TECHNOLOGY DEVELOPMENT FOR IRON FISCHER-TROPSCH CATALYSIS

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Final Report

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U.S. Department of Energy
Federal Energy Technology Center
FETC Project Manager: Richard E. Tischer
P. O. Box 10940
Pittsburgh, PA 15236-0940

Submitted By

Project Manager: Burtron H. Davis
University of Kentucky Research Foundation
Kinhead Hall
Lexington, KY 40506-0057

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Abstract

The goal of the proposed work described in this Final Report was the development of iron-based Fischer-Tropsch catalysts that combined high activity, selectivity and life with physical robustness for slurry phase reactors that will produce either low-alpha or high-alpha products. The work described here has optimized the catalyst composition and pretreatment operation for a low-alpha catalyst. In parallel, work has been conducted to design a high-alpha iron catalyst that is suitable for slurry phase synthesis. Studies have been conducted to define the chemical phases present at various stages of the pretreatment and synthesis stages and to define the course of these changes. The oxidation/reduction cycles that are anticipated to occur in large, commercial reactors have been studied at the laboratory scale. Catalyst performance has been determined for catalysts synthesized in this program for activity, selectivity and aging characteristics.

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1.0.0 Executive Summary

The work with low-alpha iron catalysts has defined formulations that have activity equal to or superior to current catalysts. For these catalysts, it has been demonstrated that the hydrocarbon productivity per unit of iron catalyst dramatically depends upon CO conversion. For CO conversions in the 30-50% range, hydrocarbon productivity exceeds 2 g h.c./g Fe-hr, a very high productivity rate. These iron catalysts are stable, with declines in CO conversions being less than 1% CO/week during five months of testing. Process schemes have been advanced to take advantage of these catalysts.

In the 30-50% CO conversion range, the fraction of CO converted to hydrocarbons with the low-alpha catalyst was in the 60-70% range. In other words, the conversion ratio for H_2/CO is in the range of 1.5-1.6; this approaches the usage ratio expected for cobalt catalysts.

Iron catalysts with adequate activity for high-alpha (heavy wax) synthesis have been prepared. These catalysts have low methane selectivity. However, the internal filters have become plugged with catalyst fines/wax so that runs exceeding 500 hours cannot be made. Wax/slurry problems must be solved if long-term testing is to be accomplished. In contrast to the iron catalysts, operation for 750 hours have been accomplished in the same reactor set-up with supported cobalt catalysts.

Low temperature (230°C), slurry phase Fischer-Tropsch synthesis (FTS) was conducted with precipitated iron-silicon catalysts under industrially relevant conditions (flow=3.1 NL $h^{-1}g-Fe^{-1}$, $H_2:CO=0.7$, $P=1.31$ MPa). The effects of activation gas (hydrogen, carbon monoxide or syngas) and promoters (potassium and copper) on activity and selectivity were explored. Optimum potassium promotion was in the range of 4-5 atomic percent, relative to iron for these high-alpha, low-temperature catalysts.

Promotion with copper lowered the reduction temperature and increased FTS activity, regardless of the activation gas used. Carbon monoxide activation gave the highest activity for a 100Fe/4.4Si/5.2K catalyst (atomic percent, relative to iron) while syngas activation was superior for a 100Fe/4.4Si/2.6Cu/5.2K catalyst. Selectivity of the FTS product was not affected by the activation gas employed or copper promotion; however, potassium promotion increased wax and alkene selectivity. A syngas activated 100Fe/4.4Si/2.6Cu/5.2K catalyst gave the best overall performance at 230°C. Alkene selectivity was greater than 75% for the C₂-C₁₁ fraction, methane selectivity was below 3 wt% and C₁₂+ selectivity was above 70 wt%.

The effect of potassium on catalyst activity, kinetic parameters and selectivity has been investigated for a precipitated iron catalyst that was employed with low H₂/CO ratio typical of a synthesis gas generated from coal. A wide range of synthesis gas conversions have been obtained by varying space velocities over catalysts with various potassium loadings. Differing trends in catalyst activity with potassium loading were observed depending on the space velocity or synthesis gas conversion. As potassium loading increased, the catalyst activity either decreased (low conversions), passed through a maximum (intermediate conversions) or increased (high conversions). This is shown to be a result of the increasing dependency of the Fischer-Tropsch synthesis on the hydrogen formed by the water-gas shift reaction with increasing synthesis gas conversions. Both the rate constant and the adsorption parameter in a common two-parameter Fischer-Tropsch rate expression decreased with potassium loading; therefore, observed maxima in Fischer-Tropsch rate with potassium loading can be due to the opposing influences of these parameters. The effect of potassium on alkene selectivity was dependent on the number of carbon atoms of the hydrocarbons as well

as the carbon monoxide conversion level. The extent of isomerization of alkene products decreased with potassium loading, while the selectivity to methane decreased with increasing potassium content at CO conversions about 50% and higher.

A consistent explanation for these activity trends has been given. The overall FTS activity is independent of the water-gas shift (WGS) reaction at low synthesis gas conversions. Potassium acts as a catalyst poison at these conversion levels as the FTS activity decreases with potassium loading. As the synthesis gas conversion increases, the hydrogen supplied to the reactor is insufficient for the FTS and the FTS increasingly depends on the hydrogen formed by the WGS reaction. Further, the extent of the WGS reaction increases with potassium loading. Thus as synthesis gas conversion increases the maximum overall FTS activity is obtained first at intermediate potassium loadings and finally at the highest potassium loading used in this study.

Unlike previous studies, the effect of potassium on catalyst selectivity has been compared at similar conversions. The effect of increasing amounts of potassium on alkene selectivity depends on the number of carbon atoms of the hydrocarbons as well as the carbon monoxide conversion level. The extent of isomerization decreases with potassium loading. The selectivity to methane in the total hydrocarbon product is affected by potassium at carbon monoxide conversions above 50% and increases with decreasing potassium loading.

The equilibrium phase compositions of iron have been calculated for gas compositions that could be encountered during the Fischer-Tropsch synthesis. The gas compositions measured experimentally for CO conversion levels in the 30-90% range show that iron should be present as the carbide phase. However, experimental characterization of iron catalysts show that a significant fraction of the iron is present as

Fe_3O_4 following synthesis for several days. A model that can account for the experimental catalyst phase composition and the gases present in the reactor would have a core of Fe_3O_4 and an outer layer of iron carbides.

Slurry phase Fischer-Tropsch Synthesis (FTS) was conducted with two precipitated iron catalysts (100Fe/3.6Si/0.71K and 100Fe/4.4Si/1.0K, atomic % relative to Fe) at 543K, 1.31MPa and a synthesis gas ($\text{H}_2/\text{CO}=0.7$) space velocity of $3.1 \text{ NL h}^{-1} \text{ g Fe}^{-1}$. The impact of activation gas (CO, $\text{H}_2/\text{CO}=0.7$ or $\text{H}_2/\text{CO}=0.1$), temperature (543K or 573K) and pressure (1.31MPa or 0.10 MPa) on the long term (>500 h) activity and selectivity of the catalysts were explored. Pretreatment with CO under the conditions employed gave highly active and stable catalysts. Catalyst performance when synthesis gas activation was used was found to be dependent upon the partial pressure of hydrogen in the activating gas with low hydrogen partial pressures resulting in the highest catalyst activity. X-ray diffraction results indicate that carbon monoxide activations and synthesis gas activations with low hydrogen partial pressure result in the formation of the carbides $\chi\text{-Fe}_5\text{C}_2$ and $\epsilon'\text{-Fe}_{2.2}\text{C}$ while activation with synthesis gas with high hydrogen partial pressure results in the formation of only Fe_3O_4 . It was found that treating the 100/3.6Si/0.71K catalyst activated with synthesis gas at 1.31 MPa and 543K, with carbon monoxide caused the activity to increase dramatically and the Fe_3O_4 to be partially converted to iron carbides. It is concluded that Fe_3O_4 is relatively inactive for FTS while the presence of some bulk iron carbide is necessary for high FTS activity to be achieved.

CO pretreatment of precipitated Fe/Si/K catalysts consistently results in high FTS activity because active carbide phases are readily formed. In the case of syngas activation, there is a relationship between the hydrogen partial pressure in the activation

gas and the initial FTS activity. During activation with syngas, the catalyst is exposed to carbon dioxide and water as well as carbon monoxide and hydrogen. It has been found that during activations with high partial pressures of hydrogen, enough water is formed to prevent the catalyst from being reduced to active iron carbide phases and only relatively inactive Fe_3O_4 is formed. The results of this study indicate that the formation of an iron carbide ($\chi\text{-Fe}_5\text{C}_2$ and/or $\epsilon'\text{-Fe}_{2.2}\text{C}$) is necessary for high FTS activity; however, based on previous Mössbauer spectroscopy experiments, the activity of iron catalysts is not related to the amount of bulk iron carbide present [3]. These results indicate that a layer of surface carbide may be responsible for FTS activity.

Iron catalysts undergo conversion from Fe_2O_3 to iron carbides during activation and a significant fraction of the carbide is converted back to Fe_3O_4 during use. Based upon X-ray densities of the compounds, contraction and/or expansion of the particle values may approach 100%, potentially creating severe strains that could cause particle disintegration. To overcome this problem, supported iron catalysts may be employed. Preliminary studies indicate the silica and alumina supports have sufficient robustness to survive testing in the CSTR without significant size reduction.

Physical measurements are currently unavailable that permit a prediction of catalyst robustness. Several typical catalyst and/or support materials and Fe_2O_3 catalyst particles were used for microhardness testing. The iron oxide sample was so soft that the standard hardness tests cannot be used to make reliable measurements, indicating that iron oxide is extremely soft.

Extensive use of electron microscopy and Mössbauer spectroscopy was made using a variety of iron catalysts collected at various times during activation and use.

However, while the results are of interest, the characterization data do not relate directly to catalyst performance.

Deactivation rates and aged catalyst properties have been investigated as a function of time on stream for iron-based Fischer-Tropsch catalysts in the presence/absence of potassium and/or silicon. There is a synergism in activity maintenance with the addition of both potassium and silicon to an iron catalyst. The addition of silicon appears to stabilize the surface area of the catalyst. Catalysts containing only iron or added silicon with or without potassium consist mainly of iron oxide at the end of the run. However, iron carbides are the dominant phase of the iron catalyst with added potassium alone. Catalyst surface areas increase slightly during synthesis. The bulk phase of the catalyst does not correlate to the catalyst activity. The partial pressure of water in the reactor is lower for potassium-containing catalysts and is not a reliable predictor of catalyst deactivation rate.

Fischer-Tropsch synthesis (FTS) was studied using a precipitated Fe/K catalyst in a improved short slurry bubble column reactor (SBCR) equipped with a satisfactory reactor-wax separation system and a continuous stirred tank reactor (CSTR) using the same experiment conditions. The catalyst in the SBCR had a lower catalytic activity. Methane and the products of the gas are higher in the CSTR. Some effects may be related to different mixing heat, mass transfer phenomena between two reactors. The C_3+ hydrocarbons ($C_3+H.C.$) with synthesis gas ($CO+H_2$) conversion ratio had similar values.

The solvent used for start-up may have impact upon the subsequent performance of the catalyst. Our study using a light (average molecular weight 420) and a heavy (average molecular weight 3000) start-up solvent produced the same

results, indicating that the viscosity and/or molecular weight do not impact the catalyst performance (activity and aging).

In comparing silica and alumina as structural promoters, it has been found that silica is superior to alumina. A catalyst containing an intermediate amount of alumina appears to provide the superior catalyst.

During these studies five different modifications have been made to the CSTR in order to remove wax when operating with precipitated, high-alpha iron catalysts. Improvements have been made; however, with 10% slurry and higher concentrations we have not been able to operate for longer than about 400-500 hours. This factor continues to be a major problem to overcome in our study of high-alpha, precipitated iron catalysts.

A technical assessment comparing published results with iron and cobalt catalysts for use with low H_2/CO ratios (coal-derived) and high H_2/CO ratios (natural gas derived) synthesis gas has been completed and is included at the end of this report.

Significant improvements in the analysis of Fischer-Tropsch products (to carbon number 90) have been made. This includes writing programs to transfer data directly to a computer and to automatically utilize this data to generate graphics.

2.0.0 Introduction

The objective of this research project is to develop the technology for the production of physically robust iron-based Fischer-Tropsch catalysts that have suitable activity, selectivity and stability to be used in the slurry phase synthesis reactor development. The catalysts that are developed shall be suitable for testing in the Advanced Fuels Development Facility at LaPorte, Texas, to produce either low- or high-alpha product distributions. Previous work by the offeror has produced a catalyst

formulation that is 1.5 times as active as the "standard-catalyst" developed by German workers for slurry phase synthesis. The proposed work will optimize the catalyst composition and pretreatment operation for this low-alpha catalyst. In parallel, work will be conducted to design a high-alpha iron catalyst this is suitable for slurry phase synthesis. Studies will be conducted to define the chemical phases present at various stages of the pretreatment and synthesis stages and to define the course of these changes. The oxidation/reduction cycles that are anticipated to occur in large, commercial reactors will be studied at the laboratory scale. Catalyst performance will be determined for catalysts synthesized in this program for activity, selectivity and aging characteristics.

