures for each reactant and product in the reactor. The forward rate estimated in this manner is shown in Figures 40a and 40b as a function of CO conversion along with the net CO_2 formation rate for the two reaction conditions used in this study. For the catalysts promoted with K, the CO_2 forward rate increases with increasing conversion, indicating that K increases the rate of the secondary CO_2 forming reactions reaction involving a water co-reactant, which increases in concentration with increasing CO conversion. Cu promotes the removal of O^* by CO^* rather than H^* , but the nearly constant forward CO_2 rate with increasing CO conversion suggests that it does not introduce active sites for secondary water-gas shift reactions. Next, we examine the effects of addition of CO_2 to synthesis gas using this formalism for estimating the effects of CO_2 on the net rate and on the rate of the forward CO_2 formation reactions.

The effects of CO_2 addition on FTS rates and selectivities were examined on Fe-Zn-K₂-Cu₁ at the two reaction conditions used for the space velocity data in Figure 37 (508 K, 2.14 MPa H_2/CO and 543 K, 0.5 MPa H_2/CO). CO conversion rates and hydrocarbon and net CO_2 formation rates are shown as a function of the average CO_2 pressure in the

reactor (the average of the inlet and outlet CO_2 pressures in the reactor) in Figures 41a and 41b. The CO conversion rates and the net CO_2 formation rates decreased with increasing CO_2 pressure, but hydrocarbon formation rates were not affected. This shows that the presence of CO_2 in the synthesis gas feed decreases the net rate of CO_2 formation without any influence in the rate of formation of hydrocarbon chains. The effect of CO_2 on the net rate of CO_2 formation is stronger at higher temperatures, apparently because of the faster forward WGS rates and the less favorable equilibrium as temperature increases. The observed decrease in the net rate of CO_2 formation may reflect the inhibition of the forward rate of CO_2 -forming reactions or merely an increase in the reverse rate of these reactions as they approach equilibrium. The relative importance of these two effects can be discerned by applying the formalism derived above to these kinetic data.

Figure 40. CO_2 forward rate as a function of CO conversion on the different Fe catalysts at (a) 508 K, 2.14 MPa, $\text{H}_2/\text{CO}=2$, and (b) 543 K, 0.5 MPa, $\text{H}_2/\text{CO}=2$. (▲): Fe-Zn, (◆): Fe-Zn-Cu₁, (■): Fe-Zn-K₂, and (●): Fe-Zn-K₂-Cu₁.

Figure 41. CO conversion rate (●), hydrocarbon formation rate (■) and CO_2 formation rate (▲), as a function of the average CO_2 pressure on the Fe-Zn-K₂-Cu₁ catalyst at (a) 508 K, 2.14 MPa, $\text{H}_2/\text{CO}=2$, and (b) 543 K, 0.5 MPa, $\text{H}_2/\text{CO}=2$.

Figure 42. Forward WGS rates (●), net WGS CO₂ formation rates (■), and the approach to equilibrium parameter, η (◇), as a function of CO₂ pressure on the Fe-Zn-K₂-Cu₁ catalyst at 543 K, 0.5 MPa, H₂/CO=2.

Figure 42 shows that forward CO₂ formation rates [$r_f = r/(1-\eta)$] at 543 K are nearly unchanged as the average CO₂ pressure (and hence η) increases. Thus, the presence of CO₂ merely increases the rate of conversion of CO₂ to CO *via* reverse WGS reactions in the exact manner predicted by Equation 10. The net rate of CO₂ formation decreases without detectable changes in the rate of the forward reaction and without the appearance of pathways that use CO₂ directly to form hydrocarbons.

Net CO₂ formation rates in Figure 42 extrapolate to zero net rates at CO₂ pressures of ~0.85 MPa (CO₂/CO = 5.5). At this CO₂ pressure, *all* of the O* species formed *via* CO dissociation would be removed as H₂O during FTS at 543 K. The required CO₂/CO ratio predicted from Equation 10 and the equilibrium constant for WGS at 543 K ($K=63.6$) is 5.2, in close agreement with the value of 5.5 obtained from the experimental data shown in Figure 42. At 508 K, the effects of CO₂ addition on the net rate of CO₂ formation were much smaller owing to the fact that the WGS reaction was significantly away from equilibrium (Figure 38a). The use of K_{WGS} values for this temperature and Equation 10 leads to a predicted value of ~2.7 MPa (CO₂/CO=4.4).

Net CO₂ selectivities and CH₄ and C₅₊ selectivities (on a CO₂-free basis) are shown as a function of the average CO₂ pressure in Figures 43a and 43b for the two reaction conditions used in these experiments. At 543 K, CO₂ leads to a slight increase in C₅₊ selectivity and to a concomitant decrease in CH₄ selectivity (Figure 43b); these effects are not detectable at lower temperatures (Figure 43a). These selectivity effects appear to reflect small changes in the H₂/CO usage ratio as the O* is increasingly removed as water (using H₂) instead of CO₂ (using CO) as the CO₂ concentration increases. They lead to slightly lower average H₂/CO ratios throughout the catalyst bed (Figures 44a and 44b), especially at higher temperatures, for which oxygen removal selectivities depend on the presence and concentration of CO₂ in the synthesis gas. H₂ and CO chemisorption are generally assumed to be quasi-equilibrated during FTS; therefore, these changes in the H₂/CO ratio lead to a concomitant increase in the surface coverages of CO* relative to

H* and to a increase in the probability of chain growth and in the average molecular weight of the products formed. These changes become detectable only at higher temperatures, for which significant reverse rates lead to appreciable changes in the synthesis gas composition. The α -olefin/ n -paraffin ratios on Fe-Zn-K₂-Cu₁ also increase with increasing CO₂ pressure (Figures 44a and 44b) for chains of all sizes at 543 K, while the effects were very small at 508 K. These changes are also consistent with the lower H₂/CO ratios and the lower expected surface H* concentrations prevalent when CO₂ is added to the synthesis gas stream.

Figure 43. Product selectivities as a function of the average CO₂ pressure on the Fe-Zn-K₂-Cu₁ catalyst at (a) 508 K, 2.14 MPa, H₂/CO=2, (b) 543 K, 0.5 MPa, H₂/CO=2; (●): C₅+, (■): CO₂ and (▲): CH₄.

Figure 44. α -Olefin/ n -paraffin ratio for different hydrocarbon chain sizes as a function of the average CO₂ pressure on the Fe-Zn-K₂-Cu₁ catalyst at (a) 508 K, 2.14 MPa, and (b) 543 K, 0.5 MPa, H₂/CO=2; (●): C₃H₆/C₃H₈, (■): *I*-C₅H₁₀/ n -C₅H₁₂, (▲): *I*-C₁₁H₂₂/ n -C₁₁H₂₄, and (○): Average H₂/CO ratio in the reactor.

These results show that the extent to which O* is removed as CO₂ during FTS can be controlled by the addition or recycle of CO₂ and that the required CO₂ concentrations can be accurately estimated using a rigorous kinetic treatment of reversible reactions as such

reactions approach equilibrium. At temperatures and reaction conditions for which WGS reactions are far away from equilibrium, the complete inhibition of CO₂ formation requires large CO₂/CO ratios. However, at higher temperatures, which lead to higher forward WGS rates and to less favorable WGS thermodynamics, the CO₂/CO ratios required to eliminate CO₂ formation become small enough for potential use of CO₂ recycle when H₂/CO mixtures derived from natural gas are used on Fe-based FTS catalysts.

8.5. *The role of CO₂ in the initiation and growth of hydrocarbon chains*

As WGS reactions approach equilibrium during FTS, CO and CO₂ become kinetically indistinguishable, because their interconversion is much faster than chain initiation and growth steps required for hydrocarbon formation. Then, a significant fraction of the C-atoms in CO₂ can contribute towards the formation of hydrocarbons, but *via* the formation of CO intermediates in reverse WGS reactions. A direct role of CO₂ in chain initiation and propagation was proposed by Xu *et al.* [57,60], but it is unclear how such conclusions could be reached from isotopic experiments influenced by significant chemical (and isotopic) interconversion of CO and CO₂ *via* WGS reactions.

Here, we report the results of experiments in which 0.1 MPa ¹³CO₂ was added to synthesis gas (P_{CO}=0.25 MPa, P_{H2}=0.50 MPa and P_{N2}=0.05 MPa) at conditions far removed from the WGS equilibrium (η =0.025). The CO conversion and product selectivities are listed in Table 12. The ¹³C contents in hydrocarbons chains of a given size were measured in order to probe the relative contributions of ¹³CO₂ and ¹²CO to chain initiation and chain growth. These results were not corrupted by any isotopic or chemical equilibration between the CO and CO₂ components in the reactant stream. As shown in Figure 45, the ¹²CO reactant exiting the reactor retains the ¹²C isotopic purity, while the initially pure ¹³CO₂ reactants retain ¹³C fractions greater than 0.5.

The ¹³C contents in CO₂, CO, hydrocarbons, oxygenates (aldehydes + alcohols) are shown in Figure 45. No ¹³C was detected in CO, suggesting that dilution of the CO reactant by CO molecules formed from CO₂ *via* reverse WGS reactions was negligible at these reaction conditions, consistent with the low value of η (=0.025). The fraction of ¹³C in CO₂ was 0.533, because CO₂ formed during O* removal using CO or *via* WGS reactions dilutes the isotopically pure ¹³CO₂ reactants. The ¹³C fraction in all C₁-C₁₀ paraffins, C₂-C₁₀ olefins, and C₁-C₈ oxygenates are much lower than in CO₂, and in most cases, well below the detection limit (~0.02-0.03) of our analytical methods. Clearly, no preferential incorporation of CO₂ is detected in any of the hydrocarbon products; exclusive chain initiation by CO₂, as proposed earlier [57,60], would have led to significant isotopic enrichment of the smaller products and to a decrease in the ¹³C content with increasing chain size, neither of which was experimentally observed in our study (Figure 45). Also, the reactivity of CO₂ in chain initiation and growth would have to be at least five times lower than that of CO, because the average ¹³C fraction in the combined CO/CO₂ pool is about 0.25, while that in the pool of hydrocarbon formed is less than 0.05, and for most of the hydrocarbons below the detection limit. Thus, the participation of CO₂ is no greater than that of CO in either the formation of monomers or

the initiation of chains, and probably much smaller. CO₂ is also not involved in alcohol formation, because the ¹³C content in alcohols was also very low and similar to that found in hydrocarbons.

Table 12. Conditions for ¹³CO₂ addition experiments performed on the Fe-Zn-K₄-Cu₂ catalyst, reaction parameters and ¹³C content in different components.