The research is divided into four major topical areas: (a) catalyst preparation and characterization, (b) product characterization, (c) reactor operations, and (d) data assessment.

To accomplish the objectives of the project, these topics have been organized into the following technical tasks:

a. Task 1.0 Development of Optimum Promoter Levels for Low- and High-Alpha Catalysts

The goal of this task is to identify and optimize procedure for the preparation of iron-based catalysts that combine high activity selectivity and life with physical robustness. Each of the subtasks address an area of considerable uncertainty in the synthesis of catalysts.

1.1 Determine Optimized Synthesis Procedure for High-Alpha Iron-Based Fischer-Tropsch Catalysts

- Role of precursor particle size on activity.

- Role of Cu in precipitated catalysts.
 - Define attrition resistance.
- 1.2 Prepare Catalysts that can be Used to Determine the Role of Promoters for Low- and High-Alpha Catalysts
- Define optimum SiO_2 .
 - Define optimum Al_2O_3 .
- 1.3 Prepare Catalysts that can be Used to Quantify the Role of K on Product Selectivity in both Low- and High-Alpha Catalysts.
- 1.4 Complete the Optimization of the Two Best Low-Alpha, Iron-Based Fischer-Tropsch Catalysts Developed during the Previous Contract.

b. Task 2.0 Definition of Preferred Pretreatment for both Low- and High-Alpha Fischer-Tropsch Catalysts.

The goals of this task are to define the preferred treatment, to define the role of Cu and K during the pretreatment on activity and selectivity and to define the chemical and physical changes which occur during the preferred pretreatment. The subtasks address each of these goals.

- 2.1 Determine the Role of Cu in the Activation of Precipitated Low- and High-Alpha, Iron-Based Fischer-Tropsch Catalysts.
- 2.2 Determine the Effect of K Content on Activation Procedures and Determine if the Method of Addition has any Effect on Catalyst Activity and Life.
- 2.3 Determine the Physical and Chemical Changes that Occur during Catalyst Pretreatment and Use and Determine how these Changes Effect the Strength of the Catalysts.

- 2.4 Evaluate the Effect of Carbon Deposition during Catalyst Activation on Activity, Selectivity and Aging Characteristics.

c. Task 3.0 Catalyst Structure and Characterization.

The goal of this task is to provide basic analyses (surface area, XRD) of all catalyst prepared and to provide additional techniques as required (Mössbauer, SEM, XPS, etc.) to answer specific questions or to provide basic required characterization data for the catalysts.

d. Task 4.0 Catalyst Testing.

The goals of this task are to operate the eight CSTR reactors, measure catalyst performance, determine the stable phases that exist during synthesis at low and high conversions and to determine the rates of interconversion of iron oxide and carbide.

- 4.1 Verify the Quality of Data Obtained from the CSTR's.
- 4.2 Measure Catalyst Performance.
- 4.3 Determine the Stable Phases that Exist during Synthesis at Low and High CO Conversion Levels.
- 4.4 Obtain Data on the Rates Involved in the Interconversion of Iron Oxide and Iron Carbide.

3.0.0 Results and Discussion

3.1.0 Task 1. Development of the Optimum Promoter Levels for Low- and High-Alpha Iron Based Fischer-Tropsch Catalysts and Task 2. The Definition of the Preferred Pretreatment of Low- and High-Alpha Catalysts

3.1.1 Activity and Selectivity of Precipitated Iron Fischer-Tropsch Catalysts

ABSTRACT

Low temperature (230°C), slurry phase Fischer-Tropsch synthesis (FTS) was conducted with precipitated iron-silicon catalysts under industrially relevant conditions (flow=3.1 NL h⁻¹g-Fe⁻¹, H₂:CO=0.7, P=1.31 MPa). The effects of activation gas (hydrogen, carbon monoxide or syngas) and promoters (potassium and copper) on activity and selectivity were explored. Optimum potassium promotion was in the range of 4-5 atomic percent, relative to iron for these high-alpha, low-temperature catalysts. Promotion with copper lowered the reduction temperature and increased FTS activity, regardless of the activation gas used. Carbon monoxide activation gave the highest activity for a 100Fe/4.4Si/5.2K catalyst (atomic percent, relative to iron) while syngas activation was superior for a 100Fe/4.4Si/2.6Cu/5.2K catalyst. Selectivity of the FTS product was not affected by the activation gas employed or copper promotion; however, potassium promotion increased wax and alkene selectivity. A syngas activated 100Fe/4.4Si/2.6Cu/5.2K catalyst gave the best overall performance at 230°C. Alkene selectivity was greater than 75% for the C₂-C₁₁ fraction, methane selectivity was below 3 wt% and C₁₂+ selectivity was above 70 wt%.

INTRODUCTION

The Fischer-Tropsch synthesis (FTS) offers the potential of converting syngas into high value chemicals [1-3]. Although several metals are active for the FTS, only

iron and cobalt catalysts appear economically feasible on an industrial scale [4]. The high water-gas shift activity of iron makes it an ideal catalyst for converting hydrogen lean syngas derived from coal [4,5]. Controlling selectivity is an important aspect of FTS catalyst development. Cobalt catalysts have a high activity for hydrogenation [1] and tend to produce linear alkanes. Iron catalysts are more versatile than cobalt catalysts, produce less methane and can be geared for the production of alkenes, oxygenates and branched hydrocarbons depending on promoters and the process conditions employed [1-3]. Sasol is currently using an iron-based catalyst in a commercial slurry reactor; high alkene selectivity relative to fixed bed reactors is reported [6].

Several factors influence the selectivity and activity of FTS catalysts. Product selectivity of iron catalysts is generally controlled by promoting with one or more alkali metals [2]. Potassium has long been known to increase wax and alkene yields while decreasing the production of undesirable methane [2,7]. Potassium also has been implicated in increasing FTS and water-gas shift activity [8]. Activation procedures also can have a large affect on the selectivity and activity of iron catalysts [9,10]. Precipitated iron catalysts are generally activated with hydrogen, carbon monoxide or syngas. Catalysts activated with carbon monoxide have been reported to produce a higher molecular weight product than syngas or hydrogen activated catalysts; however, several factors such as temperature, pressure and duration of the activation step determine the ultimate activity and stability of iron catalysts [10,11]; therefore, it is difficult to state which activation procedure is superior.

Copper has traditionally been added to precipitated iron catalysts to facilitate reduction of iron oxide to metallic iron during hydrogen activations [7]. Copper has

been shown to minimize sintering of iron catalysts when activating with hydrogen by lowering the reduction temperature [2]. The effect of copper promotion on iron catalysts activated with carbon monoxide or syngas is not as well documented although Kölbel and Ralek have reported that only 0.1 wt% of copper is necessary for successful activation of Fe/Cu/K catalysts with syngas [5].

Throughout our FTS studies, it has been found that syngas activation at elevated pressure (>0.80 MPa) requires the catalyst be promoted with copper in order to achieve reasonable activity. Previous work in our laboratory has shown that the activity of syngas activated, Fe/Si/K catalysts is related to the hydrogen partial pressure of the activation gas [10]. Low hydrogen partial pressure inhibits the formation of oxidizing water which enables active iron carbides to be formed. Likewise, we have found that copper promotion has a similar effect. Treatment of a 100Fe/3.6Si/0.71K catalyst with syngas ($H_2:CO=0.7$) for 24 h at high pressure (1.31 MPa) and 270°C resulted in syngas conversion below 18% [12]. When a 100Fe/3.6Si/2.6Cu/0.71K catalyst was treated similarly, the catalyst was found to undergo an induction period in which the syngas conversion increased to over 50% [12]. Mössbauer spectroscopy [12] analysis showed that the 100Fe/3.6Si/0.71K catalyst was composed of only Fe_3O_4 while the 100Fe/3.6Si/2.6Cu/0.71K catalyst had been partially carbided. The active species of iron-based Fischer-Tropsch catalysts has been debated since Fischer initially proposed bulk carbides were responsible for catalyst activity [13]. Emmet later demonstrated that an iron catalyst carbided with ^{14}C labeled carbon monoxide produced hydrocarbons with a lower radioactivity than the catalyst, thereby indicating that the bulk carbide was not responsible for the activity; however, he did not rule out the possibility that a surface carbide could be responsible for FTS activity [14]. Biloen et al., using ^{13}C tracers, have

proposed that a surface carbide species is responsible for FTS activity on nickel, cobalt and ruthenium catalysts [15]. Similarly, Stockwell et al. have proposed that a CH species derived from surface carbon is the active species on a supported iron catalyst [16]. Amelse et al. using Mössbauer spectroscopy [17] and more recently Shroff et al. using high resolution transmission electron microscopy [18] have proposed that the activity of iron catalysts is related directly to the extent of bulk carbide formation; however, these studies were conducted in fixed bed differential reactors at atmospheric pressure under low conversions and activity was based on the rate of methane formation. At low conversions, the $\text{H}_2:\text{H}_2\text{O}$ and $\text{CO}:\text{CO}_2$ ratios are high enough that the reactor atmosphere is reducing and iron carbides are the thermodynamically stable phases [19]. At industrially relevant conditions, *i.e.*, high conversion, enough water and carbon dioxide are present to oxidize the catalyst. Mössbauer spectroscopy and X-ray diffraction of activated and used iron catalyst samples clearly indicate that iron carbides are oxidized to magnetite at high conversion at the bottom of fixed bed reactors [20]; however, fixed bed reactors are not ideal for conducting catalyst characterization studies, because at high conversion a reducing atmosphere exists at the entrance to the reactor while an oxidizing atmosphere (high H_2O and CO_2 partial pressure) may exist at the reactor outlet. We have conducted catalyst characterization studies in the slurry phase using continuous stirred tank reactors [21,22]. In CSTR's all of the catalyst is exposed to the same reaction environment which allows for better correlation between catalyst composition and activity. We have found that a correlation between the amount of iron carbide and activity cannot always be made [22]; in some cases, peak catalyst activity is obtained when all of the bulk iron carbide appears to be oxidized to Fe_3O_4 [21].

Our research is currently directed at developing iron based catalysts for the production of wax and 1-alkenes from hydrogen-lean syngas. Herein we report results of the effect of activation gas (hydrogen, carbon monoxide or syngas) and promoters (potassium and copper) on the activity and selectivity of precipitated iron-silicon catalysts.

EXPERIMENTAL

Catalyst compositions are expressed as atomic percent relative to iron:

$$\frac{M}{M + Fe} \times 100$$

All catalysts used in this study were derived from a precipitated 100Fe/4.4Si/1.0K catalyst, unless otherwise noted. Preparation details of this catalyst are presented elsewhere [10]. Copper promotion was accomplished by impregnation with aqueous copper(II) nitrate hemipentahydrate. Additional potassium was added as potassium *tert*-butoxide during reactor loading. All FTS runs were conducted in a one liter autoclave operating as a continuous stirred tank reactor (CSTR) [10]. Catalysts were suspended in Ethylflo 164 hydrocarbon oil (Ethyl Corporation) which consists of a mixture of C₃₀ isomers. All catalyst loadings were 10 or 5 weight percent. Hydrogen and carbon monoxide 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 below the impeller blade. The 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 sintered metal filter (0.5-2.0 µm). Uncondensed effluent

was sent to an on-line Carle gas analyzer for determination of carbon monoxide, hydrogen, carbon dioxide, methane and C₂-C₄ alkanes and alkenes. An on-line Hewlett-Packard 5790 GC equipped with a Porpack-Q column was utilized for C₄-C₉ quantification. Liquid samples were analyzed with a Hewlett-Packard 5890 GC equipped with a 60 m DB-5 capillary column. The reactor was also equipped with a tube that extended below the liquid level which permitted catalyst slurry samples to be withdrawn periodically.

Catalysts were activated with carbon monoxide, hydrogen or synthesis gas (H₂:CO=0.7). In general, the activation gas flow was started at ambient conditions, the necessary reactor pressure was set and the reactor was ramped to the appropriate temperature at 2°C min⁻¹. After reaching the activation temperature, the conditions were maintained for 24 h. Carbon monoxide (2.0 NL h⁻¹g-Fe⁻¹) and syngas (3.4 NL h⁻¹g-Fe⁻¹) activations were conducted at 0.10 MPa and 270°C while hydrogen (12 NL h⁻¹g-Fe⁻¹) activations were conducted at 0.10 MPa and 220°C. The lower temperature and higher flow rate were chosen for the hydrogen activations in order to prevent sintering of the metallic iron that is formed [2]. Immediately following the activation procedure, reactors were brought to synthesis conditions: hydrogen:carbon monoxide ratio of 0.7, 3.1 NL h⁻¹g-Fe⁻¹(STP: 0°C, 0.10 MPa), 230°C or 270°C , 1.31 MPa.

Thermogravimetric analyses (TGA) were performed with a Seiko SSC/5200 instrument. Each experiment was run with 20-30 mg of sample and a calcined alumina reference. Three different reducing gases were employed: 49% hydrogen in helium (195 mL min⁻¹), 39% carbon monoxide in helium (165 mL min⁻¹) and 47% syngas (H₂:CO=0.7) in helium (190 mL min⁻¹). Samples were treated with the reducing gas at

ambient conditions for 10 minutes and then the temperature was ramped to 600°C (20°C min⁻¹) and held for 5 minutes.

RESULTS AND DISCUSSION

Catalyst Activation

Previously reported results with 100Fe/3.6Si/0.73K and 100Fe/3.6Si/2.6Cu/0.73K catalysts clearly indicate that the formation of bulk carbide is necessary to obtain substantial activity and that copper plays a role in the carbide formation [12]. Thermogravimetric experiments have been performed to better explore the effects of copper on hydrogen, carbon monoxide and syngas activation of precipitated iron catalysts. Experiments were performed on a series of catalysts containing different quantities of copper (100Fe/4.4Si/5.2K, 100Fe/4.4Si/0.5Cu/5.2K, 100Fe/4.4Si/2.6Cu/5.2K, and 100Fe/4.4Si/5.0Cu/5.2K). Hydrogen reduction resulted in substantial weight loss with two inflections (Figure 1) that have been shown by Mössbauer spectroscopy and XRD [22] to correspond to the reduction sequence: $\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4 \rightarrow \text{Fe}$. Richard et al. [23] have reported similar findings with unpromoted and promoted Fe_2O_3 catalysts. Our results show the temperature where both reduction steps occur is dependent on the level of copper promotion. The onset of the reduction sequences shifted from ~250°C and ~330°C for the 100Fe/4.4Si/5.2K catalyst to ~200°C and ~250°C for the 100Fe/4.4Si/5.0Cu/5.2K catalyst (Figure 1).

Reduction with carbon monoxide produced two weight losses (Figure 2) corresponding to the sequential reduction of Fe_2O_3 to Fe_3O_4 and Fe_3O_4 to iron carbide(s) [22]. After the formation of iron carbide(s), a rapid weight gain corresponding to the deposition of Boudouard carbon was seen ($2\text{CO} \rightarrow \text{C} + \text{CO}_2$). Reduction with syngas ($\text{H}_2:\text{CO}=0.7$) gave results nearly identical to that found for

carbon monoxide reduction (Figure 3). The similarity between carbon monoxide and syngas reduction is supported by Richard et al. who have reported that reduction of α - Fe_2O_3 with syngas ($\text{H}_2:\text{CO}=1.0$) is analogous to reduction with diluted carbon monoxide [23]. As was found with hydrogen reduction, the reduction steps for the carbon monoxide and syngas treated catalysts generally occurred at lower temperatures with increasing levels of copper.

It has been proposed that reduction of metal oxides to the zero valent state by hydrogen can be described by either a nucleation model or a contracting sphere model [24]. Only metal oxides that are reduced according to the nucleation mechanism have the reduction temperature affected by promoters, *i.e.* iron oxide promoted with copper. In the nucleation model, metal nuclei form by the removal of oxide ions from the lattice and the reduction process accelerates as previously formed nuclei grow and new nuclei are formed [24]. The reduction temperature of copper(II) oxide is approximately 150-200°C lower than the reduction temperature of iron oxide. During the reduction of iron oxide promoted with copper oxide, the copper oxide will reduce to the metallic state first and will form sites of nucleation that accelerate the reduction of iron oxide [24]. Wachs et al. have studied the effects of copper and silver on the hydrogen reduction of low surface area α - Fe_2O_3 [25]. Copper was found to lower the temperature where reduction is initiated from ~300°C to ~150°C; however, promotion with silver had no effect on the catalyst reduction. Copper was found to be much more dispersed on the catalyst surface than silver and was concluded to provide more sites of nucleation for reduction to occur. A similar process may occur for reduction with carbon monoxide or syngas. Shroff et al. have shown by transmission electron microscopy that reduction of a commercial iron oxide catalyst ($\text{Fe}_2\text{O}_3/\text{CuO}/\text{K}_2\text{O}$) with carbon monoxide proceeds by

first reducing rapidly to Fe_3O_4 and then slowly to iron carbide(s) [18]. The iron carbide(s) were clearly shown to form as small nuclei on the surface of the Fe_3O_4 crystallites. Kölbel and Ralek report that only a small amount of copper is necessary to promote the reduction of iron oxide [5]. The results presented here show that the reduction with hydrogen, carbon monoxide or syngas is accelerated with increasing levels of copper promotion. This is in agreement with more nucleation sites being available with an increasing amount of copper.

Activity and Selectivity

We have developed a precipitated FT catalyst, 100Fe/4.4Si/1.0K, that shows high activity and stability [10]. With the proper activation, this catalyst has an initial carbon monoxide conversion greater than 90% and deactivates at a rate of 0.6% (CO conversion) per week when operating at 270°C, 1.31 MPa, and a space velocity of 3.1 $\text{NL h}^{-1}\text{g-Fe}^{-1}$ [10]. Activation with carbon monoxide (0.10 or 1.31 MPa) or syngas ($\text{H}_2:\text{CO}=0.7$, 0.10 MPa) at 270°C results in carbon monoxide conversion above 90%; however, activations with hydrogen are only successful when the catalyst is promoted with copper (Figure 4). Carbon monoxide conversion of the 100Fe/4.4Si/1.0K catalyst activated with hydrogen started at 20% and gradually increased to ~60% during the first 600 h at synthesis conditions. In contrast, hydrogen activation of the same catalyst with copper promoter (100Fe/4.4Si/2.6Cu/1.0K) resulted in an initial carbon monoxide conversion higher than 80%. This hydrogen activated catalyst showed stability equal to that of the carbon monoxide or syngas activated 100Fe/4.4Si/1.0K catalyst; a deactivation rate of less than 0.9% per week was achieved for over 3500 h. Bukur et al. have shown by XPS that carbon monoxide is more effective at reducing the surface of a commercial iron oxide catalyst promoted with copper, potassium and silica [26].

Richard et al. have shown that reduction of Fe_3O_4 to Fe_5C_2 by carbon monoxide is more thermodynamically favored than reduction of Fe_3O_4 to $\alpha\text{-Fe}$ by hydrogen [23]. As a result, copper promotion is necessary to ensure the formation of metallic iron when activating with hydrogen. High activity is then obtained when the metallic iron is converted to iron carbide(s) during synthesis.

We have generally found that catalysts activated with carbon monoxide have higher selectivity for high molecular weight products than catalysts activated with syngas or hydrogen [10]. Bukur et al. report carbon monoxide and syngas activations result in a heavier product distribution when a fixed bed reactor is used [21] while carbon monoxide activation results in lower methane selectivity than hydrogen or syngas activations in a slurry reactor [9]. However, all activation procedures using the 100Fe/4.4Si/1.0K catalyst resulted in a product distribution optimized for gasoline and light gases, not high value chemicals, *i.e.* wax and alkenes when FTS was conducted at 270°C. Several factors are known to affect the selectivity of iron based catalysts in addition to the activation procedure. Alkali promotion, *i.e.* potassium has been well established as being critical for increasing alkene and wax yields while lowering the reaction temperature has been shown to decrease methane and increase wax production [2]. Increasing reaction pressure will also increase wax selectivity; however, it has been reported that catalyst stability decreases [9].

Since it is well known that decreasing FTS temperature and optimizing alkali promotion are effective at increasing wax and alkene yields, four low temperature runs were conducted at 230°C on a 100Fe/4.4Si catalyst in which the potassium content was varied. The highest syngas conversion, after carbon monoxide activation, was obtained with a potassium loading between 4 and 5 atomic percent (Figure 5). Interestingly, at

270 °C the maximum conversion for a similar catalyst was obtained with a potassium loading of ~1.0 atomic percent. Potassium is a FTS promoter because it increases the rate of dissociation of the C-O bond of carbon monoxide [27,28]. As the temperature is decreased it is harder to dissociate the C-O bond so a higher potassium loading is required. This is fortuitous, because the high potassium content needed at 230°C also decreased methane and ethane production (Figure 5). Despite the improved selectivity, the activity of all of the 100Fe/4.4Si/xK catalysts were unacceptably low at 230°C. The rate of hydrocarbon production relative to the amount of iron is a good measure of FTS activity. The rate of hydrocarbon production for a 100Fe/4.4Si/5.2K catalyst increased with respect to activation gas according to the order: hydrogen < syngas < carbon monoxide. The activity of the carbon monoxide activated catalyst underwent an induction period in which the rate of hydrocarbon production reached 0.30 g h⁻¹g-Fe⁻¹ after 72 h (Figure 6). The hydrogen activated catalyst also went through an induction period; however, the activity was less than half that obtained when activation was conducted with carbon monoxide (Figure 6). The syngas activated catalyst deactivated slowly from a maximum rate of 0.24 g h⁻¹g-Fe⁻¹ (Figure 6).

Bukur et al. have reported that copper promotion increases FTS activity of precipitated iron catalysts and that there is a synergistic effect when both potassium and copper are used [8]. Soled et al. have claimed promotion with both potassium and copper is essential to obtain the highest activity, lowest methane selectivity and highest alkene selectivity with a precipitate iron-zinc catalyst [29]. In an effort to improve FTS activity at 230°C, the 100Fe/4.4Si/5.2K catalyst was promoted with copper to give a composition of 100Fe/4.4Si/2.6Cu/5.2K. It was found that copper promotion significantly increased FTS activity for the carbon monoxide, syngas and hydrogen

activated catalysts (Figure 6). The maximum rate of hydrocarbon production achieved with the different activation gases increased in the order: hydrogen (0.25) < carbon monoxide (0.38) < syngas (0.43 g h⁻¹g-Fe⁻¹). Maximum syngas conversion followed similar trends; hydrogen (38%) < carbon monoxide (56%) < syngas (64%) (Figure 7).

Carbon dioxide selectivity was found to be higher for the catalyst with copper (Figure 8) which indicates that copper is a promoter for the water-gas shift reaction. Carbon dioxide selectivity obtained for the 100Fe/4.4Si/2.6Cu/5.2K catalyst varied according to the activation gas as follows: carbon monoxide < syngas < hydrogen (Figure 9). Bukur et al. also report that hydrogen activation leads to higher water-gas shift activity when operating at 260 °C [9].

Product selectivities for the 100Fe/4.4Si/5.2K and 100Fe/4.4Si/2.6Cu/5.2K catalysts are shown in Table 1. Methane selectivity was low and wax selectivity was high for all runs. The best overall performance, based on syngas conversion and selectivity, was achieved by the syngas activated 100Fe/4.4Si/2.6Cu/5.2K catalyst. This is unlike the runs made at 270°C with the 100Fe/4.4Si/1.0K catalyst which had similar activity when activated with carbon monoxide or syngas. Methane selectivity less than 3 wt% (based on total hydrocarbon product), wax selectivity greater than 70 wt% and high alkene yields were obtained at moderately high carbon monoxide conversion (>60%). The syngas activated 100Fe/4.4Si/2.6Cu/5.2K catalyst showed reasonable stability with total conversion greater than 50% maintained for over 300 h. Contrary to FTS activity, alkene selectivity is not appreciably affected by the activation gas or the presence of copper. Alkene selectivity for the C₂-C₁₁ product fraction was typically above 70 wt%. Much interest of the commercial viability of iron based FTS catalysts has focused on their ability to produce 1-alkenes for chemical feedstocks. We

have found that over 95% of the alkene fraction is composed of 1-alkenes for the 100Fe/4.4Si/xCu/5.2K catalysts ($x=0$ or 2.6) when FTS is conducted at 230°C. Table 1 shows the selectivity of the C₂-C₁₁ 1-alkenes, relative to the total FTS product. Although geared for the production of wax and transportation fuels, the 100Fe/4.4Si/2.6Cu/5.2K catalyst also produces significant amounts of light alkenes, in fact, ethylene and propylene and 1-butene are the most abundant of all products by mass.

CONCLUSIONS

Moderately high FTS activity has been achieved in the slurry phase under industrially relevant conditions with a precipitated iron-silicon catalyst at 230°C. Optimum potassium promotion for a 100Fe/4.4Si/xK catalyst is in the range of 4-5 atomic %, relative to iron. In general, syngas and carbon monoxide activations at 270°C and 0.10 MPa result in better catalyst performance than hydrogen activation at 220°C. Low methane and high wax and alkene selectivities have been achieved for 100Fe/4.4Si/xCu/5.2K catalysts ($x=0$ or 2.6).

The major difference between running at 270°C and 230°C has been a rapid deactivation after approximately 300 h on stream for the 230°C runs. Work in progress suggests that the deactivation is linked to the difficulty of separating the catalyst from the heavy wax that accumulates in the reactor. Eventually all of the runs reported here were stopped because the reactors had become filled with wax soon after plugging of the internal filter. Work in progress has shown a lower catalyst loading (<5 wt%) to reduce wax production has enabled us to run for longer times and verify that the 100Fe/4.4Si/2.6Cu/5.2K catalyst is stable for over 500 h. A study of catalyst deactivation will be reported elsewhere.