Temperature (K)	508
Synthesis Gas Pressure (MPa) (H ₂ /CO=2)	0.8
¹³ CO ₂ pressure (MPa)	0.1
CO conversion (%)	21.1
CO ₂ selectivity (%)	35.9
η^*	0.025
<i>Selectivity (CO₂-free, %)</i>	
CH ₄	3.5
C ₅₊	81.8

*: as defined in Equation 1

Figure 45. ^{13}C fraction in CO, CO₂, paraffins, olefins and oxygenates during $^{13}\text{CO}_2$ addition runs on the Fe-Zn-K₄-Cu₂ catalyst at 508 K, 0.8 MPa, H₂/CO=2, 0.1 MPa $^{13}\text{CO}_2$.

In summary, an investigation of the CO₂ formation and reaction pathways during Fischer-Tropsch synthesis (FTS) has been carried out on a co-precipitated Fe-Zn catalyst promoted with Cu and K. The removal of adsorbed oxygen formed during CO dissociation steps can occur by primary and secondary pathways. Primary pathways for oxygen removal include reactions with adsorbed hydrogen to form H₂O and with adsorbed CO to form CO₂. The relative probability of oxygen removal either as H₂O or CO₂ is determined by the reaction temperature and the presence of promoters (Cu and K). H₂O formed by primary pathways can undergo readsorption followed by its subsequent reaction with CO-derived intermediates leading to the formation of CO₂. The forward rate of CO₂ formation increases with an increase in residence time, while the net CO₂ formation rate decreases due to the approach towards WGS reaction equilibrium. CO₂ addition during FTS does not influence CO₂ forward rates, but increases the rate of their reverse steps leading to the attainment of WGS equilibrium; and hence it can result in the minimization of CO₂ formation during FTS and to the preferential removal of oxygen as H₂O. CO₂ addition also results in lower H₂/CO ratios in the reactor, which in turn resulted in higher C₅₊ selectivities and olefin content. From our experimental data and the predictions from our thermodynamic treatment, it was found that at 543 K, the addition of 0.85 MPa CO₂ to synthesis gas (H₂/CO=2, 0.50 MPa) could eliminate CO₂ formation during FTS and lead to the complete removal of dissociated oxygen formed during FTS as H₂O. These studies also suggest that the recycle of CO₂ formed during FTS can be used as a tool to improve the carbon efficiency on Fe catalysts, which in turn adds to their advantage of being cheaper and more flexible than Co catalysts. Finally, the addition of ¹³CO₂ to H₂/¹²CO reactants showed that the hydrocarbon products had a negligible ¹³C content, indicating that CO₂ is much less reactive than CO towards chain initiation and growth. Our studies also show that except at WGS reaction equilibrium, where CO and CO₂ become kinetically indistinguishable from each other, CO₂ does not appear to compete with CO towards chain initiation and growth reactions.

9. Investigation of the kinetic isotope effects during FTS Reactions on Fe catalysts

Isotope effects were determined by performing FTS reactions on the Fe-Zn-K₂-Cu₁ catalyst with CO/H₂/N₂ (31/62/7) and CO/D₂/N₂ (31/62/7) mixtures (H₂/CO=D₂/CO=2.0) at 508 K and 2.14 MPa. The deuterium content in hydrocarbon products (up to C₈) and in water were measured by a Hewlett-Packard 5890 gas chromatograph coupled with a 5972 A mass selective detector, while the D content in hydrogen isotopomers was determined by online mass spectrometry (Leybod Inficon Instruments Co., Inc.). The D contents were calculated using matrix techniques that correct for ion fragmentation [61].

9.1. H₂/D₂ effects on FTS rates

Figures 46 and 47 show hydrocarbon formation rates and CO₂ formation rates as a function of CO conversion on the Fe-Zn- K₂-Cu₁ catalyst. Hydrocarbon formation rates were much higher with D₂/CO than with H₂/CO. In contrast, CO₂ formation rate was lower with D₂/CO than with H₂/CO. It has been proposed previously that the formation of higher molecular weight hydrocarbons on Fe-based catalyst during FTS reactions is initiated by the addition of a methyl group to a methylene group and that further chain growth occurs by the reaction of the methylene group with adsorbed alkyl groups. The alkyl groups then react to form olefins and paraffins via either hydrogen elimination or addition. Consistent with these views of CO hydrogenation, one would expect to observe a normal isotopic effect if D₂ were used instead of H₂.

Figure 46. Hydrocarbon formation rate as a function of CO conversion on the Fe-Zn- K₂-Cu₁ catalyst (Zn/Fe=0.1, K/M=0.02, Cu/M=0.01) at 508 K, 2.14 MPa, H₂/CO=D₂/CO=2.

However, we observed an inverse isotopic effect as D₂ was used instead of H₂. The overall isotopic effect for CO hydrogenation could arise from a combination of kinetic and equilibrium isotope effects, the former favoring the reaction of H₂ and the latter favoring the reaction of D₂. If the chemisorption characteristics of H₂ and D₂ on Co were

to be different so as to result in a higher surface coverage of D* than H*, this would lead to a thermodynamic isotope effect that would be opposite in magnitude to the kinetic isotope effect. The inverse isotopic effects of our observations suggested a dominant role of the thermodynamic effects.

Figure 47. CO₂ formation rate as a function of CO conversion on the Fe-Zn- K₂-Cu₁ catalyst (Zn/Fe=0.1, K/M=0.02, Cu/M=0.01) at 508 K, 2.14 MPa, H₂/CO=D₂/CO=2.

The isotopic effect can be expressed by the ratio of r_H/r_D , where r_H and r_D are FTS rates for H₂ and D₂ respectively, at the same CO conversion. Since experimental values for both r_H and r_D were not obtained at the same CO conversion, these values were obtained by extrapolation from the respective rate vs CO conversion curves. A reaction rate expression proposed [65] for FTS is

$$-r_{CO+H_2} = \frac{kP_{CO}P_{H_2}^2}{P_{CO}P_{H_2} + bP_{H_2O}}$$

Where b is the adsorption parameter and k is the rate constant. Based on this rate expression, hydrocarbon formation rate ($-r_{CO+H_2}$) increases almost linearly with hydrogen pressure at low CO conversions. Since the surface hydrogen concentration is determined by hydrogen pressure (*i.e.* H₂ dissociation is quasi-equilibrated), higher surface hydrogen concentrations result in higher hydrocarbon formation rates. Therefore, hydrocarbon formation rates were higher with D₂ at the same CO conversion, as shown in Figure 46. The lower CO₂ formation rates with D₂ were also due to the higher surface deuterium concentration since hydrogen is one of the products of the water-gas shift reaction (Figure 47). The higher surface D₂ concentration is due to its larger adsorption equilibrium coefficient. This result is in agreement with previous studies. Soller [66] observed that the adsorption of D₂ was about 1.4 times higher than that of H₂ on Cu powder at 398 K. Larger adsorption coefficients were also obtained for D₂ than for H₂ on Ni during the hydrogenation of acetylene [67] and of CO₂ [68].

Figure 48 shows the r_H/r_D ratios for CO conversion, hydrocarbon and CO₂ formation as a function of CO conversion. The r_H/r_D ratio for hydrocarbon formation was about 0.5 and

slightly decreases with increasing CO conversion. The isotope effect (r_H/r_D) for CO consumption is about 0.6, and independent of CO conversion. This value is similar to that reported by Sakharov and Dokukina [69]. The r_H/r_D ratio for CO_2 formation was greater than 1. The inverse isotopic effect for hydrocarbon formation ($r_H/r_D < 1$) and the normal isotopic effect for CO_2 formation ($r_H/r_D > 1$) are expected because higher surface hydrogen concentration was present when D_2 was used. The slight decrease in the r_H/r_D ratio for hydrocarbon formation with increasing CO conversion could be associated with small changes in the partial pressure of hydrogen with CO conversion.

Figure 48. r_H/r_D ratios for CO conversion, hydrocarbon and CO_2 formation as a function of CO conversion for H_2/CO or D_2/CO reactants on the Fe-Zn- K_2 -Cu₁ catalyst (Zn/Fe=0.1, K/M=0.02, Cu/M=0.01) at 508 K and 2.14 MPa.

9.2. H_2/D_2 effects on α -olefin/*n*-paraffin ratios

Figure 49 shows α -olefin/*n*-paraffin ratios as a function of the carbon number. The increase in surface H_2 or D_2 concentration on the catalyst increases the probability of hydrogen addition of the adsorbed alkyl to form paraffins and decrease the probability of hydrogen elimination of the adsorbed alkyl to form olefins. Hence, lower α -olefin/*n*-paraffin ratios are observed with D_2 than H_2 . The isotopic effect for *l*-butene and *n*-butane is illustrated in Figure 50. The r_H/r_D ratios for *l*-butene were higher than that for *n*-butane, suggesting that the inverse isotopic effect is more evident for paraffins than for olefins. This is because the probability of paraffin formation increased due to higher surface hydrogen concentrations when D_2 was used.

Figure 49. α -Olefin/*n*-paraffin ratio as a function of CO conversion for H₂/CO or D₂/CO reactants on the Fe-Zn-K₂-Cu₁ catalyst (Zn/Fe=0.1, K/M=0.02, Cu/M=0.01) at 508 K and 2.14 MPa.

Figure 50. r_H/r_D ratios for *l*-butene, *n*-butane and total C₄ as a function of CO conversion for H₂/CO or D₂/CO reactants on the Fe-Zn-K₂-Cu₁ catalyst (Zn/Fe=0.1, K/M=0.02, Cu/M=0.01) at 508 K and 2.14 MPa.

II. FISCHER-TROPSCH SYNTHESIS ON COBALT CATALYSTS

1. Background

In contrast with Fe, Co catalysts work at relatively lower reaction temperatures and pressures with slightly higher selectivity to linear paraffins in the C₅₊ range and much lower water-gas-shift activity [4]. We have previously developed a *reaction-transport model* [13] of chain growth and termination for FTS with Co and Ru-based catalysts. The aim of this project at Berkeley is to utilize a combination of activity and selectivity measurements in a high-pressure reactor along with in situ characterization tools such as FTIR and X-ray absorption spectroscopies, as well as the use of isotopes in order to investigate mechanistic implications of FTS reactions on Co-based catalysts. In contrast to Fe catalysts, H₂O is the primary oxygenate product on Co catalysts. The commercial practice of FTS requires that Co catalysts withstand long-term operation at high conversions, where water concentrations can approach their saturation levels and even condense within catalyst pores. This warrants a detailed study of its effects on the FTS rates and selectivities, as well as the chemical characteristics of the Co surface. In this project, we have utilized silica- and titania-supported Co catalysts in order to probe the kinetics of the FTS reaction as well as the effect of water on the FTS performance of Co catalysts. We have also utilized isotopic mixtures in order to test the reversibility of hydrogen and water dissociation steps in the proposed FTS mechanisms and to determine if water participates in the kinetically relevant steps of CO activation and hydrocarbon chain growth.

2. Catalyst synthesis and characterization

The Co/SiO₂ catalysts (12.7 and 21.9 wt.%) and Co/TiO₂ (15 wt.%) were prepared by incipient wetness impregnation of an aqueous solution of Co nitrate (Aldrich 98%) onto SiO₂ support (PQ Co. CS-2133; treated in dry air at 673 K for 3 h) and TiO₂ (Degussa; treated in dry air at 673 K for 3 h) respectively. These samples were dried at 333 K in ambient air for 24 h and treated in flowing H₂ (1.2×10^4 cm³/h.g-cat) by increasing the temperature from 293 K to 423 K at 0.17 K/s and from 423 K to 623 K at 8.3×10^{-3} K/s and then holding at 623 K for 1 h. The samples were then passivated in a 1% O₂/He at ambient temperature before exposure to ambient air. Cobalt dispersions were measured using H₂ chemisorption (AutoSorb-1; Quantachrome) at 373 K, after passivated samples were reduced in H₂ at 598 K, evacuated to $< 10^{-3}$ Pa at 598 K, and cooled to 373 K. A 1:1 H/Co titration stoichiometry was used to calculate cobalt dispersions, which were found to be 6.3% and 4.2% for 12.7% Co/SiO₂ and 21.9% Co/SiO₂, respectively [70].

3. FTS activity and selectivity measurements

FTS reaction rates and selectivities were measured at 473 K and 2 MPa using a single-pass fixed-bed reactor (SS 304, 0.95 cm O.D. and 0.5 cm I.D.), held within a three-zone furnace and controlled by three temperature controllers. Axial temperature profiles were measured using a type K movable thermocouple contained within a 0.32 cm thermowell, and they were within ± 0.5 K of the average bed temperature. All lines were heat-traced to

433-553 K and two vessels, one at 408 K after the reactor to collect liquid products, and the other at ambient pressure and temperature to collect water and light fractions were used. Analysis of reactants and products were conducted using a HP 5890 GC-Series II and the procedure is described in detail in Section 4.4. Flow of synthesis gas (62% H₂, 31% CO, 7% N₂ internal standard; Praxair: 99.9% H₂, 99.9% CO, 99.99% N₂) and hydrogen (Bay Air gas: 99.999%) were metered using mass flow controllers (Brooks, Model 5850-CAB1AF1A3). H₂/D₂ kinetic isotope effects were studied by running FTS with mixtures of CO/N₂ (Matheson, UHP, 81.5/18.5, molar ratio) with H₂ or D₂ (Cambridge Isotope Laboratories, Inc., 99.8%). Studies were also conducted with the addition of H₂O to synthesis gas using a ISCO 400D pump.

4. Effect of water on FTS rate and selectivities on Co catalysts

The Co site-time yields for the 12.7 and 21.9 wt.% Co/SiO₂ catalysts at 473 K and 2 MPa are shown as a function of the average water pressure in Figure 1. These data points include both space velocity and water addition runs (0.2, 0.4 and 0.8 MPa) at the lowest CO conversion. These data indicate that both indigenous and added water enhances FTS rates.

Figure 1. Water effects on FTS reaction rate (Co/SiO₂ catalysts, 473 K, 2 MPa, H₂/CO=2; Open symbols: space velocity runs; Filled symbols: water addition runs at the lowest CO conversions; water partial pressure is the average of the inlet and the exit values).

These results are consistent with those observed previously on Co/SiO₂ and Co/TiO₂ [14,71], and Co-Mg-Th-Aerosil [72]. However this behavior is in contrast to results reported on Co supported on Mn and Al oxides, which showed that water inhibits FTS rates [73-75]. Higher water concentrations also led to lower CH₄ and higher C₅₊ selectivities on Co-based catalysts as shown in Figures 2 and 3 and also as previously reported [14, 71-72, 76-78]. Iglesia *et al.* proposed that FTS rate and C₅₊ selectivity enhancements might reflect higher CO diffusion rates through a water-rich intrapellet phase stabilized by capillary effects [14].

The evidence considered was indirect and based on the influence of the support pore structure on these water effects and on the well-documented effects of intrapellet transport restrictions on FTS chemistry. Large pores would require larger H₂O concentrations to form a water-rich condensed phase, while smaller pores could stabilize such a phase even at all water concentrations prevalent in the experimental CO conversion range covered in these studies [14]. On TiO₂-supported Co catalysts, TiO_x overlayers can form during pre-reduction; these overlayers are removed in more oxidizing environments [78]. Thus, a role of water on such catalysts may be to remove TiO_x overlayers at high water concentrations. Such overlayers, however, do not form on silica, which also show water enhancement effects on large-pore supports. It is also

possible that water may: (1) participate in kinetically relevant steps in the reaction mechanism, or (2) enhance the active site density. In this project, we have tested both these hypotheses. The first approach involves the formulation of reaction mechanisms that involve water participating in the rate-determining steps, followed by fitting the reaction data obtained using non-linear regression to the obtained rate expressions.

Figure 2. Water effects on CH₄ selectivity (Co/SiO₂ catalysts, 473 K, 2 MPa, H₂/CO=2; Open symbols: space velocity runs; Filled symbols: water addition runs at the lowest conversions; water partial pressure is the average of the inlet and the exit values)

Figure 3. Water effects on C₅₊ selectivity (Co/SiO₂ catalysts, 473 K, 2 MPa, H₂/CO=2; Open symbols: space velocity runs; Filled symbols: water addition runs at the lowest conversions; water partial pressure is the average of the inlet and the exit values)

5. Kinetic studies to explore effect of water on the reaction mechanism

5.1. H_2 - D_2 Exchange and D_2O Tracer Experiments

D_2 - H_2 exchange was carried out by performing FTS reactions at 473 K and 2 MPa with a $CO/H_2/D_2/N_2$ mixture (31% CO , 31% D_2 , 31% H_2 , 7% N_2). The deuterium content in hydrocarbon products (up to C_8) and in water were measured by a GC-MS (Hewlett-Packard 5972), while the D content in hydrogen isotopomers was determined by mass spectrometry (Leybod Inficon Instruments Co., Inc.). The D contents were calculated using matrix techniques that correct for ion fragmentation [61]. The formation rate of the HD was compared to the rate of hydrogen converted to hydrocarbons (Figure 4). The isotopic exchange rates presented here have been calculated by subtracting those measured in a blank run using SiO_2 . Hydrogen exchange rate decreased from 450 h^{-1} to 200 h^{-1} as the CO conversion increased from 6% to 15% (by decreasing bed residence time), while the rates of hydrogen conversion to hydrocarbons were less than 50 h^{-1} . At zero CO conversion, the D_2 - H_2 exchange rate (590 h^{-1}) is almost 20 times larger than the conversion rate (30 h^{-1}). It is also observed that the isotopic exchange nearly reaches equilibrium at CO conversions of 6-15%. Therefore, the results of these H_2 - D_2 exchange experiments show that the H_2 dissociation step is quasi-equilibrated during FTS.

Figure 4. Hydrogen conversion rate to hydrocarbons (♦), HD formation rate (□), and expected rate for equilibrium HD formation (Δ) in the D_2 - H_2 exchange reaction at FTS conditions on a 21.9 wt.% Co/SiO_2 catalyst (473 K, 2 MPa, $H_2/D_2/CO = 1/1/1$).

In order to explore the reversibility of water dissociation step during FTS, D_2O tracer studies were carried out by co-feeding 0.2 MPa D_2O with 2 MPa syngas (13.8% D in the feed) using a ISCO 400D series pump. The deuterium content in hydrocarbon products (up to C_8) and in water were measured by a Hewlett-Packard 5890 gas chromatograph coupled with a 5972 A mass selective detector, while the D content in hydrogen isotopomers was determined by online mass spectrometry (Leybod Inficon Instruments Co., Inc.). The D contents were calculated using matrix techniques that correct for ion fragmentation as mentioned earlier. The results are shown in Figure 5. The D content in

water decreases with increase in the bed residence time, because more H₂O formed at longer bed residence times, *i.e.*, at higher conversions. The D contents in all the primary products (C₄-C₈) and in the H₂ isotopomers increase with increasing bed residence time, suggesting the D content in surface H-D pool increases with bed residence time. The water dissociation steps during FTS are as follows:

1. $O^* + H^* \leftrightarrow OH^* + *$
2. $OH^* + H^* \leftrightarrow OH_2^* + *$
3. $OH_2^* \leftrightarrow H_2O + *$

Figure 5. Deuterium content in FTS products (21.9 wt% Co/SiO₂ catalysts, 473 K; H₂/CO/N₂ = 62/31/7, 2 MPa; D₂O added, 2 atm)

These may influence the H/D ratio on surface. Assuming the step (3) is quasi-equilibrated, at least one of the steps (1) and (2) must be away from equilibrium. Otherwise, the D content in all hydrocarbons and H₂ isotopomers would be independent of bed residence time. Also, extrapolating the data in Figure 5 to zero bed residence time, we find that the D content in hydrocarbons and H₂ isotopomers are ~0.03. This is an indication that water dissociation is reversible, but not quasi-equilibrated during FTS.

In the following section, we propose a series of reaction mechanisms that could involve the participation of water in monomer formation pathways. A set of kinetic data was obtained using the procedure described in Section 6.3, where in the partial pressure of CO, H₂ or H₂O was varied holding the pressures of the other two components to a constant value at 473 K and 2 MPa on a 21.9 wt.% Co/SiO₂ catalyst. We also fit our kinetic data to the rate expressions obtained using non-linear multivariate regression.

5.2. Formulation of reaction mechanisms and derivation of rate expressions

The Fischer-Tropsch synthesis is a polymerization reaction, although the mechanism and the nature of the intermediates remain a subject of active discussion [13,79,80]. The surface carbide mechanism, which was originally proposed by Fischer and Tropsch [2], is

the currently accepted route for the formation of monomers. This mechanism assumes that CO dissociates on surface metal sites to form carbon adatoms. Subsequently, carbon adatoms undergo hydrogenation to form surface CH_x groups, which are the monomers in chain growth processes leading to hydrocarbons (olefins, paraffins and oxygenates) with a broad range of chain length and functionality.