Copper promotion has been found to be imperative for low temperature FTS or when hydrogen activations are utilized. Hydrocarbon productivity increased by as much as a factor of two with copper promotion. Copper has been found to increase the activity of hydrogen activated catalysts by lowering the reduction temperature which in turn reduces sintering of the metallic iron that is formed [2]. However, this does not explain why FTS activity of carbon monoxide and syngas activated catalysts is increased dramatically by copper promotion. Carbon monoxide and syngas activation generally reduce iron oxide catalysts to a mixture of iron carbides which are not as susceptible to sintering as metallic iron. Thermogravimetric analyses clearly show that copper lowers the reduction temperature of hydrogen, carbon monoxide and syngas treated catalysts. In addition, it has been found that the temperature of the reduction onset is correlated with the amount of copper. Based on previous reports, it can be speculated that increasing copper content increases the number of nucleation sites for the reduction process [25].

The FTS reaction requires a 2:1 hydrogen:carbon monoxide ratio, so catalysts must have good water-gas shift activity if syngas with low levels of hydrogen is used, *i.e.* $H_2:CO=0.7$. One possibility for the increase in FTS activity we observe with copper promotion is that copper increases the water-gas shift activity. This is consistent with copper being used in commercial low temperature water-gas shift catalysts. We have also found that copper promotion appears to favor the formation of iron carbides [12]. It may be possible that copper increases the activity of iron catalysts by increasing the number of active sites that are formed. Assuming that the active site(s) is a zero valent surface species, copper may serve as a means of preventing oxidation of the active metallic iron or iron carbide.

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Table 1						
Selectivity of 230°C FTS Runs						
Activation Gas	H ₂		CO		H ₂ :CO = 0.7	
Catalyst ^a	I	II	I	II	I	II
TOS/h	168	168	168	192	624	192
Conversion/mol %						
CO	17	35	40	39	25	68
H ₂	17	31	42	38	22	58
CO + H ₂	17	34	41	39	24	64
Water-Gas Shift						
H ₂ :CO Usage	0.69	0.60	0.73	0.68	0.64	0.60
K _p ^b	4	9	3	4	4	11
CO ₂ selectivity/%, C basis	44	42	43	42	44	45
Productivity						
Total HC/gm ⁻³ feed	35	71	83	84	51	138
C ₃ + HC/gm ⁻³ feed	33	65	78	79	45	130
C ₃ + HC/gm ⁻³ converted	194	191	190	202	188	203
Total HC/g h ⁻¹ g-Fe ⁻¹	0.10	0.22	0.25	0.26	0.15	0.42
Selectivity/wt.% ^c						
C ₁	2.6	3.8	2.9	2.2	5.7	2.2
C ₂ -C ₄ (alkene) ^d	10	14(72)	15(82)	12(80)	21(79)	11(77)
C ₅ -C ₁₁ (alkene) ^d	20	37(66)	27(78)	25(76)	34(75)	15(78)
C ₁₂ +	67	44	55	60	39	72
1-alkene/wt.% ^c						
C ₂	2.0	2.9	3.4	2.6	5.2	2.5
C ₃	2.8	4.1	4.9	3.9	6.4	3.4
C ₄	2.2	3.2	3.8	3.2	4.4	2.1
C ₅	1.8	4.2	3.1	2.6	4.8	2.3
C ₆	2.1	3.2	3.0	2.6	3.9	1.4
C ₇	1.4	2.4	2.9	2.1	4.1	1.3
C ₈	1.3	2.2	2.3	2.2	2.8	1.2
C ₉	0.96	2.5	1.9	1.9	2.8	1.2
C ₁₀	1.2	2.2	1.6	1.6	2.0	1.1
C ₁₁	1.2	2.1	1.4	1.6	1.9	1.1
a. I, 100 Fe/4.4 Si/5.2 K; II, 100 Fe/4.4 Si/2.6 Cu/5.2 K b. $K_p = (p_{CO} p_{H_2}) / (p_{CO} p_{H_2O})$ c. Based on total hydrocarbon product d. Wt.% of hydrocarbon fraction

Figure 1. Weight change measured by thermogravimetric analysis of 100Fe/4.4Si/5.2K (—), 100Fe/4.4Si/0.5Cu/5.2K (---), 100Fe/4.4Si/2.6Cu/5.2K (.....) and 100Fe/4.4Si/5.0Cu/5.2K (—...—) catalysts reduced with hydrogen.

Figure 2. Weight change measured by thermogravimetric analysis of 100Fe/4.4Si/5.2K (—), 100Fe/4.4Si/0.5Cu/5.2K (---), 100Fe/4.4Si/2.6Cu/5.2K (.....) and 100Fe/4.4Si/5.0Cu/5.2K (—...—) catalysts reduced with carbon monoxide.

Figure 3. Weight change measured by thermogravimetric analysis of 100Fe/4.4Si/5.2K (—), 100Fe/4.4Si/0.5Cu/5.2K (---), 100Fe/4.4Si/2.6Cu/5.2K (.....) and 100Fe/4.4Si/5.0Cu/5.2K (—...—) catalysts reduced with syngas ($H_2:CO=0.7$).

Figure 4. Carbon monoxide conversion as a function of time on stream for a 100Fe/4.4Si/1.0K catalyst ($\square$) and a 100Fe/4.4Si/2.6Cu/1.0K catalyst ($\circ$). Activation conditions: H_2 flow rate= $12 \text{ NL h}^{-1}\text{g-Fe}^{-1}$, 220°C , 0.10 MPa , 24 h . Synthesis conditions: $H_2:CO=0.7$, $3.1 \text{ NL h}^{-1}\text{g-Fe}^{-1}$, 270°C , 1.31 MPa .

Figure 5. Syngas conversion (○), C₂-ethylene selectivity (Δ) and methane selectivity, wt% of hydrocarbon product (□) as a function of potassium loading for a 100Fe/4.4Si catalyst. Synthesis conditions: H₂:CO=0.7, 1.0 NL h⁻¹g-Fe⁻¹, 230°C and 1.31MPa.

Figure 6. Hydrocarbon production rate for 100Fe/4.4Si/5.2K (○) and 100Fe/4.4Si/2.6Cu/5.2K (□) catalysts. Activation conditions: (a) hydrogen flow rate=12 NL h⁻¹g-Fe⁻¹, 220°C, 0.10 MPa for 24 h, (b) carbon monoxide flow rate=2.0 NL h⁻¹g-Fe⁻¹, 270°C, 0.10 MPa for 24 h, (c) H₂:CO=0.7 at 3.1 NL h⁻¹g-Fe⁻¹, 270°C, 0.10 MPa for 24 h. Synthesis conditions: H₂:CO=0.7, 3.1 NL h⁻¹g-Fe⁻¹, 230°C and 1.31MPa.

Figure 7. Syngas conversion for 100Fe/4.4Si/5.2K (○) and 100Fe/4.4Si/2.6Cu/5.2K (□) catalysts. Activation conditions: (a) hydrogen flow rate=12 NL h⁻¹g-Fe⁻¹, 220°C, 0.10 MPa for 24 h, (b) carbon monoxide flow rate =2.0 NL h⁻¹g-Fe⁻¹, 270°C, 0.10 MPa for 24 h, (c) H₂:CO=0.7 at 3.1 NL h⁻¹g-Fe⁻¹, 270°C, 0.10 MPa for 24 h. Synthesis conditions: H₂:CO=0.7, 3.1 NL h⁻¹g-Fe⁻¹, 230°C and 1.31MPa.

Figure 8. Carbon dioxide selectivity/% of CO converted versus time of synthesis (h) for 100Fe/4.4Si/5.2K (○) and 100Fe/4.4Si/2.6Cu/5.2K (□) catalysts. Activation conditions: H₂:CO=0.7 at 3.1 NL h⁻¹g-Fe⁻¹, 270°C, 0.10 MPa for 24 h. Synthesis conditions: H₂:CO=0.7, 3.1 NL h⁻¹g-Fe⁻¹, 230°C and 1.31MPa.

Figure 9. Carbon dioxide selectivity for 100Fe/4.4Si/2.6Cu/5.2K catalyst activated with hydrogen ($\square$), syngas ($\text{H}_2:\text{CO}=0.7$) ($\circ$) and carbon monoxide ($\diamond$). Synthesis conditions: $\text{H}_2:\text{CO}=0.7$, $3.1 \text{ NL h}^{-1}\text{g-Fe}^{-1}$, 230°C and 1.31MPa .

3.1.2 Effect of Potassium Promotion on Iron-Based Catalysts For Fischer-Tropsch Synthesis

ABSTRACT

The effect of potassium on catalyst activity, kinetic parameters and selectivity has been investigated for a precipitated iron catalyst that was employed with low H_2/CO ratio typical of a synthesis gas generated from coal. A wide range of synthesis gas conversions have been obtained by varying space velocities over catalysts with various potassium loadings. Differing trends in catalyst activity with potassium loading were observed depending on the space velocity or synthesis gas conversion. As potassium loading increased, the catalyst activity either decreased (low conversions), passed through a maximum (intermediate conversions) or increased (high conversions). This is shown to be a result of the increasing dependency of the Fischer-Tropsch synthesis on the hydrogen formed by the water-gas shift reaction with increasing synthesis gas conversions. Both the rate constant and the adsorption parameter in a common two-parameter Fischer-Tropsch rate expression decreased with potassium loading; therefore, observed maxima in Fischer-Tropsch rate with potassium loading can be due to the opposing influences of these parameters. The effect of potassium on alkene selectivity was dependent on the number of carbon atoms of the hydrocarbons as well as the carbon monoxide conversion level. The extent of isomerization of alkene products decreased with potassium loading, while the selectivity to methane decreased with increasing potassium content at CO conversions about 50% and higher.

INTRODUCTION

The Fischer-Tropsch Synthesis (FTS) converts synthesis gas, a mixture of carbon monoxide and hydrogen, to hydrocarbons. The FTS reaction can be represented as:

where n is the average H/C ratio of the hydrocarbons produced. Iron-based catalysts possess activity for the water gas shift (WGS) reaction. This property allows the direct processing of synthesis gas with a low H_2/CO ratio (as produced by coal gasification in advanced gasifiers) without an additional WGS reactor. The WGS reaction provides the extra hydrogen needed for the FTS.

Typical iron-based catalysts contain small amounts of potassium along with binders such as silica or alumina. The role of potassium on iron-based catalysts has been previously studied; however, the results of the effect of potassium on catalyst activity vary considerably with different researchers, different temperatures and with the presence/amount of binders used (1-4). Potassium has been shown to increase catalytic activity (1, 2, 4), decrease activity (2, 3), and in some cases the activity has been shown to reach a maximum with increasing potassium loading and then decline with further addition of potassium (1, 2). Further, systematic studies of possible reasons for catalyst activity trends have rarely been performed.

A reaction rate expression proposed (5) for the FTS is

$$-r_{CO+H_2} = \frac{kP_{CO}P_{H_2}^2}{P_{CO}P_{H_2} + bP_{H_2O}} \quad (3)$$

Based on this rate expression, changes in catalyst FTS activity could be due to changes in: (i) rate constant, k , (ii) adsorption parameter, b , and (iii) partial pressure of water. In addition, the rate and extent of the WGS reaction has a major effect on the FTS activity, especially for a low H_2/CO ratio synthesis gas. Studies of the effect of potassium loading on the kinetic parameters of the Fischer-Tropsch Synthesis or the effect of the WGS reaction on the FTS activity have not been previously reported in detail.

Addition of potassium has been found to affect the catalyst selectivity. Potassium apparently increases the alkene content of the hydrocarbon products, increases the rate of the WGS reaction and suppresses methane formation. However, these selectivity comparisons have often been made at different synthesis gas conversion levels (3, 4). It is known that selectivity changes with synthesis gas conversion and thus a comparison at equal conversion levels would be more appropriate to discern selectivity changes (6).

In this study, a systematic comparison of the effect of increasing potassium levels on iron-based catalyst activity and selectivity is conducted. Data were obtained for each potassium level over a wide range of synthesis gas conversions by varying feed space velocities. Thus, the effect of potassium on kinetic parameters has been determined and selectivity comparisons made at equal conversion levels. An attempt is made to discern the reason(s) for changes in catalyst activity with increasing potassium levels.

EXPERIMENTAL

Catalysts

The base catalyst used was a precipitated iron-silica catalyst with atomic ratio 100Fe/4.6Si. The preparation of this catalyst using a continuous precipitation procedure has been described previously (7). Various levels of potassium were added by incipient wetness impregnation with aqueous potassium nitrate. Final catalyst compositions in atomic ratio were: 100Fe/4.6Si/0.36K, 100Fe/4.6Si/1.4K and 100Fe/4.6Si/2.2K.

Reaction System

A 1-liter autoclave 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. More details of the reaction system used and product analysis have been reported previously (8).

Procedure

Approximately 5 g of catalyst was mixed with 300 g of melted octacosane (purified to remove halogens) in the CSTR. The reactor pressure was increased to 13.1 MPa with carbon monoxide at a flow rate of 13 NL h⁻¹ (20 °C, 0.10 MPa). The reactor temperature was increased to 270 °C at a rate of 120 °C h⁻¹. These activation conditions were maintained for 24 h.