Table 1. Kinetic rate expressions of the FTS on cobalt-based catalysts

Reference	Catalyst	Overall kinetic expression*
van der Baan, <i>et al.</i> , [81]	Co/ Al_2O_3	$-\text{r}_{\text{CO}} = a\text{P}_{\text{H}_2}\text{P}_{\text{CO}}^{1/2}/(1 + b\text{P}_{\text{CO}}^{1/2})^3$
Wojciechowsky, <i>et al.</i> , [82]	Co/Kieselguhr	$-\text{r}_{\text{CO}} = a\text{P}_{\text{H}_2}^{1/2}\text{P}_{\text{CO}}^{1/2}/(1 + b\text{P}_{\text{H}_2}^{1/2} + c\text{P}_{\text{CO}}^{1/2})^2$
Satterfield, <i>et al.</i> , [83]	Co/MgO/ SiO_2	$-\text{r}_{\text{CO}+\text{H}_2} = a\text{P}_{\text{H}_2}\text{P}_{\text{CO}}/(1 + b\text{P}_{\text{CO}})^2$
Pannell, <i>et al.</i> , [84]	Co/ La_2O_3 / Al_2O_3	$-\text{r}_{\text{CO}+\text{H}_2} = a\text{P}_{\text{H}_2}^{0.55}\text{P}_{\text{CO}}^{-0.33}$
Yang, <i>et al.</i> , [85]	Co/CuO/ Al_2O_3	$-\text{r}_{\text{CO}+\text{H}_2} = a\text{P}_{\text{H}_2}\text{P}_{\text{CO}}^{-0.5}$

* a, b, and c in these equations are temperature-dependent constants.

Some kinetic rate expressions FTS reported in the literature for cobalt-based are shown in Table 1. According to these studies, the FTS rates exhibit a positive order in H_2 , while the influence of CO varies from negative to mildly positive depending on the CO concentration. However, none of these rate expressions contain a water partial pressure term, implying that these authors did not notice an effect of water. In addition, none of these expressions can be obtained rigorously by pseudo-steady state analyses of a set of elementary steps.

In our studies, the Langmuir-Hinshelwood type rate expressions were obtained by assuming that the rate-determining step involves the formation of surface methylene groups (CH_2^*) from adsorbed C^* and H^* . We observed the enhancement of the synthesis rate by water on cobalt catalysts. To explain the positive water effect, an additional pathway for C^* consumption must be considered and this pathway must be influenced by gas phase water. From the D_2O tracer study, we know that the concentration of surface OH_2^* depends on the relative amount of water in the gas mixture. It is expected that surface C^* may react with OH_2^* to form CHOH^* species. The latter species may be hydrogenated or may react with partially hydrogenated C_n^* species. In fact, the presence of species containing C-O-H bands on cobalt FTS catalysts has been confirmed by IR spectroscopy [86]. Of course, other pathways may also lead to species containing C-O-H bands. The concentration of OH_2^* will increase with water partial pressure, increasing the C^* consumption through the proposed water-aided pathway. However, the hydrogenation of C^* using hydrogen remains operative and it is the dominant route when the water concentration is low. The corresponding elementary steps for FTS on cobalt are as follows:

Mechanism 1:

1. $\text{H}_2 + 2^* \leftrightarrow 2\text{H}^*$
2. $\text{CO} + 2^* \leftrightarrow \text{C}^* + \text{O}^*$
3. $\text{C}^* + \text{H}^* \rightarrow \text{CH}^* + ^*$
4. $\text{C}^* + \text{OH}^* \rightarrow \text{COH}^* + ^*$
5. $\text{O}^* + \text{H}^* \leftrightarrow \text{OH}^* + ^*$
6. $\text{OH}^* + \text{H}^* \leftrightarrow \text{OH}_2^* + ^*$
7. $\text{OH}_2^* \leftrightarrow \text{H}_2\text{O} + ^*$

The dissociative H_2 adsorption (Step 1) is a quasi-equilibrated step (based on the results of D_2 - H_2 exchange). In addition, it is not likely to be a rate-determining step because the FTS rate has a positive order in CO partial pressure for low CO concentrations [82], which would not be present if hydrogen dissociation on free sites were to be the only kinetically relevant step. CO chemisorbs molecularly and then dissociates to produce adsorbed C and O, respectively. The extent to which these processes are reversible remains unresolved [79]. Here, we assume that CO adsorption (Step 2) is also quasi-equilibrated. We also conceive two parallel pathways that consume surface C^* , namely, C^* reacting with H^* (Step 3) and with OH_2^* (Step 4). We have the synthesis rate, $r_{\text{CO}} = k_3[\text{C}^*][\text{H}^*] + k_4[\text{C}^*][\text{OH}_2^*]$. We assume that the important surface species are unoccupied sites and adsorbed C^* , O^* , OH_2^* and H^* . Other species, though present, are not important in the stoichiometric balance of surface sites. Applying the pseudo-steady state approximation to step 1 through 7 leads to a Langmuir-Hinshelwood type expression.

$$r_{\text{CO}} = aP_{\text{CO}}^{1/2}P_{\text{H}_2}^{1/4}(bP_{\text{H}_2}^{1/2} + cP_{\text{H}_2\text{O}})^{1/2}/(1 + dP_{\text{H}_2}^{1/2} + eP_{\text{H}_2\text{O}} + fP_{\text{CO}}^{1/2})^2, \text{ in which,}$$

$$a = (K_1^{1/2}K_2 k_5)^{1/2}$$

$$b = K_1^{1/2}k_3$$

$$c = k_4K_{-7}$$

$$d = (K_1)^{1/2}$$

$$e = K_{-7}$$

$$f = (K_2(k_5/k_3 + k_3/k_5))^{1/2}$$

Since CO adsorption is much stronger than the adsorption of H_2 and water on cobalt [13,82], the term in the denominator containing CO partial pressure becomes much larger than the others if the CO partial pressure in the gas phase is not too low. Then, the rate expression simplifies to

$$r_{\text{CO}} = aP_{\text{CO}}^{-1/2}P_{\text{H}_2}^{1/4}(bP_{\text{H}_2}^{1/2} + cP_{\text{H}_2\text{O}})^{1/2}, \text{ in which,}$$

$$a = k_1^{1/4}k_5^{1/2}/(K_2^{1/2}(k_5/k_3 + k_3/k_5))$$

$$b = K_1^{1/2}k_3$$

$$c = k_4K_{-7}$$

Another mechanism was also considered to account for the positive water effects. Earlier studies suggest that the Co surface is covered almost entirely by non-dissociated CO during FTS [4,79]. Hydrogen-assisted CO dissociation has also been considered as a rate-

limiting step in FTS [86]. Here, we have assumed that both H_2 and H_2O can react with adsorbed CO. Then, we have the follow elementary steps.

Mechanism 2

1. $H_2 + 2* \leftrightarrow 2H^*$
2. $CO + * \leftrightarrow CO^*$
3. $CO^* + H^* \rightarrow C^* + OH^*$
4. $CO^* + OH_2^* \rightarrow C^* + 2OH^*$
5. $O^* + H^* \leftrightarrow OH^* + *$
6. $OH^* + H^* \leftrightarrow OH_2^* + *$
7. $OH_2^* \leftrightarrow H_2O + *$

A rate expression was obtained according to the proposed mechanism by applying the pseudo-steady state hypothesis with quasi equilibrium assumptions.

$$r_{CO} = (aP_{CO}P_{H_2}^{1/2} + bP_{CO}P_{H_2O}) / (1 + cP_{H_2}^{1/2} + dP_{H_2O} + eP_{CO})^2, \text{ where,}$$

$$\begin{aligned} a &= K_1^{1/2} K_2 k_3 \\ b &= K_2 k_4 (K_7)^{-1} \\ c &= K_1^{1/2} \\ d &= (K_7)^{-1} \\ e &= K_2 \end{aligned}$$

A modification of the second mechanism was also considered by including an additional step that allows the formation of CH^* directly during hydrogen-assisted CO dissociation as shown below.

Mechanism 3:

1. $H_2 + 2* \leftrightarrow 2H^*$
2. $CO + * \leftrightarrow CO^*$
3. $CO^* + H^* \rightarrow C^* + OH^*$
4. $CO^* + H^* \rightarrow CH^* + O^*$
5. $CO^* + OH_2^* \rightarrow COH^* + 2OH^*$
6. $COH^* + * \rightarrow C^* + OH^*$
7. $O^* + H^* \leftrightarrow OH^* + *$
8. $OH^* + H^* \leftrightarrow OH_2^* + *$
9. $OH_2^* \leftrightarrow H_2O + *$

The parallel pathways for CO dissociation are described by the steps 3, 4 and 5. Using similar procedures as above, this mechanism led to the following rate expression:

$$r_{\text{CO}} = \frac{(aP_{\text{CO}}P_{\text{H}_2}^{1/2} + bP_{\text{CO}}P_{\text{H}_2\text{O}})}{\left(1 + cP_{\text{H}_2}^{1/2} + dP_{\text{H}_2\text{O}} + eP_{\text{CO}} + \frac{fP_{\text{CO}}P_{\text{H}_2\text{O}}}{P_{\text{H}_2}^{1/2}}\right)^2}$$

where the rate is given in h^{-1} and the individual pressures in atm. The experimental data was also used to test the above expression in the regression program and determine the various constants.

5.3. Kinetic studies and mathematical fitting of data to rate expressions

FTS kinetic data were obtained over a broad range of H_2/CO ratios (1.3 to 8.5) and pressures (1.3 to 3.3 MPa) and space velocities, and with different concentration of H_2O , at 473 K and 2 MPa on the 21.9 wt.% Co/ SiO_2 catalyst. The experimental results are presented in Table 2. For this set of data, it was difficult to do a regression using only the two adjustable parameters, P_{CO} , P_{H_2} . Thus, it was decided that the rate expression should also include $P_{\text{H}_2\text{O}}$. These data were first fitted using a multilinear regression, leading to a power law rate expression: $r_{\text{CO}} = 56.3\text{H}_2^{0.43}\text{CO}^{-0.53}\text{H}_2\text{O}^{0.38}$.

Figure 6. A comparison of predicted rates from Mechanism 2 with the measured rates for a 21.9% Co/ SiO_2 catalyst at 473 K and 2 MPa, $\text{H}_2/\text{CO}=2$.

Figure 7. A comparison of predicted rates from Mechanism 3 with the measured rates for a 21.9% Co/ SiO_2 catalyst at 473 K and 2 MPa, $\text{H}_2/\text{CO}=2$.

A sample of this data was then regressed using nonlinear least squares method and fitted to the above proposed mechanisms in order to obtain the best possible fit. A comparison between the measured rates and predicted rates is plotted for the above-mentioned mechanisms 2 and 3 are shown in Figures 6 and 7. In both cases, the predicted rates are within 95% of the measured rates and hence both the mechanisms are consistent with the FTS reaction kinetics on Co/ SiO_2 and can explain the positive water effect on these catalysts. The parameters obtained in both these cases are listed in Table 3.

Table 2. Experimental results of FTS kinetic study over 21.9 wt.% Co/SiO₂ catalyst*

No	Partial pressure (atm)			CO conversion	CO conversion	CH ₄ formation	C ₅ + synthesis
	H ₂	CO	H ₂ O	(%)	rate (h ⁻¹)	rate (h ⁻¹)	rate (h ⁻¹)
1	11.6	5.4	0.5	17.2	48.3	4.6	41.8
2	11.6	5.7	0.3	8.7	36.9	4.2	28.7
3	9.3	6.0	0.2	7.7	29.9	2.8	24.1
4	18.3	6.0	0.1	4.5	32.3	5.8	17.8
5	17.2	5.1	0.6	20.4	64.7	8.8	53.7
6	17.9	5.9	0.2	8.0	42.5	6.6	29.8
7	24.0	5.3	0.5	16.6	70.4	12.1	51.1
8	25.0	6.0	0.2	7.6	50.1	10.0	29.3
9	11.9	5.8	0.2	7.4	41.8	5.2	32.2
10	11.3	5.3	0.6	21.3	59.7	5.2	50.8
11	11.9	5.9	0.2	6.6	37.2	5.2	27.5
12	10.8	2.6	0.3	20.4	57.2	7.3	42.7
13	11.5	2.8	0.1	7.7	43.9	8.0	30.8
14	10.2	2.3	0.5	32.9	68.6	9.4	58.1
15	11.8	5.8	0.2	5.3	30.1	4.4	22.2
16	11.4	5.5	0.5	17.1	54.0	4.9	43.4
17	11.2	5.2	0.6	21.5	60.4	5.4	50.4
18	11.4	1.4	0.1	10.0	57.0	13.1	--
19	10.6	1.3	0.2	23.1	64.7	12.6	--
20	9.7	1.2	0.3	38.5	80.3	16.4	60.4
21	11.3	5.2	0.6	20.4	57.2	5.3	47.5
22	11.6	8.7	0.2	4.8	27.4	3.2	20.6
23	11.3	8.6	0.3	6.6	30.4	3.0	22.9
24	11.7	5.4	0.5	18.0	50.5	5.1	42.5

* Reaction conditions: 473 K, H₂/CO ratios from 1.3 to 8.5, pressures from 13 to 33 atm, water partial pressure is the average of water pressures at the reactor inlet and outlet.

Table 3. Values of Parameters in rate expressions, obtained by best fit for two mechanisms listed above.

Parameter	Mechanism 2	Mechanism 3
a (atm ^{-3/2} hr ⁻¹)	59.8	45.3
b (atm ⁻² hr ⁻¹)	527.1	443.4
c (atm ^{-1/2})	2.3*10 ⁻¹⁴	8.8*10 ⁻⁸
d (atm ⁻¹)	1.8	1.5*10 ⁻⁸
e (atm ⁻¹)	1.0	0.9
f (atm ^{-3/2})	-	1.0

6. Determination of the Kinetic isotope Effect (KIE) during FTS on Co catalysts

Isotope effects were determined by performing FTS reactions with CO/H₂/N₂ and CO/D₂/N₂ mixtures. Rates of CO consumption as a function of the average H₂O partial pressure within the reactor are shown for experiments with both CO/H₂ and CO/D₂ over the 21.9 wt.% Co/SiO₂ catalyst in Figure 8. In both cases, the FTS rate increases with increasing CO conversion (and hence water concentration). The isotope effects (r_H/r_D) for overall CO consumption were obtained by comparing the synthesis rate with CO/H₂ to that using CO/D₂ at each conversion level (Figure 9). The isotope effect (r_H/r_D) for CO consumption is about 0.8, and independent of CO conversion. This value is almost identical to that reported by Sakharov and Dokukina [65]. If C-H bond formation is a rate-determining step, this will result in a normal isotope effect ($k_H/k_D > 1$). On the other hand, if the chemisorption characteristics of H₂ and D₂ on Co were to be different so as to result in a higher surface coverage of D* than H*, this would lead to a thermodynamic isotope effect that would be opposite in magnitude to the kinetic isotope effect. Hence, the inverse isotope effect observed can reflect on a combination of kinetic and equilibrium isotope effects.

Figure 8. Rate of CO consumption versus CO conversion:◆ H₂, □ D₂ (21.9 wt% Co/SiO₂, 473 K, 2 MPa, H₂/CO or D₂/CO = 2).

The fact that the observed isotope effect is almost independent of which hydrogen isotope is used indicates that it is unlikely for water to play a direct kinetic role that would account for the observed rate enhancement. This is because at higher CO conversions, the water concentration is larger and would lead to a greater contribution of H₂O-mediated pathways and to a different KIE value than at the low H₂O concentrations that prevail at low CO conversions. This result indicates that H₂O does not play a role in the reaction mechanism and hence the turnover rate enhancement due to an increase in the H₂O concentration could reflect instead an increase in the active site density (either CO-binding sites or the total amount of active carbon on the catalyst surface). We test this hypothesis in the next section.

Figure 9. Isotope effect for CO consumption versus CO conversion (21.9 wt% Co/SiO₂, 200°C, 20 atm, H₂/CO or D₂/CO = 2).

7. Possible effects of water on the number of CO-binding sites available during FTS

7.1 Introduction

The isotopic studies discussed in the previous section have failed to detect, however, any shift in CO activation pathways when H₂O is present. H₂O can also influence FTS rates by increasing the number of exposed Co surface atoms available for CO adsorption and for monomer formation and chain growth during FTS. This could be possible due to water possibly removing or preventing the formation of less reactive forms of C-containing intermediates. Previous studies have shown that H₂O inhibits FTS reaction rates in some cases [73-75] and XPS studies [73] detected surface oxidation processes on Co/Al₂O₃ samples exposed to high H₂O concentrations during FTS. Bulk oxidation to CoO or Co₃O₄ is not thermodynamic feasible, but metal-oxygen bonds at metal surfaces are significantly stronger than in bulk oxides and small Co clusters strongly interacting with Al₂O₃ may show a greater tendency to oxidize than large Co crystallites. None of these studies however, have probed structural and compositional changes *during* Fischer-Tropsch synthesis.

In this section, we apply two techniques well suited for the detection of any such changes during reaction with the specific objective to measure changes in the oxidation state and in the availability of Co surface sites as H₂O concentrations change during FTS. *In situ* infrared spectra of CO adsorbed during FTS on Ru, Co and Fe have been reported, but typically at low pressures and high temperatures, which lead to methane as the predominant reaction product [87-91]. Stretching modes for linearly adsorbed CO, for –CH₂ and –CH₃ groups, and for surface formates were detected on Ru/Al₂O₃ [87]. A bridged CO adsorbed species was also detected on Ru/SiO₂ [88]. The –CH₂ and –CH₃ groups arise from growing chains [88,89] and from hydrocarbons physisorbed or condensed within catalyst pores. These adsorbed species have also been reported in less detailed infrared studies of Co/Al₂O₃ catalysts [90,91]. These previous infrared studies did not address the effect of reaction conditions, and specifically of H₂O concentration, on the surface coverage or frequency of these adsorbed species. The surface of Co catalysts is covered mostly by adsorbed CO during FTS [92]. Therefore, the intensity of the CO infrared bands reflects the number of Co surface atoms capable of chemisorbing CO during FTS.

X-ray absorption spectroscopy (XAS) can probe the local structure in solids during catalytic reactions. It has been used to examine the structure of Co [93,94], Co-Ru [43,95] and Co-Re [96] FTS catalysts. We present here the results of *in situ* characterization studies of Co/SiO₂ catalysts using infrared and X-ray absorption spectroscopy at various H₂O concentrations in the synthesis gas reactant stream. These studies probed a possible role of water in increasing the fraction of the Co surface atoms available for reactions and in changing the oxidation state of the Co metal crystallites initially present in supported Co catalysts after pre-treatment and before FTS reactions.

7.2. FTS activity and selectivity measurements at 0.5 MPa

At first, FTS activity and selectivity measurements were carried out at 0.5 MPa and 473 K, because these conditions are more accessible during in situ infrared and X-ray absorption spectroscopy studies. The Co site-time yields shown in Figure 10 as a function of the average water partial pressure in the reactor confirmed the presence of similar H₂O effects at these lower synthesis gas pressures. As in the case of the 2.0 MPa runs shown in Section 4, space velocity and water addition results fall in a single curve in the data shown in Figure 10. CH₄ selectivities decreased and C₅₊ selectivities increased with increasing water concentration at these lower pressures (Figure 11, Table 4). Water addition at these lower pressures also decreased the paraffin and internal olefin contents in FTS products (Figure 12, Table 4).

Several plausible roles of H₂O in FTS have been proposed [14]. For example, an intrapellet water phase, favored at high H₂O partial pressures, can increase transport rates for CO, because the solubility and diffusivity of CO is higher in water than in hydrocarbon liquids [97]. Intrapellet CO concentration gradients lead to lower FTS rates and C₅₊ and olefin selectivity; thus, an increase in CO diffusion rates could lead to the concurrent changes in rates and selectivities observed at high H₂O partial pressures. Higher transport rates mediated by intrapellet aqueous or water-rich phase, which prevails at higher H₂O pressures within the pores of the support, would be consistent with the observed effects of H₂O on FTS rates and selectivity. They would also account for the unexplained effect of support structure on the magnitude of the rate enhancements [14] and for the contradictory reports of the effect of water on rates (but not on selectivity) from various research groups. For example, the addition of water catalysts did not influence reactions rates on Co-Ru/ZrO₂/Aerosil [72], but led to lower rates on Co-Re/Al₂O₃ [73]. Co/SiO₂ catalysts with larger pores showed marked rate enhancements with H₂O, while rates on Co supported on SiO₂ with smaller pores were unaffected [14].

Figure 10. Cobalt site-time yield (h⁻¹) as a function of the average water partial pressure on a 12.7% Co/SiO₂ catalyst at 473 K, 0.5 MPa, H₂/CO=2. (Open symbols: Space velocity runs, Filled symbols: Water addition runs).

Figure 11. CH₄ selectivities (○,●) and C₅₊ selectivities (□,■) as a function of the average water partial pressure on a 12.7% Co/SiO₂ catalyst at 473 K, 0.5 MPa, H₂/CO=2. (Open symbols: Space velocity runs, Filled symbols: Water addition runs).

Figure 12. 1-pentene/*n*-pentane ratios (○,●) and 1-octene/*n*-octane ratios (□,■) as a function of the average water partial pressure on a 12.7% Co/SiO₂ catalyst at 473 K, 0.5 MPa, H₂/CO=2. (Open symbols: Space velocity runs, Filled symbols: Water addition runs).

In the next section, we explore the effects of water on the density of CO-binding sites by collecting infrared spectra during FTS reaction using synthesis gas reactants with and without added water.

Table 4. Effect of water concentration on the performance of a 12.7% Co/SiO₂ catalyst at 473 K, 0.5 MPa and H₂/CO=2.