At the end of the activation period, synthesis gas flow was started at a H₂/CO ratio of 0.67. During the entire run the reactor temperature was 270 °C, the pressure was 13.1 MPa and the stirring speed was maintained at 750 rpm. About two days were required before the catalyst reached steady state as evidenced by the constant

conversion of synthesis gas. Subsequently, the space velocity of the synthesis gas was varied between 5 and 65 NL h⁻¹ g-Fe⁻¹. The conversions of carbon monoxide, hydrogen, and the formation of various products were measured with a period of approximately 24 hours at each space velocity. The H₂/CO ratio of the feed synthesis gas was kept constant at 0.67 at all the space velocities. Periodically during the run, the catalyst activity was measured at pre-set "standard" conditions (a space velocity of 10 NL h⁻¹ g-Fe⁻¹) to check for catalyst deactivation.

RESULTS

The results for three potassium levels (0.36, 1.4 and 2.2) are presented. Representative runs for the 0.36 K and 1.4 K catalysts lasted for 500 hours during which the catalyst activity was constant as measured at pre-set "standard" conditions. Preliminary data for the 2.2 K catalyst showed that this catalyst deactivated after about 250 hours of time on stream. Hence, data for this catalyst were obtained in multiple runs lasting for a maximum of 250 hours. The synthesis gas conversion as measured in multiple runs was accurate to about +/- 1.5%.

Conversions

The syngas conversion is a rough measure of the overall Fischer-Tropsch activity of an iron-based catalyst. The syngas conversion for the three levels of potassium studied is shown in Figure 1. It is immediately evident that the trends in synthesis gas conversion with potassium loading are dependent on the space time (reaction time) or the conversion level. At low synthesis gas conversion levels or low space times, the catalyst with the lowest potassium loading (0.36 K) exhibited the highest synthesis gas conversion. At intermediate conversion levels, the catalyst with an intermediate potassium loading (1.4 K) exhibited the highest synthesis gas

conversion. At the highest conversion levels, the synthesis gas conversion exhibited by all three of the catalysts closely approached each other.

This is more clearly shown in Figure 2 where the synthesis gas conversion is plotted against potassium loading at various space velocities. At high space velocities, potassium appears to act as a catalyst poison. At the lowest space velocities, potassium appears to slightly enhance the synthesis gas conversion. At intermediate space velocities, there appears to be an optimum potassium level for maximum synthesis gas conversion.

The same trends obtained for synthesis gas conversion are also evident for the hydrocarbon production rate with potassium loading (Figure 3). This confirms that synthesis gas conversion is a good measure of the overall FTS activity.

Product/Reactant Partial Pressures

The partial pressure of water is an important parameter in the FTS. Water has been shown to inhibit the FTS reaction rate (Equation 3). As shown in Figure 4, the partial pressure of water in the reactor exhibits the behavior of a reaction intermediate, i.e., the water partial pressure is high initially and then decreases with reaction time. This is not surprising as the water formed by the FTS can be subsequently consumed in the WGS reaction. In general, the partial pressure of water in the reactor decreases with potassium loading.

The reaction rate expression given in Equation (3) can be rearranged as

$$-r_{CO+H_2} = \frac{kP_{H_2}}{1 + b \left(\frac{P_{H_2O}}{P_{CO}P_{H_2}} \right)} \quad (4)$$

In contrast to the water partial pressure, the value of the partial pressure ratio,

$$\frac{P_{H_2O}}{P_{CO}P_{H_2}}$$

increases monotonically with reaction time as shown in Figure 5. The value of the partial pressure ratio increases, in general, with potassium loading.

Reaction Rates of FTS and WGS

The individual rates of reaction of the FTS (r_{FTS}) and WGS (r_{WGS}) can be calculated from experimentally observed quantities by:

$$r_{WGS} = r_{CO_2} \quad (5)$$

and

$$r_{FTS} = r_{CO} - r_{CO_2} \quad (6)$$

where r_{CO_2} is the rate of carbon dioxide formation and r_{CO} is the rate of carbon monoxide conversion.

These calculated rates of the two reactions are shown in Figure 6 for the three potassium levels. At low reaction times, the rate of the FTS is much greater than the rate of the WGS reaction; however, the rate of the WGS reaction closely approaches the rate of the FTS at high reaction times. The trends in the FTS rate at different potassium loadings are similar to the variation of synthesis gas conversions with potassium loading (Figure 1).

At low reaction times, there are marked differences between the WGS reaction rates for different potassium loadings. The catalyst with intermediate potassium loading (1.4 K) exhibits the highest WGS reaction rate at the low reaction times; however, at

high reaction times the rates of the WGS for the three potassium loadings are quite similar.

Extent of WGS

One measure of the extent of the WGS reaction can be obtained by following the WGS reaction quotient (RQ_{WGS}).

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

As shown in Figure 7, the value of the reaction quotient is small at low carbon monoxide conversions and increases considerably at higher carbon monoxide conversions. The value of the reaction quotient increases with potassium loading at the same carbon monoxide conversions. Hence, the extent of the WGS reaction measured in this way appears to increase with potassium loading.

The FTS reaction produces water which is a necessary reactant for the WGS reaction to proceed. Thus the rate/extent of the WGS reaction is limited by the amount of water formed by the FTS. Since water is not supplied to the reactor, the stoichiometry of the FTS and WGS reactions (Equations (1) and (2)) dictates that

$$r_{WGS} \leq r_{FTS} \quad (8)$$

Hence, a more reliable measure of the extent of the WGS reaction is to compare the relative rate of the WGS to the rate of the FTS to see how closely the rate of the WGS approaches that of the FTS. As shown in Figure 8, the ratio of the FTS rate to the WGS reaction rate increases with carbon monoxide conversion and approaches a value of one. This is consistent with the data shown in Figures 6 and 7. Figure 8

clearly shows that the extent of the WGS reaction increases substantially with potassium loading at carbon monoxide conversions less than 80%. However, at high carbon monoxide conversions the increase in the extent of the WGS reaction with potassium loading is small.

Kinetics

The reaction rate expression given in Equation (3) can be linearized by rearrangement as

$$\frac{P_{H_2}}{-r_{CO-H_2}} = \frac{1}{k} + \frac{b}{k} \frac{P_{H_2O}}{P_{CO}P_{H_2}} \quad (9)$$

Hence a plot of $\frac{P_{H_2}}{-r_{CO-H_2}}$ versus $\frac{P_{H_2O}}{P_{CO}P_{H_2}}$ should give a straight line whose intercept is given by $(1/k)$ and whose slope is given by (b/k) .

The data for the three potassium loadings studied are plotted in this manner in Figure 9. It is evident that the results do not lie on a single straight line for any of the catalysts studied. The regression lines shown in Figure 9 have been drawn through the data obtained at low conversions. This situation is analyzed in the Discussion section.

Alkene Selectivity

Figure 10 illustrates the alkene selectivity of the light hydrocarbon products (C_2 and C_3) obtained. Both the C_2 and C_3 alkene selectivities decrease with carbon monoxide conversion for all the catalysts studied. The selectivity to C_2 alkene increases with potassium loading at similar carbon monoxide conversions. This is true over the entire range of carbon monoxide conversions obtained in this study. However, the effect of increasing potassium amounts on the selectivity to C_3 alkenes depends on the carbon monoxide conversion level; at lower carbon monoxide conversions the

highest alkene selectivity is obtained over the 0.36 K catalyst, while at higher conversions the highest alkene selectivity is exhibited by the 1.4 K and 2.2 K catalysts.

1-Alkene Selectivity

The isomerization ability at different potassium levels can be compared from the selectivity of the 1-alkene relative to the total alkenes (1-alkene + cis-2-alkene + trans-2-alkene) produced. This is illustrated for the butenes in Figure 11 for the three potassium levels as a function of carbon monoxide conversion. The selectivity to 1-butene decreases with increasing carbon monoxide conversion and increases with increasing potassium loading at similar carbon monoxide conversions.

Methane Selectivity

As shown in Figure 12, the methane selectivity was constant and similar for all the catalysts studied at low carbon monoxide conversions. Above 50% carbon monoxide conversion, the methane selectivity increased with increasing conversion. The selectivity to methane increased with decreasing potassium loading.

DISCUSSION

Effect of Increase in Potassium on WGS and FTS

For synthesis gas with a low H_2/CO ratio, the extent and/or rate of the WGS is extremely important to achieve a high conversion of carbon monoxide. For example, if there was no WGS, then according to Equations (1) and (2) the maximum carbon monoxide conversion would be 31%, assuming $n = 2.3$ (actual values of n or the average H/C ratio of the hydrocarbon products are between 2.2 and 2.4). In the case of all three of the catalysts studied, there is always some accompanying WGS reaction. In order to illustrate the importance of a high WGS reaction rate, it is necessary to

calculate the rate of hydrogen consumed by the FTS reaction. This can be calculated from the stoichiometry of the FTS (Equation 1) as

$$H_2 \text{ consumed by FTS} = r_{FTS}(1 + (n/2)) \quad (10)$$

Figure 13 shows a comparison of the hydrogen consumed by the FTS and the hydrogen supplied to the reactor for the three potassium loadings as a function of reaction time. The hydrogen supplied to the reactor varies with space velocity and is the same for each catalyst at the same space velocity. The hydrogen supplied to the reactor is sufficient for the FTS up to a space time of about 0.07 to 0.09 h g(Fe) NL⁻¹; however, at higher space times (or reaction times) the hydrogen supplied to the reactor is lower than that consumed by the FTS. The extra hydrogen consumed by the FTS must be formed by the WGS reaction.

The same data can be plotted with respect to carbon monoxide conversion instead of reaction time (Figure 14). The hydrogen supplied to the reactor is now different for each catalyst as the carbon monoxide conversions are different at the same space velocities. Similar to Figure 13, the hydrogen supplied to the reactor is sufficient for the FTS at low carbon monoxide conversions (less than 50%). Further, at higher carbon monoxide conversions, part of the hydrogen needed by the FTS must be obtained from the WGS reaction due to the insufficient hydrogen supply to the reactor. This illustrates that a high rate of the WGS reaction is necessary to supply the extra hydrogen in order to have a high rate of the FTS for synthesis gas containing a low H₂/CO ratio.

There is an increasing need for hydrogen formed by the WGS reaction with increasing carbon monoxide conversion (Figure 14). Further, the extent of the WGS

reaction increases substantially with potassium loading (Figure 8). These two factors can explain the variation in the effect of potassium on synthesis gas conversion (or activity) with reaction time (Figure 2).

At low carbon monoxide conversions or reaction times the extent/rate of the WGS reaction is not critical. The hydrogen supplied to the reactor is more than sufficient for the FTS. At these conversion levels, the only determinant of the overall FTS activity is the FTS reaction (Equation 1). As shown in Figure 2, the overall FTS activity of the catalyst (given by the synthesis gas conversion) decreases with potassium loading. Hence, potassium apparently acts as a catalyst poison for the FTS reaction.

As the carbon monoxide conversion increases, the extent/rate of the WGS becomes increasingly critical. The overall FTS activity is increasingly dependent on the hydrogen formed by, and thus the rate of, the WGS reaction. The overall FTS activity is then determined not only by the FTS reaction (Equation 1) but also by the WGS reaction (Equation 2). The highest overall FTS activity (synthesis gas conversion) at intermediate carbon monoxide conversions should then be exhibited by a catalyst which has an acceptably high rate for both the FTS reaction (Equation 1) as well as the WGS reaction (Equation 2). Since, the extent of the WGS reaction increases with potassium loading, the overall FTS activity should be a maximum at intermediate potassium loadings at these intermediate carbon monoxide conversions levels. This is exactly the situation at intermediate carbon monoxide conversion levels (Figure 2) where the synthesis gas conversion is the highest for the catalyst with an intermediate potassium loading (1.4 K).

At high carbon monoxide conversions, the overall FTS activity is increasingly dominated by the WGS reaction rather than the FTS reaction. Hence, the overall FTS activity should be higher for catalysts having a high rate for the WGS reaction. Since the extent of the WGS reaction increases with potassium loading, this implies that the overall FTS activity should be the highest for the catalyst with the highest potassium content. As shown in Figure 2, at high carbon monoxide conversions the synthesis gas conversion is maximum for the 2.2 K catalyst.

In summary, the above reasoning provides a consistent explanation for the experimental results of varying optimum potassium loadings with space velocity (Figure 2). According to this explanation, potassium actually inhibits the rate of the FTS reaction (Equation 1). Varying optimum potassium loadings with synthesis gas conversion level are due to the enhancement of the WGS reaction by potassium.

Effect of Water Partial Pressure

The partial pressure of water or the ratio of the partial pressure of water to the product of the partial pressures of carbon monoxide and hydrogen inhibit the FTS rate according to Equation (3). A possible explanation for changes in catalyst activity with potassium loading is the corresponding change in the water partial pressure or the partial pressure ratio with potassium loading. However, a comparison of Figures 4 or 5 with Figure 1 does not show any correlation between the partial pressures and synthesis gas conversion for the three potassium loadings studied. For instance, the water partial pressure decreases with potassium loading at the same space velocity whereas the synthesis gas conversion does so only at high space velocities and does not at low and intermediate space velocities.