Space velocity cm ³ /g.s	Average H ₂ O Pressure MPa	CO conversion (%)	Co site-time yield h ⁻¹	CH ₄ selectivity %	C ₅₊ selectivity %	<i>l</i> -C ₅ H ₁₀ / <i>n</i> - C ₅ H ₁₂ ratio	<i>l</i> -C ₈ H ₁₆ / <i>n</i> - C ₈ H ₁₈ ratio	<i>l</i> -C ₅ H ₁₀ /2- C ₅ H ₁₀ ratio
0.08	0.07	56.8	16.9	6.4	88.2	0.46	0.10	2.1
0.17	0.02	26.7	16.8	7.1	86.4	0.80	0.17	3.8
0.25	0.02	18.2	16.6	7.4	85.9	1.12	0.24	5.4
0.35	0.01	13.1	16.8	7.3	86.3	1.47	0.32	7.3
0.50	0.01	9.8	17.8	7.4	84.9	1.69	0.38	8.4
0.50	0.06	10.2	18.5	5.9	87.2	2.77	0.84	19.5
0.50	0.11	11.4	20.8	5.6	87.6	3.52	1.23	34.4
0.50	0.16	13.5	24.6	5.2	89.2	3.36	1.20	31.0
0.50	0.21	14.1	25.7	3.4	92.3	3.74	1.56	38.1
0.50	0.26	13.9	25.3	3.2	92.9	3.78	1.64	41.0

7.3. *In situ* infrared spectra during FTS

In situ infrared spectra were acquired using a Mattson RS-18000 Spectrometer in the transmission mode at a resolution of 2 cm^{-1} using a stainless steel cell (Figure 10). The sample consisted of a thin wafer held in the beam path by a holder. The optical path was minimized by using packed CaF_2 windows on both sides of the pellet, which also minimized the dead volume in the flow manifold. The cell temperature was held constant using a resistive heater surrounding the cell; the cell windows were kept to 353 K using a continuous water flow. The reaction temperature was monitored with a K-type thermocouple (Omega, 0.08 cm diameter, 10 cm length) placed within 1 mm of the center of the sample wafer. Wafers (20 x 1 mm) were prepared by pressing a mixture of Co/SiO₂ (0.07 g, 12.7 wt.%) and Al₂O₃ (Alon, 0.03 g) at ~100 MPa. The sample was treated in O₂/He flow ($3.6 \times 10^3\text{ cm}^3/\text{h}$) at 623 K for 0.5 h in order to remove any species adsorbed during exposure to ambient air. The cell was then flushed briefly with He at 623 K and the sample wafers reduced in H₂ ($3.6 \times 10^3\text{ cm}^3/\text{h}$) at 623 K for 2 h. The temperature of the cell was then decreased to 473 K in H₂ and a background spectrum was collected. Synthesis gas (H₂:CO=2:1, $4.8 \times 10^3\text{ cm}^3/\text{h}$) was introduced and the cell was pressurized to 0.5 MPa. Spectra were collected at 453 K and 473 K with and without external H₂O addition. Water was added by using an Isco 500D pump. All heating and cooling cycles were carried out at 0.082 K s^{-1} in order to prevent damage to the CaF_2 windows. All spectra were corrected for gas phase CO contributions by subtracting the spectrum obtained without a catalyst wafer at each temperature.

In situ infrared spectra collected on the 12.7 wt. % Co/SiO₂ catalyst at 473 K and 0.5 MPa (H₂/CO=2) are shown in Figure 11 as a function of time on stream. Several strong bands for adsorbed species were detected and their frequency and assignment resemble those reported in previous studies on Ru and Co catalysts [87-90]. The band at 1590 cm^{-1} (symmetric –OCO- stretches) and a doublet at 1390 (-CH deformation mode) and 1377 cm^{-1} (asymmetric –OCO- stretching vibrations) obscured by intense hydroxyl SiO₂ bands, arise from surface formate species adsorbed on SiO₂. The 2067 cm^{-1} band corresponds to linear CO species adsorbed on Co [87,89]. This band initially weakens and shifts slightly (to 2057 cm^{-1}) with time, and then reaches the steady-state intensity value in ~1 h. The two intense bands observed at 2927 cm^{-1} and 2855 cm^{-1} are assigned to symmetric and asymmetric C-H vibrations in methylene groups [87,88] and the band at 1450 cm^{-1} arises from C-H bending modes in –CH₂ groups. The weak shoulder at 2959 cm^{-1} is typical of symmetric C-H stretches; the antisymmetric modes are likely to be masked by the intense –CH₂ stretches [88-90]. As observed in Figure 11, these IR bands for methyl and methylene groups become more intense with time on stream, suggesting that they arise from growing chains or adsorbed hydrocarbons formed from synthesis gas; previous reports have shown that they are likely to be adsorbed growing chains because these bands are not observed when fresh samples are exposed to FTS hydrocarbon mixtures [88]. A very weak band was also detected in our samples at $\sim 1900\text{ cm}^{-1}$; this band is characteristic of bridged –CO- stretching vibrations on metal surfaces.

Figure 10. Schematic representation of the in situ FTIR spectroscopic cell

Figure 11. Evolution of FTIR spectra as a function of time under reaction conditions on a Co/SiO₂ catalyst at 473 K and 0.5 MPa (H₂/CO=2, 3.6 x 10³ cm³/h flow rate). (a) 1 min, (b) 10 min, (c) 20 min, (d) 40 min, and (e) 66 min.

Figure 12. Effect of water addition on steady state FTIR spectra under reaction conditions on a Co/SiO₂ catalyst, (473 K, 0.5 MPa, H₂/CO=2, 3.6 x 10³ cm³/h flow rate). (a) no water added, (b) 0.05 MPa H₂O, (c) 0.1 MPa H₂O, (d) H₂O stopped.

Figure 13. Effect of added water on the area of the CO adsorption peak at (a) 473 K, no water, (b) 473 K, 0.05 MPa H₂O, (c) 473 K, 0.1 MPa H₂O, (d) 473 K, H₂O stopped, (e) 453 K, no water, (f) 453 K, 0.05 MPa H₂O, and (g) 453 K, 0.1 MPa H₂O. (0.5 MPa, H₂/CO=2, 3.6 x 10³ cm³/h flow rate).

Isotopic switch studies have shown that active Co and Ru surfaces are predominately covered by adsorbed CO during FTS, even near ambient pressures [92]. As a result, the adsorbed CO band intensity reflects the relative number of active sites involved in FTS turnovers. After steady-state spectra were collected at 473 K and 0.5 MPa, H₂O (0.05 MPa) was added and infrared spectra were acquired until CO infrared bands reached a constant intensity. The H₂O concentration was then increased to 0.1 MPa and infrared spectra were again collected until the intensity of all bands again reached constant values. After this, H₂O was removed from the synthesis gas stream and infrared spectra again collected until the system again reached steady state. The steady-state spectra for the initial and final dry synthesis gas experiments and for the two water concentrations are shown in Figure 12. The addition of water led to an initial slight decrease in the frequency of the adsorbed CO band (from ~2070 to ~2050 cm⁻¹) and to the appearance of an intense band at 1628 cm⁻¹, which corresponds to deformation vibrations in molecularly adsorbed water [88-91]. This band was also present on the pure SiO₂ support when water was added to the synthesis gas stream. The CO bands did not revert to their original frequency upon water removal, but adsorbed water bands disappeared gradually when H₂O was removed from the synthesis gas stream. After these experiments, the sample temperature was decreased to 453 K, spectra were collected, and H₂O (0.05 MPa) was added. The spectra and conclusions were similar to those obtained at 473 K. The area under the infrared CO band is shown in Figure 13 for the experiments described above.

At 473 K, the presence of H₂O (0.05 MPa) increased the initial CO band intensity by ~15% and then by another 5% when the H₂O pressure was increased to 0.1 MPa. These changes are much smaller in magnitude than the changes in FTS rates of 30% and 45% observed when these water concentrations were added to synthesis gas at 473 K and 0.5 MPa. Clearly, this rate enhancement cannot reflect a larger steady-state density of Co sites active for FTS when H₂O was added. The observed initial increase in CO band intensity upon H₂O does not appear to be related in fact to the FTS rate enhancements. These rate enhancements were fully reversed upon water removal, but the CO infrared band did not return to its initial intensity when H₂O was removed from the synthesis gas stream at 473 K (Figure 13). This band also did not change in intensity when 0.05 MPa H₂O was added during subsequent experiments at 453 K. The initial changes in the CO band intensities appear to reflect a gradual approach to a steady-state Co surface with a slightly lower adsorption capacity than fresh Co/SiO₂. High H₂O concentrations (0.25 MPa) led to a marked irreversible change in the CO infrared band. The infrared spectra before H₂O addition was not recovered upon removal of water from the synthesis gas stream. These high H₂O/H₂ ratios appear to lead to the surface oxidation of Co metal particles. Below these H₂O/H₂ ratios, the availability of CO binding sites was unchanged by H₂O partial pressures that markedly influenced FTS rates and selectivities.

These studies appear to rule a scavenging effect of H₂O on inactive adsorbed species or their precursors. They also cast some doubt on a role of water in removing transport restrictions, because the removal of these restrictions would have led to reversible effects of water on intrapellet CO concentrations and thus on the intensity of CO-related infrared bands. While inhibition of FTS rates caused by transport require very severe diffusional limitations, selectivity effects are noticeable even with very small intrapellet gradients, which would have not been detected in our on situ infrared studies. In the next section, we show that the structure and the oxidation state of the Co crystallites in Co/SiO₂ remain unchanged during FTS at 0.1 MPa H₂/CO, 0-0.015 MPa H₂O, and 473 K using *in situ* X-ray absorption spectroscopy.

7.4. *In situ* X-ray absorption spectroscopy during reactions of CO/H₂ and CO/H₂/H₂O on Co/SiO₂

X-ray absorption spectra were measured at the Co K-edge using a wiggler side-station (beamline 4-1) at the Stanford Synchrotron Radiation Laboratory (SSRL). The storage ring was operated at 30-100 mA and 3.0 GeV during the experiments. Two Si (111) crystals, detuned by 20% in order to minimize harmonics, were used as the monochromator. The X-ray beam intensities incident on the sample (*I*₀), leaving the sample (*I*₁), and after a 5 μ Co foil (*I*₂), were measured using three N₂-filled ion chambers, and the sample (*I*₀/*I*₁) and reference (*I*₁/*I*₂) spectra were collected simultaneously. The most restrictive aperture along the beam path was a 0.2×12 mm slit, which set an energy resolution of 2 eV at the Co K-edge (7.709 keV). Co₃O₄ (Alfa Aesar, 99.997%) was used as the reference. The catalyst sample (10 mg., 21.9 wt.% Co/SiO₂, 100-180 μ) was placed within a quartz capillary cell described in earlier sections and treated in H₂ by increasing the temperature to 608 K at 0.167 K/s, holding at 608 K for 1 h, and cooling to 473 K. Synthesis gas (Praxair: 62% H₂, 31% CO, 7% N₂; 3.6-7.4 × 10³

cm³/h.g-cat) was introduced and spectra were collected for 10 h during FTS. H₂O was then added to the synthesis gas reactants (H₂O/CO=0.05-0.1; 7.4 x 10³ cm³/h.g-cat of synthesis gas) using a syringe pump (Cole Palmer, 74900 Series) and X-ray absorption spectra were collected during FTS reaction. X-ray absorption data were analyzed using the WinXAS code (version 1.2). Raw spectra were calibrated by aligning the first inflection point in spectrum for Co foil with the reported absorption energy for Co metal (7.709 keV). The background was subtracted using linear fits in the pre-edge region (7.500-7.700 keV) and a sixth-order polynomial normalization for the post-edge region (7.840-8.720 keV). The fine structure spectra were analyzed after background subtraction and Fourier transform of k⁻¹-weighted data in the 3-16 Å⁻¹ wavenumber range.

Figure 14. *In situ* XANES of a pre-reduced 21.9 wt.% Co/SiO₂ catalyst under (a) H₂ (12 x 10³ cm³/h.g-cat), 608 K, (b) H₂/CO (7.5 x 10³ cm³/h.g-cat), 473 K, (c) H₂/CO/H₂O (7.5 x 10³ cm³/h.g-cat, H₂O/CO=10 %), 473 K, and (d) reference Co₃O₄.

Near-edge spectra for pre-reduced Co/SiO₂ (21.9 wt.% of Co) after treatment in H₂ (Figure 14a) and after exposure to synthesis gas without H₂O (Figure 14b) and with H₂O added (0.015 MPa H₂O, Figure 14c) are compared in Figure 14. Samples were treated in H₂ at 608 K for 1 h before exposure to synthesis gas. The reduced catalysts show lower absorption edge energy than Co₃O₄ (Figure 14d). During reduction in H₂, an absorption feature emerged at 7.709 keV along with the disappearance of the pre-edge feature present in Co₃O₄, indicating the formation of Co metal. No detectable spectral changes were detected after exposing the sample to synthesis gas (H₂/CO=2, 0.1 MPa; 1.02-2.05 cm³/g-s). The subsequent addition of H₂O to the synthesis gas (0.005-0.015 MPa) also did not lead to detectable changes in the near-edge spectra. These data clearly indicate that the structure, composition, and oxidation state of the Co metal crystallites present after reduction in H₂ are not changed during FTS and that the addition of amounts of water that lead to detectable change in FTS rates and selectivities also do not influence the nature of these Co metal particles. These conclusions are illustrated by the difference

spectra shown in Figure 15. In this figure, the spectrum of the reduced sample (Figure 14a) was subtracted from the spectra obtained in CO/H₂ (Figure 14b) and CO/H₂/H₂O (Figure 14c) reactant mixtures. The nearly flat and identical difference spectra clearly show that Co metal particles retain their structure and oxidation state during reactions of synthesis gas with and without water added.

Figure 15. Difference X-ray absorption spectra of a 21.9% Co/SiO₂ catalyst under (a) H₂/CO and (b) H₂/CO/H₂O with respect to a reduced catalyst; 473 K, 0.1 MPa, H₂/CO=2, H₂O=0.01 MPa.

The analysis of the extended X-ray absorption fine structure (EXAFS) of these samples (Figure 16) confirms these conclusions. Figure 16 shows the radial structure functions of Co₃O₄ (Figure 16a), Co foil (Figure 16e), and of Co/SiO₂ after reduction in H₂ (Figure 16b) and during FTS with CO/H₂ (Figure 16c) and CO/H₂/H₂O (Figure 16d) reactant mixtures. The spectra of reduced Co catalysts resemble Co metal and do not change in synthesis gas and in the presence of H₂O. The consistent results with XANES and EXAFS analysis of Co catalysts coupled with our IR studies indicate that the chemical nature of the CO-binding Co sites are unchanged with increasing H₂O concentrations up to a threshold value.

Based on our IR and XAS results, it appears that water does not appear to modify the density of CO-binding sites during reaction as well as change their chemical characteristics. During FTS reactions on Co catalysts, the chemical environment near the catalyst surface is determined by hydrocarbon chains that are formed, as well as CO-binding sites. And since previous studies on CO hydrogenation reactions on Ru and Co catalysts have pointed out to the possible existence of active and inactive forms of carbon on the surface, it is conceivable that water could affect the relative concentrations of the different forms of carbon, which in turn would bring about an increase in the rate. In addition, a decrease in the CH₄ selectivity and increase in C₅₊ selectivity with increase in

H₂O concentration can also be explained by the possible difference in the ways chains terminate on these different forms of carbon. We have attempted to investigate this effect in a parallel study in which the CH₄ transient obtained during the switch of flow from synthesis gas (FTS conditions) at steady state to H₂ was utilized to obtain the total amount of active carbon on the catalyst surface, at different H₂O concentrations, as discussed in the next section.

Figure 16. *In situ* EXAFS of (a) reference Co₃O₄ and a pre-reduced 21.9 wt.% Co/SiO₂ catalyst under (b) H₂ (200 cm³/min, g-cat), 608 K, (c) H₂/CO (125 cm³/min g-cat), 473 K, (d) H₂/CO/H₂O (125 cm³/min g-cat, H₂O/CO=10 %), 473 K, and (e) Co foil.

7.5. Carbon coverage measurements during FTS

7.5.1. Introduction

An alternate unexplored explanation for the autocatalytic effect of water on Co/TiO₂ and Co/SiO₂ catalysts during FTS is that the presence of H₂O could affect the relative amounts of reactive and less reactive carbon on the catalyst surface. In the previous section we have shown with the help of *in situ* FTIR spectroscopy that the density of CO-binding sites was unchanged with changes in water concentration. In section, we present our studies in which we test whether water influences the concentration of carbonaceous species on the catalyst under reaction conditions.

Various researchers have presented techniques to estimate the amount of reactive carbon present on the catalytic surface. Winslow and Bell [98] determined the carbon coverage on a Ru/TiO₂ catalyst at 463 K and 0.08 MPa by titration with D₂, by following the

evolution of CD₄ (attributed to the hydrogenation of chemisorbed carbon) with time. Two CD₄ peaks were detected, the first one being representative of reactive carbon (named by the authors as Carbon α). The authors, following Bianchi *et al.* [99,100], who performed similar studies on an iron catalyst at atmospheric pressure, stated that the second peak is due to hydrogenation of a pool of less reactive carbon (Carbon β). In a different approach, Winslow and Bell [92] estimated the amount of carbon α from the decay with time of the flow rate of ¹³CO after the feed of the reactor was changed from a ¹³CO/H₂ mixture to a ¹²CO/H₂ mixture; CD₄ that was observed upon feeding D₂ to the reactor after the first transient was completed, was attributed to hydrogenation of carbon β . A similar isotope exchange approach was also adopted by De Pontes *et al.* [101] on Ru/TiO₂ and Ru/SiO₂ to detect the presence of two pools of adsorbed carbon. Biloen *et al.* [102] presented data collected on an unsupported Co catalyst at 488 K, 0.3 MPa and a H₂/CO ratio of ~5:1, with ¹²CO/H₂-¹³CO/H₂ switch experiments, similar to the ones previously described. Finally, Mims and McCavendish [103] have also performed carbon coverage with an identical approach on a Co/SiO₂ catalyst. Despite the fact that Co is one of the most important and widely used catalyst for FTS, very few studies have been carried out at high-pressure reaction conditions to estimate the number of active carbon atoms during FTS on these catalysts. Here, we present our studies performed to determine if the observed rate enhancements by water would reflect an increase in the active carbon coverage on Co catalysts, based on switch transient measurements at high pressure conditions.

7.5.2. Catalyst synthesis and measurement of steady state and transient FTS kinetics

The 15 wt.% Co/TiO₂ sample was prepared by impregnation of standard solutions of CoNO₃·5H₂O onto TiO₂ (Degussa) respectively. The impregnated sample was dried in air at 333 K for 24 h. and subsequently reduced in flowing hydrogen (15 x 10³ cm³/h, 0.0167 K/s from 313 K to 673K, hold for 16 h). The catalyst sample was then passivated with 1% O₂ in He for 1 h at ambient temperature.

The reactor setup was identical to the one used for all the other experiments listed in Sections 3-6. In addition, the flow of synthesis gas or H₂ was directed either to the reactor or to the vent with a 4-port valve, mounted close to the reactor inlet. A 1/16" capillary tube was positioned under the bed and was utilized to divert a part of the effluent stream (~10 %) into a differentially pumped atmospheric sampling system connected to a quadrupole mass spectrometer (Leybold Inficon Instruments Co., Inc.), allowing to continuously collect gas samples during the runs. This step minimized the total dead volume between the reactor and the mass spectrometer. Also, two needle valves were utilized in order to maintain the desired pressure drop between the reactor zone (at high pressure) and the tube to the mass spectrometer (under vacuum). Active carbon coverage measurements were conducted at steady state FTS conditions, by performing rapid switches of the feed to the reactor from synthesis gas to H₂ at high pressure, followed by monitoring of the transients of different components with the mass spectrometer.

The experiments performed on the Co/TiO₂ catalyst at 473 K and 2 MPa showed that the CO reaction rate increased significantly with increase in the average water partial

pressure in the reactor (Figure 17). An increase in water concentration decreased methane selectivities and correspondingly increased C_{5+} selectivities (Figure 18). The effect of the partial pressure of internally generated water on olefin selectivity is affected by the parallel effect of contact time. The combined result is reported in Figure 19 for *l*-pentane to *n*-pentane ratios; the observed decrease in olefin content with partial pressure of water produced is to be attributed to extensive readsorption of α -olefins into the growing chain mechanism at higher contact times [13]. The details related to calculation of the active carbon coverage are presented in the next section.

Figure 17. Rate of CO consumption as a function of the average water partial pressure. Full symbols: water internally generated, Open symbols: added water. (15 wt.% Co/TiO₂, 473 K, 2.0 MPa, H₂/CO=2).

Figure 18. Methane (◆) and C_{5+} (%) selectivities as a function of the average water partial pressure. Full symbols: water internally generated, Open symbols: added water. (15 wt.% Co/TiO₂, 473 K, 2.0 MPa, H₂/CO=2).

Figure 19. *I*-Pentene/*n*-pentane molar ratio as a function of the average water partial pressure. Filled symbols: water internally generated, Open symbols: added water. (15 wt.% Co/TiO₂, 473 K, 2.0 MPa, H₂/CO=2).