Effect of Potassium on Kinetic Parameters

Figures 13 and 14 clearly show that the FTS reaction must depend increasingly on the hydrogen formed by the WGS reaction as the reaction time or carbon monoxide conversion increases. Thus the overall FTS rate is increasingly affected by the rate/extent of the WGS reaction at high conversions. Only at lower conversions is the overall FTS rate unaffected by the WGS reaction. Hence, there is a change in the rate limiting step of the overall FTS reaction (Equation 1 or Equation 2) with carbon monoxide conversion. This provides an explanation for the non-linearity of the experimental results when plotted (Figure 9) according to the linearized version of Equation 3. The results at carbon monoxide conversions of less than 60% lie on a straight line; however, results at higher carbon monoxide conversions deviate substantially.

Since, the rate of the FTS reaction is of importance in this study, regression lines have been drawn in Figure 9 for the data at carbon monoxide conversions below 60%. Information obtained from these regression lines then correspond only to the FTS reaction (Equation 1) and not to any influence of the WGS reaction (Equation 2). The intercept and slope of the regression lines can be used to calculate the rate constant (k) and the adsorption parameter (b) with potassium loading.

The rate constant (k) decreases with potassium loading as shown in Figure 15. This decrease in the rate constant is more than an order of magnitude between loadings of 0.36 K and 2.2 K. This result is consistent with the explanation offered for varying optimum potassium loadings with conversion level wherein the potassium was shown to be a poison or decrease the catalyst activity for the FTS reaction (Equation 1).

The adsorption parameter (b) also decreases with potassium loading as shown in Figure 16. Similar to the extent of decrease in the rate constant, the adsorption parameter decreases by over an order of magnitude between 0.36 K and 2.2 K loadings. The adsorption parameter has been shown to be given by (5)

$$b = \frac{K_{H_2O}}{K_{CO}} \quad (11)$$

where K_{H_2O} and K_{CO} are adsorption equilibrium constants for water and carbon monoxide respectively. Thus a decrease in the adsorption parameter (b) can be due to a decrease in the adsorption equilibrium constant for water and/or an increase in the adsorption equilibrium constant for carbon monoxide. Several previous studies (3,9,10) have shown that potassium causes an increase in the adsorption equilibrium constant for carbon monoxide. The observed decrease in the adsorption parameter (b) with potassium loading is consistent with the results of these studies.

A decrease in the rate constant (k) with potassium loadings implies a decrease in the FTS rate with potassium loading. In contrast, a decrease in the adsorption parameter (b) with potassium loading implies an increase in the FTS rate with potassium loading. This provides a possible explanation for a maximum in FTS activity with potassium loading. Thus an optimum potassium loading would be one for which the rate constant (k) is not too low and the adsorption parameter (b) not too high.

Effect of Potassium on Selectivity

As illustrated in Figure 10, increasing the amount of potassium on the catalyst appears to increase the selectivity to ethene. This is in conformity to previous studies. However, the selectivity to propene depends on the carbon monoxide conversion level.

This is in contrast to previous studies and illustrates the importance of comparing selectivities at similar carbon monoxide conversion.

Since the selectivity to 1-butene relative to total butenes increases with increasing potassium loading (Figure 11), the isomerization ability of the catalyst decreases with increasing amounts of potassium. Similarly, the selectivity to methane decreases with increasing potassium loading at carbon monoxide conversions greater than 50%.

CONCLUSION

A systematic evaluation of the effect of potassium on FTS activity and selectivity has been carried out in this study. A major observation of this study is that the trends in FTS activity with potassium loading are dependent on the space velocity and synthesis gas conversion level. At low synthesis gas conversions, the FTS activity decreases with potassium loading. At intermediate synthesis gas conversions, there is a maximum in FTS activity with potassium loading. At high synthesis gas conversions, potassium slightly enhances the FTS activity.

A consistent explanation for these activity trends has been given. The overall FTS activity is independent of the WGS reaction at low synthesis gas conversions. Potassium acts as a catalyst poison at these conversion levels as the FTS activity decreases with potassium loading. As the synthesis gas conversion increases, the hydrogen supplied to the reactor is insufficient for the FTS and the FTS increasingly depends on the hydrogen formed by the WGS reaction. Further, the extent of the WGS reaction increases with potassium loading. Thus as synthesis gas conversion increases the maximum overall FTS activity is obtained first at intermediate potassium loadings and finally at the highest potassium loading used in this study.

The effect of potassium on kinetic parameters for the FTS has also been determined in this study. The FTS activity depends on a rate constant and an adsorption parameter according to a previously proposed rate expression (5). The rate constant decreases by more than an order of magnitude when the potassium loading is increased from 0.36 K to 2.2 K. Thus potassium acts as a catalyst poison for the FTS. The adsorption parameter also decreases by over an order of magnitude with increasing potassium loadings between 0.36 K and 2.2 K. Since decreases in the rate constant and the adsorption parameter affect the FTS rate in opposite directions, these results provide a reasonable explanation for a maximum in FTS activity with potassium loading. Hence, an optimum potassium loading is one for which the rate constant is not too low and the adsorption parameter not too high.

Unlike previous studies, the effect of potassium on catalyst selectivity has been compared at similar conversions. The effect of increasing amounts of potassium on alkene selectivity depends on the number of carbon atoms of the hydrocarbons as well as the carbon monoxide conversion level. The extent of isomerization decreases with potassium loading. The selectivity to methane in the total hydrocarbon product is affected by potassium at carbon monoxide conversions above 50% and increases with decreasing potassium loading.

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Figure 1. Synthesis gas conversion as a function of potassium loading. (○) 0.36 K, (□) 1.4 K, and (◇) 2.2 K.

Figure 2. Synthesis gas conversion as a function of potassium loading. (○) 5 NL h⁻¹ g(Fe)⁻¹, (□) 10 NL h⁻¹ g(Fe)⁻¹ and (◇) 50 NL h⁻¹ g(Fe)⁻¹.

Figure 3. Hydrocarbon production rate as a function of reciprocal flow rate. (○) 0.36 K, (□) 1.4 K, and (◇) 2.2 K.

Figure 4. Water partial pressure as a function of reciprocal flow rate. (○) 0.36 K, (□) 1.4 K, and (◇) 2.2 K.

Figure 5. Partial pressure ratio, $\frac{P_{H_2O}}{P_{CO}P_{H_2}}$ (psia⁻¹) as a function of reciprocal flow rate 1/space velocity (h g(Fe)NL⁻¹). (○) 0.36 K, (□) 1.4 K, and (◇) 2.2 K.

Figure 6. Fischer-Tropsch (open symbols) and water-gas shift (closed symbols) rates as a function of reciprocal flow rate. (○) FT; 0.36 K, (●) WGS; 0.36 K, (□) FT; 1.4 K, (■) WGS; 1.4 K, (◇) FT; 2.2 K, and (◆) WGS; 2.2 K.

Figure 7. Water-gas shift reaction quotient as a function of reciprocal flow rate. (○) 0.36 K, (□) 1.4 K, and (◇) 2.2 K.

Figure 8. Ratio of rate of Fischer-Tropsch synthesis to rate of water-gas shift reaction as a function of reciprocal flow rate. (○) 0.36 K, (□) 1.4 K, and (◇) 2.2 K.

Figure 9. Plots of the linearized version of equation 3. (○) 0.36 K, (□) 1.4 K, and (◇) 2.2 K.

Figure 10. Alkene selectivity of C_2 (open symbols) and C_3 (closed symbols) hydrocarbons. (○) C_2 ; 0.36 K, (●) C_3 ; 0.36 K, (□) C_2 ; 1.4 K, (■) C_3 ; 1.4 K, (◇) C_2 ; 2.2 K, and (◆) C_3 ; 2.2 K.

Figure 11. Fraction of 1-butene in total linear alkenes as a function of carbon monoxide conversion. (○) 0.36 K, (□) 1.4 K, and (◇) 2.2 K.

Figure 12. Methane selectivity as a function of carbon monoxide conversion. (○) 0.36 K, (□) 1.4 K, and (◇) 2.2 K.

Figure 13. Need for water-gas shift reaction shown as a comparison of hydrogen supplied to the reactor and hydrogen used by the FTS. (—) hydrogen supplied to reactor, (○) hydrogen used by 0.36 K catalyst, (□) hydrogen used by 1.4 K catalysts, and (◇) hydrogen used by 2.2 K catalyst.

Figure 14. Need for water-gas shift reaction with increasing carbon monoxide conversion. Open symbols: hydrogen supplied to reactor. Closed symbols: hydrogen used by FTS. (○, ●) 0.36 K, (□, ■) 1.4 K, and (◇, ◆) 2.2 K.

Figure 15. Fischer-Tropsch rate constant as a function of potassium loading.

Figure 16. Adsorption parameter (b) from equation 3 as a function of potassium loading.

3.1.3 Fischer-Tropsch Synthesis. Compositional Changes in an Iron Catalyst During Activation And Use

ABSTRACT

The equilibrium phase compositions of iron have been calculated for gas compositions that could be encountered during the Fischer-Tropsch synthesis. The gas compositions measured experimentally for CO conversion levels in the 30-90% range show that iron should be present as the carbide phase. However, experimental characterization of iron catalysts show that a significant fraction of the iron is present as Fe_3O_4 following synthesis for several days. A model that can account for the experimental catalyst phase composition and the gases present in the reactor would have a core of Fe_3O_4 and an outer layer of iron carbides.

INTRODUCTION

The CHO system is of great importance in many areas of modern technology, including combustion, gasification, fuel cell and the Fischer-Tropsch (F-T) synthesis process. The species most likely to be present in the greatest amounts are those which are most stable under the conditions of interest, i.e., those having the lowest values of the free energy of formation. For the system containing carbon, hydrogen and oxygen in the temperature ranges of 298K to 1500K and a pressure of one atmosphere, the most stable species are carbon, carbon oxide, carbon dioxide, hydrogen, water and methane (1). For the F-T synthesis reaction, an iron catalyst is frequently employed. On contacting with the pretreating and/or synthesis gases, the iron or iron oxides can form an iron carbide, which is a catalyst for F-T synthesis. It is of interest to define the gas phase compositions where the iron carbide is thermodynamically favored during the course of catalyst activation and synthesis.

A convenient and informative method for the presentation of the iron carbide or iron oxide formation boundaries for the ternary CHO system is a set of triangular coordinates. The generality of the phase diagram becomes clear when it is recognized that C:H:O ratios of the system completely determine whether or not carbon, iron oxide and/or iron carbide will form for a given composition of gases. The usefulness of the phase diagram has been demonstrated by Manning and Reid (2) in their study of the iron-iron oxide system, Sacco and Reid (3) for the Bosch reaction system, and Sacco et al. (4) who studied the formation of carbon on iron.

This study considers the CHO gas phase compositions in equilibrium with iron and/or graphite (C) over the temperature range of interest for Fischer-Tropsch synthesis (200°C - 300°C) at pressures of 1 and 15 atmospheres. Different forms of iron oxide, i.e., Fe_3O_4 , Fe_2O_3 and FeO , and iron carbide, i.e., Fe_3C , $\text{Fe}_{2.2}\text{C}$ and Fe_2C , may be present during F-T synthesis. However, for simplicity and the availability of thermodynamic data, only Fe_3O_4 and Fe_3C are used to represent the iron compounds in these calculations.

In the F-T synthesis using an iron catalyst, Fe_3C , Fe_3O_4 , and C may form by reactions (1), (2) and (3), respectively:

The gas components are also subject to the water-gas shift reaction:

and methane is included as follows:

Also, hydrocarbons may be formed as, for example:

RESULTS

Three pertinent equilibria, C/gases, Fe/Fe₃O₄/gases and Fe/Fe₃C/gases were considered in the calculations. A modification of the method presented by Cairns and Tevebaugh was employed (1). Details of the calculation are given in Appendix A. Figures 1 to 3 are phase diagrams showing the Fe/Fe₃O₄/gases (□), Fe/Fe₃C/gases (Δ) and C/gases (○) at 15 atm. total pressure and temperatures of 300, 200 and 270°C, respectively. These graphs are on a molar basis of C, O and H; thus, an equimolar mixture of H, C and O (0.33 moles of each) requires a syngas with H₂/CO = 0.5. From these diagrams, one can delineate regions where Fe₃C, Fe₃O₄ and/or C would be expected to form when iron is in contact with different gas mixtures composed of hydrogen, oxygen and carbon at different temperatures. For example, for a gas mixture represented by a position which is located above the upper line (□) in Figures 1-3, Fe₃C is the solid iron phase that is thermodynamically favored. Carbon could also be formed in this region if Fe₃C catalyzed carbon formation at a rate comparable to F-T; i.e., reaction (3) would proceed to the right. The tie line for syngas of different H₂/CO mole ratios is also included in Figure 1. This tie line clearly shows that in order to have iron present only as Fe₃C, the H₂/CO mole ratio of the syngas must be less than about 0.75 at 300°C.