7.5.3. Measurement and estimation of carbon coverage

When the reactor feed is changed from syngas to hydrogen, the carbon adsorbed on the surface of the catalyst during the reaction is hydrogenated mostly to methane; while at the same time, the flow rates of CO and Ar decrease to zero, and that of H₂ increases and reaches a steady value. The transients of CO, H₂ and CH₄ after a switch from syngas to hydrogen and back to syngas are presented in Figure 20. The hydrodynamics of the system is described by the following equation:

$$F(t) = F_1 + (F_2 - F_1) \cdot \left(1 - e^{-\frac{t - t_D}{\tau}} \right) \quad (1)$$

where: $F(t)$ is the flow rate of an inert species as a function of the time t , F_1 is the flow rate of the same species before the switch to H₂ and F_2 is the flow rate when the transient is completed. Equation 1 results from the application of a non-stationary mass balance in the absence of reaction on a system that is combination of a plug flow reactor followed by a continuously stirred reactor. The Ar contained in the syngas mixture is the inert and internal hydrodynamic standard of the system: its flow rate transient is utilized to estimate the parameters t_D and τ in Equation 1. This model fits the decay profile of the Ar flow rate very well for all the experimental data collected as illustrated in Figure 21. Once a reliable model for the hydrodynamics of the system is devised, the peak of methane evolved from the catalyst surface is analyzed in order to deconvolute it into two contributions; one derived from hydrogenation of a more active pool of adsorbed carbon and the other from reaction of hydrogen with a less active form of carbon on the catalyst.

In order to estimate only the amount of active carbon from the methane peak, Equation 1 is applied to the decay of methane after the attainment of the maximum value in the methane flow rate profile. In fact assuming that the kinetic of formation of methane is first order with the carbon coverage and with the hydrogen coverage, and supposing that after the maximum of methane flow rate, there is no change in the concentration of adsorbed hydrogen on the catalytic surface, the decay of methane with time should follow an exponential law with a time constant τ_{CH_4} . However, when the linearized flow rate $\ln[(F(t)/(F_{peak}))]$ is plotted as a function of time (where $F(t)$ is the actual methane flow rate, F_{peak} the rate corresponding to the maximum of the methane flow rate), two slopes are visible, for all the experiments conducted, corresponding to two different time constants for the consumption of adsorbed carbon. An example of the presence of two distinct slopes is presented in Figure 22; from the first part of the curve a time constant of 40 s is estimated, while from the second part, the resulting value of τ_{CH_4} is 315 s. The first part of the curve can be attributed to hydrogenation of active carbon, whereas the second part derives from reaction of hydrogen with some form of less reactive carbon. Since in the absence of CO, secondary reactions of FTS products are inhibited on Co catalyst at high pressure, the methane detected likely derives from hydrocracking of heavy waxes contained in the catalyst pores. Once the time constant for hydrogenation of active carbon is calculated from the first part of the methane decay, Equation 1 can be used to extrapolate the curve until the transient is completed.

$$F_{\alpha}(t) = F_{peak} \cdot \left(1 - e^{-\frac{t-t_D}{\tau}} \right) \quad (2)$$

Here, $F_{\alpha}(t)$ is the methane flow rate thus calculated, and $B(t)$ is the hydrodynamic decay that methane should follow in the absence of a reaction from F_{peak} to zero:

$$B(t) = F_1 \cdot \left(1 - e^{-\frac{t-t_D}{\tau}} \right) \quad (3)$$

The amount of active carbon adsorbed on the catalyst at the time of the switch is determined from the area between $F_{\alpha}(t)$ and $B(t)$ (Figure 23), after the transient is completed.

$$C^* = \int_{t_D}^{\infty} [F_{\alpha}(t) - B(t)] dt \quad (4)$$

If the Co loading and the dispersion of the catalyst are known, it is possible to calculate the percentage of the superficial Co sites occupied by active carbon.

Figure 20. Transient of CO, H₂ and CH₄ flow rates after switch from syngas to methane. (15 wt.% Co/TiO₂, 473 K, 2.0 MPa, H₂/CO=2, residence time = 1.7 sec, CO conversion = 6.3 %, CH₄ selectivity = 9.6 %).

Figure 21. Transient of Ar flow rate after switch from syngas to methane. (◆): experimental, (no symbols): model. (15 wt. % Co/TiO₂, 473 K, 2.0 MPa, H₂/CO=2, residence time = 1.7 sec, CO conversion = 6.3 %, CH₄ selectivity = 9.6 %).

Figure 22. Normalized flow rate of CH₄ after switch from syngas to methane. (15 wt. % Co/TiO₂, 473 K, 2.0 MPa, H₂/CO=2, residence time = 1.7 sec, CO conversion = 6.3 %, CH₄ selectivity = 9.6 %).

Figure 23. Flow rate of CH₄ after switch from syngas to methane. (◆): experimental, (—): model; (15 wt.% Co/TiO₂, 473 K, 2.0 MPa, H₂/CO=2, residence time = 1.7 sec, CO conversion = 6.3 %, CH₄ selectivity = 9.6 %).

Data obtained from the carbon coverage measurements on the Co/TiO₂ catalyst are shown in Table 5. The estimates of the carbon coverage (θ_C) for which an effect on

selectivity was observed, estimated with the titration technique are between 15% and 24% and are of the same order of magnitude of the ones reported in the literature. For example, Winslow *et al.* [98] estimated a number of active carbon at steady state for a Ru/TiO₂ catalyst is $0.8 \cdot 10^{-7}$ mol, resulting in a coverage of superficial cobalt atoms by active carbon at steady state calculated by us of about 1.5%; the value obtained by Winslow *et al.* for the same catalyst [92] is 12%, whereas Mims *et al.* [103] obtained a value of 18500 mol_C/g_{cat} on a Co/SiO₂ catalyst leading to a coverage of superficial Co, from our calculations, of about 17%. Biloen *et al.* [102] also found the carbon coverage to be 4% on an unsupported Co catalyst and 14% on a Ru/ γ -Al₂O₃ catalyst.

In order to perform a more thorough statistical analysis, repeated measurements were collected at two different space velocities and by adding water at the higher space velocity: the results of these experiments are reported in Table 5. From those data it is evident that to an increase of the water partial pressure from 0.17 atm to 3.04 atm, at which the rate increases from 1.51 mmol/h/g to 2.83 mmol/h/g and the methane selectivity decreases from 9.1 % to 5.3 %, the active carbon coverage detected by the switch method does not change significantly. The hypothesis that the number of active carbon in the presence of water is greater than in dry conditions was also verified by a statistical test and rejected. These results suggest that both the higher activity and the changes in selectivity observed on the Co/TiO₂ catalyst cannot be attributed to a significantly greater number of active carbon adsorbed on the surface. The higher rate of CO consumption could hence be explained by hypothesizing a higher reactivity of the same amount of carbonaceous species, which may not be observed by the titration technique here adopted. Indeed, if water played a role in activating the carbon adsorbed on the surface during FTS, a switch to a pure hydrogen stream would not be able to detect it.

Alternatively, since the direct involvement of water into the mechanism of CO consumption was ruled out by the kinetic isotope effect experiments discussed in Section 6, the enhancement of the rate of CO consumption at high water partial pressure could derive from the easier transport of the reactants to the catalytic sites through the liquid waxes filling the pores. This phenomenon might be due to the formation of an aqueous phase, which would facilitate the transport of CO and H₂ [14]. Assuming a dependence of the CO consumption rate as $r_{CO} = k \cdot p_{H_2}^{0.74} \cdot p_{CO}^{-0.24}$ [70], an equal increase of the amount of CO and H₂ dissolved in the liquid, due to a minor transport limitation of H₂ and CO, would positively affect the velocity, whereas the change in the concentration of adsorbed CO with respect to hydrogen could be such as to decrease the methane formation. The fact that the carbon coverage is not greatly affected by the presence of water might be explained if we consider that the amount of adsorbed carbon is much greater than the coverage by hydrogen. Hence, to a decrease of the number of carbon, to which the titration method here used may not be sensible enough, would correspond a significant increase of the adsorbed hydrogen, leading eventually to a higher rate. Still, further investigations are needed to understand the effect of water on activity and selectivity of cobalt catalysts.

Table 5. Results from the experiments on the 15 wt.% Co/TiO₂ catalyst at 2.0 MPa, 473K, H₂/CO = 2

	SV = 36.3 min ⁻¹			SV = 28.2 min ⁻¹			SV = 36.3 min ⁻¹		
p _{H2O} (MPa)	1.7·10 ⁻²	±	2.4·10 ⁻³	2.0·10 ⁻²	±	6.5·10 ⁻³	3.1·10 ⁻³	±	2.9·10 ⁻³
r _{CO} (mmol/h/g)	1.51	±	0.20	1.35	±	0.44	2.83	±	0.22
CH ₄ selectivity (%)	9.11	±	0.82	8.79	±	1.27	5.31	±	0.53
C* (μmol)	23.4	±	3.31	24.8	±	4.75	25.93	±	5.10

8. Conclusions

Water enhances FTS rates, decreases CH_4 selectivity and increases product molecular weight and olefin content on Co-based FTS catalysts. We have carried out extensive studies with the use of isotopic tracers, in situ FTIR and XAS spectroscopies, and carbon coverage measurements based on site titration with H_2 switch, to investigate the possible causes of this positive water effect. Studies with CO/D_2 and CO/H_2 mixtures showed the existence of an overall inverse isotope effect, which resulted from a combination of kinetic and equilibrium isotope effects. The isotope effect was unchanged with changes in the average water pressure in the reactor, which pointed out to a lack of participation of water in the kinetically relevant steps in the FTS reaction mechanism. In situ FTIR spectroscopic measurements showed that increase in water concentrations in the reactor did not lead to a significant change in the total number of CO-binding sites, which points out the lack of existence of a correlation between FTS rates and site density. X-ray absorption spectroscopic measurements showed that the Co surface remains unoxidized under typical reaction conditions, contrary to what has commonly been reported in the literature. The carbon adsorbed on the surface during the reaction was measured by means of hydrogen titration at real FTS conditions (i.e. high temperature and pressure) on both catalysts. The amount of active carbon adsorbed on the catalytic surface was found to be independent of water partial pressure, according to our investigation. Therefore the autocatalytic effects of water on Co catalysts may not be attributed to a higher coverage of the surface by active carbon. The effect of water could derive either from a higher reactivity of the same number of carbon species, or from the formation of an intrapellet aqueous phase which would enhance the transport of the reactants to the catalytic sites. This we recommend as one of the few remaining avenues for research in the area of FTS reactions on Co-based catalysts.

III. APPENDIX

1. References

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Task 12. Reporting/Project Management

The submission of this final report completes all reporting requirements for the project.