After activation with CO, the iron should be present only as, or predominantly as, the carbide. Experimental data show the 90% or greater is present as iron carbide following a 24 hr activation period (5-7) (Figure 4). During the course of F-T synthesis, gas compositions change to produce a catalyst in which some Fe₃C is converted to

Fe_3O_4 (Figure 4, from ref. 5). Previous studies produced data to show that the formation of H_2O during the F-T synthesis, i.e., reaction 6, is a major reason that Fe_3C will change phase to Fe_3O_4 (8). For a particular feedstock that defines the ratio of H_2/CO , the composition of all gases can be calculated by using material balance equations for each conversion level of CO and H_2 .

Using equations 8 and 9 for the reaction stoichiometry, one can calculate the minimum time required to convert Fe_3C to Fe_3O_4 at particular reaction conditions.

or

This is done for typical F-T synthesis conditions (catalyst loading, 15 g Fe, $T = 270^\circ\text{C}$, $\text{H}_2/\text{CO} = 0.67$, flow rate = 3.1 L/hr./g.Fe, $\alpha = 0.7$) where the H_2 and CO conversions are approximately 86 and 90%, respectively (9,10). Using these data, it is calculated that it would take approximately 4 hours to have sufficient reactants pass through the catalyst to convert Fe_3C to an equilibrium mixture of Fe_3C and Fe_3O_4 . The actual time needed to convert iron carbides present following activation to a mixture of iron carbides/iron oxide has been determined experimentally for several catalysts (5-7) and is much longer than the minimum. The presence of promoters provides a complicating factor to the conversion and stability of the iron carbide phases. Thus, for a comparison with the calculation of the minimum time for the conversion of iron carbide to iron oxide, data for an iron catalyst that does not contain promoters are shown in Figure 4. It is emphasized that for the iron catalyst, data similar to that shown in Figure 4 have been obtained for several runs.

In addition to the data shown in Figure 4, data have also been reported for Mössbauer and XRD characterization of promoted and unpromoted iron catalysts withdrawn from the reactor at various times (5-7,9,10). While the extent of oxidation as well as the rate of oxidation of catalysts utilized in laboratory CSTRs and the LaPorte pilot plant may differ for these catalysts, the compositional changes that occur follow a trend that can be represented by the data in Figure 4.

The forms of the carbon present in the actual FTS catalyst is difficult to define. Certainly for operation in the high temperature range of FTS, free carbon may be deposited (11). In fact, these carbon deposits can be so large as to cause disintegration of the catalyst particle and its formation has reduced the iron catalyst particles to very fine "bug dust" (12).

Small iron carbide particles can be prepared using a laser pyrolysis technique (13) and these particles are surrounded by pyrolytic carbon with $d = 0.35$ nm spacing between ordered layers. These carbon coated iron carbide particles have catalytic activity for FTS (10). Furthermore, the particles, depending upon preparative conditions, may initially be either Fe_7C_3 or Fe_3C but, in either case, the carbide phase gradually converts to the oxide phase during use for FTS. Starting with large (100-1,000 nm) particles of Fe_2O_3 , it has been shown that organized carbon layers form on the small particles of iron carbides that are formed during catalyst activation (14). The deposition of these organized pyrolytic carbon layers is not restricted to iron carbides. Nolan et al. (15) showed that organized carbon layers are present on both nickel and cobalt carbides. While the form of this organized carbon has not been conclusively defined, the use of graphite to represent this carbon seems reasonable.

A catalyst prepared by activation with CO at 270°C for 24 hours contains about twice the amount of carbon that is needed to form Fe₅C₂ and is presumably present as organized "pyrolytic carbon" on the surface of the iron carbide particles. Similar results have been obtained using a 1-L CSTR, a 2" slurry bubble column reactor and the 22.5" i.d. slurry bubble column reactor at the LaPorte pilot plant (16). Following pretreatment in CO, the iron is essentially in the form of iron carbides.

Comparison with Experimental Data

The compositional changes occurring with iron carbide catalysts during synthesis using conditions outlined in the manuscript have been documented in previous publications (5-7,9,10) and are representative of those shown in Figure 4.

F-T synthesis was effected at various CO conversion levels using a slurry reactor. Details of the experimental set-up, procedures and analytical methods are provided elsewhere (17,18). In one study (17), the molar ratio of syngas feed (H₂/CO=0.67), pressure (175 psi), and temperature (270°C) were held constant while flow rates of syngas were varied between 9.5 and 75.6 NL/hr-gFe for CO (6.4 and 50.6 NL/hr for CO). The composition of the gas phase exiting the reactor for each conversion level is shown in Table 1. The hydrocarbons formed (i.e., C₁ to C₃₅) during the reaction are reported in this table as an average value of C_x H_y. The mean carbon number of the hydrocarbon products is given by equation 10 (19):

$$x = 1 / (1 - \alpha) \quad (10)$$

where α refers to chain growth probability. Since the α value for this particular run is about 0.75 (17,18), the mean carbon number, x , is 4. The mean hydrogen number in the products can be calculated by:

$$y = \{ \sum [H/C]_i \cdot N_i / \sum N_i \} \cdot x \quad (11)$$

where the mean carbon number $x = 4$, i denotes hydrocarbon with carbon number equal to i , and N denote the molar fraction of each hydrocarbon. The data in Figure 5 indicate that at higher conversion levels, ($X_{CO} = 0.69$ to 0.86), Fe_3C is the solid iron phase that is favored by thermodynamics. However, at lower conversion levels ($X_{CO} = 0.23$ to 0.46) both Fe_3C and Fe_3O_4 are thermodynamically favored. The data in Table 1 show that the concentration of H_2O increases to a maximum level and then decreases with increasing CO conversion. On the other hand, the concentration of CO_2 increases with increasing CO conversion.

The data in Figure 6 indicate that the conversion of CO and H_2 are approximately equal (i.e., $X_{CO} = X_{H_2} = 0.69$) at a total flow rate ($CO+H_2$) of 31.3 NL/hr-gFe; this equal conversion is designated the equivalence point. At flow rates lower than the one that corresponds to the equivalence point, the conversion of H_2 is greater than that of CO while the conversion of CO is greater than that of H_2 above the equivalence point. This is due to the effect of WGS reaction since it consumes CO to generate H_2 . For flow rates slower than the one corresponding to about the equivalence point, Fe_3C is the iron phase that is thermodynamically favored. However, for flow rates faster than the one corresponding to the equivalence point, both Fe_3C and Fe_3O_4 are thermodynamically favored.

The solubility of the F-T gaseous reaction products, CO_2 and H_2O , in the F-T reactor wax product is reported to be higher than CO and H_2 by about a factor of ten; however, the solubilities of CO and H_2 increase remarkably with temperature which is in contrast to the product gases where the solubilities decrease with increases of temperature (20). Knowing the partial pressure of gas phase compounds and assuming that vapor-liquid equilibrium occurs, the solubility of each gas can be

calculated using the data reported in references 17 and 20. The total amounts of the compounds (CO , H_2O , CO_2 , CH_4) present in the reactor in both the gas and liquid phases can be calculated; these are shown in Figure 7. The data which represent both gas and liquid phase compounds are similar to the results in Figure 5, which represent only gas phase compounds.

DISCUSSION

The thermodynamic data indicate that activation in CO or H_2/CO at compositions with a ratio of 0.7 or lower should produce a nearly pure iron carbide phase. The experimental data generated during a 24 hour activation in CO at 270°C (1 or 12 atm.) show nearly pure iron carbide is formed (Figures 4 and 8). However, during about 24 hours of CO activation in a CSTR at 270°C , about twice as much carbon is deposited as is required to produce an iron carbide. Thus, it is apparent that a form of free carbon is deposited as well during the 24 hour activation. It is a common feature to observe a carbon film on nanometer sized metal particles (13,15). Carbon films have also been observed for large-particle iron Fischer-Tropsch catalysts (14).

The reduction of the catalyst to iron is not expected in a static system at temperatures of 300°C and lower. In agreement with this expectation, only about 30% of the iron is present as Fe^0 following 24 hour at 270°C in **flowing** hydrogen which continuously removes water (e.g., 5). Under reaction conditions, even at high conversion levels to produce high H_2/CO ratios, the presence of significant water (and CO_2) will prohibit the reduction of the iron to Fe^0 . In agreement with the calculations, metallic iron has not been observed in the catalyst samples withdrawn from the reactor during synthesis. Any metallic iron present following activation for 24 hours in H_2 was converted to metal carbides within 2 hours exposure to synthesis gas (5).

Under conditions of synthesis with $H_2/CO = 0.7$, the calculated data based on the exit gas phase composition, and even including the excess CO and H_2O held in the liquid phase in the reactor, based upon measured solubilities, the iron catalyst should be present as the carbide phase (Figure 7). One of the reasons for the deviation of the experimental data from the equimolar C and O tie-line is that oxygen present in methanol, ethanol and other oxygenates have not been included in the calculation. However, a significant fraction of the iron in the catalyst is present as Fe_3O_4 following long-term use in Fischer-Tropsch synthesis (5-7,9,10).

One possibility to account for the presence of both iron carbides and Fe_3O_4 during Fischer-Tropsch synthesis is that errors in the thermodynamic data cause the actual region for the presence of both iron carbides and Fe_2O_3 to extend to a higher carbon region than shown in Figures 1-3, 5 and 7.

A more likely possibility is inhomogeneity in the individual catalyst particles. In the interior of the individual porous particle and in the agglomeration of particles, the conversion of H_2 and CO will produce CO_2 and H_2O in addition to liquid hydrocarbons. The combination of reaction rates and product diffusion can combine to increase the concentration of H_2O and CO_2 to levels that are higher than are present in the bulk gas phase. Thus, the individual catalyst particles could be present with a core of predominantly Fe_3O_4 and with a surface layer of predominantly iron carbides coating the Fe_3O_4 core.

This model provides an explanation for the lack of a direct correlation between bulk catalyst composition and catalytic activity/selectivity. In many of the early studies with the fused iron catalyst, it was necessary to reduce the mass to essentially pure metallic iron, and this was found to be the case for the C-73 catalyst provided by United

Catalyst Inc. (22). Results of the changes that occur when this catalyst is placed in the syngas is illustrated in Figure 9 (11). In a lecture in 1974, Emmett (21) summarized what happens to this type of catalyst during synthesis. He noted that, "The story of what happens to the iron is rather straightforward... Immediately one builds up a concentration of carbide - the carbide which is formed is Fe_2C and it builds up rather quickly to a considerable extent and the iron content of course very well drops, and then a somewhat slower reaction builds up Fe_3O_4 . After a while the catalyst is largely Fe_3O_4 , Fe_2C and iron. The interesting thing is that it chugs along producing synthetic fuels at just about the same rate as it did initially. All of which reveals the fact that the surface composition is maybe distributed between iron, Fe_2C and Fe_3O_4 and this is the thing that determines the activity of the catalyst and these various phases within the catalyst are simply bulk phases that form by-products that are not particularly concerned with the reaction...There is evidence that until these carbides build up very little hydrocarbons are synthesized. In other words, it is necessary to build up these carbides and oxides in order to block the center of the iron catalyst crystals so that the carbon that is formed momentarily on the surface is as some Fe_2C compound...So we have a catalyst that, when all is simply said and done, we simply have to conclude is a combination of iron, iron carbide and iron oxide and possibly the surface is made up of such a combination."

Various studies at the CAER have shown that a sample activated to produce a material that is predominantly Fe_3O_4 has a much lower catalytic activity than one that is predominantly an iron carbide. Furthermore, the phases present are in a dynamic situation that depends upon the conversion levels of CO and H_2 . Thus, at the surface of the catalyst particle, the CO appears to serve to imitate and to grow the hydrocarbon

chains as well to serve as a source of carbon to maintain at least the surface region of the catalyst particle as an iron carbide phase.

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Appendix 1

Method for Calculation

For a balanced chemical process, the change in thermodynamic property can be calculated by adding together the tabulated values of the property for the substances present in the final state minus the sum of the values of the properties for the substances in the initial state, each value being property multiplied by the appropriate stoichiometric coefficient. The procedures for calculating the equilibrium constant for a chemical reaction utilized obtains thermodynamic properties from reference (1). The equilibrium constants for each temperature were calculated from Gibbs free energy, obtained for the ΔH° and ΔS° fractions using the assumption of ΔC_p° is constant in the temperature range utilized.

Equilibrium Calculation for Different Systems

The calculation for the system of C (graphite) and gases (CO, H₂, CO₂, H₂O, CH₄) equilibria, equations (3), (4) and (5) can be utilized. One material balance equation and three equilibrium constants collectively include all six species in equations (3), (4) and (5).

Material Balance		
Species	Moles at Start	Moles at Equilibrium
CO ₂	CO _{2,0}	CO _{2,0} - x + y
H ₂	H _{2,0}	H _{2,0} - x - 2z
C	0	y - z
CH ₄	0	z
H ₂ O	0	x
CO	0	x - y

The variable x, y, and z can be calculated by substituting expressions from material balance into the equilibrium constant equations:

$$\frac{z}{(H_{2,0} - x - 2z)^2} = K_3 \quad (11)$$

$$\frac{(CO_{2,0} - x + y)}{(x - 2y)^2} = K_2 \quad (12)$$

$$\frac{x(x - 2y)}{(CO_{2,0} - x + y)(H_{2,0} - x - 2z)} = K_1 \quad (13)$$

with three equations and three variables, values for x, y and z can be obtained.

For the equilibria involving Fe_3O_4/Fe and gases (CO , H_2 , CO_2 , H_2O , CH_4) equation (4) and the following equations are applicable:

The appropriate compositions and equations are:

Material Balance		
Species	Initial	At Equilibrium
CO_2	0	$x - y - 4z$
H_2	$H_{2,0}$	$H_{2,0} = 2x - y$
CO	$CO_{i,0}$	$CO_{i,0} - 2x + y + 4z$
Fe	$Fe_{i,0}$	$Fe_{i,0} - 3z$
H_2O	0	y
CH_4	0	x
Fe_3O_4	0	z

$$K_1 = \frac{[y] [CO_{,0} - 2x+y+4z]}{[H_{2,0} - 2x-y] [x-y-4z]} \quad (21)$$

$$K_{2,3} = \frac{[x] [x-y-4z]}{[H_{2,0} - 2x-y]^2 [CO_{,0} - 2x+y+4z]^2} \quad (22)$$

$$k_4 = \frac{[CO_{,0} - 2x+y+4z]^4}{[x-y-4z]^4} \quad (23)$$

The above allows one to obtain values for x, [CO₂] and [CH₄].

Table 1									
Composition of the Gas Phase Exiting the Reactor for Each Conversion Level									
Data #	H ₂ (psi)	CO (psi)	H ₂ O (psi)	CO ₂ (psi)	C ₄ H _y (psi)	y	X,CO (%)	X,H ₂ (%)	CO+H ₂ (NL/hr)
1	25.4	26.7	4	78	55	8.63	0.86	0.8	15.9
2	32	43	6	72	36	8.52	0.78	0.76	21
3	39.4	60.1	8.49	61.1	20.154	8.48	0.685	0.692	31.3
4	50.3	89.5	10.7	32.6	5.27	8.44	0.46	0.54	63.1
5	54.8	102.4	10.3	18.8	3.14	8.43	0.32	0.45	91.6
6	59.24	107.3	9.23	11.8	1.82	8.36	0.23	0.37	126.2

Figure 1. Ternary phase diagram for the solid phase(s) present for graphite/gases (○), Fe/Fe₃O₄/gases (□) and Fe/Fe₃C/gases mixtures at equilibrium at 300°C and 15 atm. (Region A: Fe₃C and C; Region B: Fe₃O₄, Fe₃C and C; Region C: Fe₃O₄ and C; Region D: Fe₃O₄; "—": tie line) (gases = H₂O, CO, CO₂, H₂ and CH₄).

Figure 2. Ternary phase diagram for the solid phase(s) present for graphite/gases (○), Fe/Fe₃O₄/gases (□), Fe/Fe₃C/gases mixtures at equilibrium at 200°C and 15 atm. (△) (gases = H₂O, CO, CO₂, H₂ and CH₄).

Figure 3. Ternary phase diagram for the solid phase(s) present for graphite/gases (○), Fe/Fe₃O₄/gases (□) and Fe/Fe₃C/gases mixtures at equilibrium at 250°C and 15 atm. (gases = H₂O, CO, CO₂, H₂ and CH₄).

Figure 4. Change in composition of an activated iron catalyst during synthesis. Fe₃O₄ (■), Fe₂O₃ (○), and Fe carbides (▲) (high surface, 300 m²/g, 3.0 nm Fe₂O₃) (from ref. 5).

Figure 5. The gas phase composition during synthesis at various flow rates plotted on the ternary phase diagram of Figure 1. Data #1 in Table 1 (●), data #2 (□), data #3 (△), data #4 (◇), data #5 (▽), data #6 (○) and feed composition of $H_2/CO = 0.67$ (●).

Figure 6. The variation of the conversion of H_2 and CO with flow rate ($H_2/CO = 0.7$, 270°C and 170 psig) (from ref. 9) (X, H_2 (△) and X, CO (□)).

Figure 7. The gas phase composition during synthesis at various flow rates plotted on the ternary phase diagram of Figure 1 (both liquid and gaseous CO , H_2 and CO_2 and H_2O are included in the calculation). Data #1 in Table 1 ($\bullet$), data #2 ($\square$), data #3 ($\triangle$), data #4 ($\diamond$), data #5 (∇), data #6 ($\circ$) and feed composition of $\text{H}_2/\text{CO} = 0.67$ ($\bullet$).

Figure 8. Rate of generation of CO_2 during activation of an iron catalyst at 270°C in a flow of CO in a 2 inch x 6 foot slurry bubble column reactor. CO_2 in exit ($\square$) and accumulated CO_2 ($\triangle$) represented by CO_2 formed/ CO_2 formed to produce Fe_3C .

Figure 9. The change in the composition of iron catalysts during the FT reaction. The phases are those which are present according to X-ray diffraction analysis. At time zero the catalyst is 100% metallic Fe. The units are defined since the rates of the phase changes depend on alkali content. The figure is only intended to illustrate the trends (from ref. 11).

3.1.4 Activation Study of Precipitated Iron Fischer-Tropsch Catalysts

ABSTRACT

Slurry phase Fischer-Tropsch Synthesis (FTS) was conducted with two precipitated iron catalysts (100Fe/3.6Si/0.71K and 100Fe/4.4Si/1.0K, atomic % relative to Fe) at 543K, 1.31MPa and a synthesis gas ($H_2/CO=0.7$) space velocity of $3.1 \text{ NL h}^{-1} \text{ g Fe}^{-1}$. The impact of activation gas (CO, $H_2/CO=0.7$ or $H_2/CO=0.1$), temperature (543K or 573K) and pressure (1.31MPa or 0.10 MPa) on the long term (>500 h) activity and selectivity of the catalysts were explored. Pretreatment with CO under the conditions employed gave highly active and stable catalysts. Catalyst performance when synthesis gas activation was used was found to be dependent upon the partial pressure of hydrogen in the activating gas with low hydrogen partial pressures resulting in the highest catalyst activity. X-ray diffraction results indicate that carbon monoxide activations and synthesis gas activations with low hydrogen partial pressure result in the formation of the carbides $\chi\text{-Fe}_5\text{C}_2$ and $\epsilon'\text{-Fe}_{2.2}\text{C}$ while activation with synthesis gas with high hydrogen partial pressure results in the formation of only Fe_3O_4 . It was found that treating the 100/3.6Si/0.71K catalyst activated with synthesis gas at 1.31 MPa and 543K, with carbon monoxide caused the activity to increase dramatically and the Fe_3O_4 to be partially converted to iron carbides. It is concluded that Fe_3O_4 is relatively inactive for FTS while the presence of some bulk iron carbide is necessary for high FTS activity to be achieved.

INTRODUCTION

The activation procedure used for iron based Fischer-Tropsch synthesis (FTS) catalysts has a great influence on their activity and selectivity [1]. Reduction of fused magnetite catalysts with hydrogen at high temperatures (>673K) and high linear flow

rates is necessary to produce a substantial surface area necessary for good activity; however, reduction with synthesis gas or carbon monoxide is ineffective [2]. In contrast, activation of precipitated iron catalysts is not understood as well. Precipitated catalysts have been reported to be successfully activated with carbon monoxide [3,4] hydrogen [2,5] or synthesis gas [6-8].

Several research groups have reported that pretreatment of precipitated iron oxide with carbon monoxide is the preferred activation procedure. Bukur et al. have reported that pretreatment of doubly promoted Fe/Cu/K catalysts with carbon monoxide or synthesis gas ($H_2:CO \sim 0.7$ or 2.0) results in higher initial activity and a heavier product than activation with hydrogen; however, hydrogen pretreatments were reported to result in more stable catalysts [4,5]. Pennline et al. found that activation of a precipitated iron-manganese catalyst with carbon monoxide was superior to activation with hydrogen or synthesis gas at 15 MPa and 548 K; furthermore, they report little temperature or pressure affects when activating with carbon monoxide [9]. During the initial German work on FTS, the Kaiser Wilhelm Institute favored pretreating catalysts with carbon monoxide at subatmospheric pressure [10]. In addition, Huang et al. have reported that an ultrafine iron oxide catalyst has superior activity when pretreated with carbon monoxide than with hydrogen or synthesis gas ($H_2:CO=1.0$) at 533 K and 0.79 MPa [11].

Although pretreatment of precipitated iron catalysts with carbon monoxide leads to active catalysts, hydrogen pretreatment is more favorable on an industrial scale, because it is less expensive and easier to purify. In general, pure hydrogen can be prepared from synthesis gas using a membrane separation process that allows only hydrogen to pass; however, this separation will not lead to pure carbon monoxide, but

instead will produce a carbon monoxide rich synthesis gas. SASOL utilizes hydrogen pretreatment of precipitated iron catalysts used in its commercial FT reactors [2]. In addition, much of the early German work utilized hydrogen pretreatment, i.e., Ruhrchemie AG, IG Farbenindustrie AG and Lurgi [10]. Hydrogen pretreatment has the disadvantage that the metallic iron that is formed is susceptible to sintering. High flow rates are needed to keep the partial pressure of water low and low temperatures are necessary to insure that a high surface area is maintained [2,5].

The development of a pretreatment procedure utilizing synthesis gas that would consistently lead to active catalysts would be attractive, because pretreatments could be performed with the same gas that is used in the FTS, thereby eliminating the need for a pure hydrogen or carbon monoxide stream. Kölbel and Ralek [6] and Mobil [7,8] have reported high activity and good stability with precipitated Fe/Cu/K catalysts in laboratory and demonstration plant slurry reactors using *in situ* synthesis gas activation. Pretreatment conditions appear to be crucial in determining the ultimate FT activity of synthesis gas activated catalysts. Kolbel and Ralek report that the temperature of the synthesis gas pretreatment is critical to the final activity and selectivity of the catalyst; too high a temperature will result in “supercarbonization” and too low a temperature will prevent activation [6]. In addition, pressure may also affect the ultimate activity; many of the German companies preferred activation at a low pressure when using synthesis gas pretreatments [10].

The catalyst phase that exists is strongly dependent on the activation procedure employed. Activation with hydrogen, carbon monoxide or synthesis gas generally result in the rapid formation of Fe_3O_4 [3]. With additional time, the Fe_3O_4 is converted to metallic iron in the case of hydrogen pretreatment or various iron carbides (usually χ -

Fe_5C_2 or $\epsilon\text{'-Fe}_{2.2}\text{C}$) with carbon monoxide or synthesis gas pretreatment [1-3,5]. During synthesis, metallic iron is rapidly converted to iron carbide and with longer times on stream the iron carbide may be oxidized to Fe_3O_4 [1-3,5]. Several studies have been made to correlate catalyst composition with activity [3,12-15]. Some reports claim iron carbides are active for FTS [12] while others claim an oxide species is responsible for activity [16]. In contrast, it has also been reported that a correlation between catalyst activity and bulk phase composition cannot be made [1-3].

The present study is aimed at providing a better understanding of the relationship between pretreatment, FTS activity and the phase composition of precipitated iron catalysts used in a slurry reactor. A comparison is made between pretreatment with carbon monoxide and synthesis gas ($\text{H}_2:\text{CO}=0.7$ or 0.1) with particular attention being paid to the affect of temperature and pressure used during the activation procedure on the resulting FTS activity.

EXPERIMENTAL

Catalysts were prepared by continuous precipitation of amorphous ferric oxyhydroxide from aqueous iron(III) nitrate nonahydrate (1.17M) and concentrated ammonium hydroxide (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 the desired level of silicon. 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 393 K and crushed to -300 mesh. The composition of this catalyst in terms of atomic percent relative to Fe is 100Fe/3.6Si. During loading into the slurry reactor, the catalyst

was treated with sufficient potassium *t*-butoxide to make the composition 100Fe/3.6Si/0.71K. A large 75 kg catalyst batch was also prepared; however, this catalyst was prepared by adding potassium nitrate to the slurry, spray dried and calcined in air at 623 K. The composition of this catalyst was 100Fe/4.4Si/1.0K.

All FTS runs were conducted in a one liter autoclave operating as a continuous stirred tank reactor (CSTR). Catalysts were suspended in Ethylflo 164 hydrocarbon oil (Ethyl Corporation) which is reported to be a C₃₀ 1-decene homopolymer. All catalysts loadings were 10 weight per cent unless otherwise noted. A schematic of the reactor system is shown in Figure 1. Hydrogen and carbon monoxide feed gas 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 333 K and 273 K. Accumulated reactor wax was removed daily through a tube fitted with a porous metal filter (0.5 µm). Uncondensed effluent was sent to an on-line Carle gas analyzer for determination of carbon monoxide, hydrogen, carbon dioxide, methane and C₂-C₄ alkanes and alkenes. An on-line Hewlett-Packard 5790 GC equipped with a Porpack-Q column was utilized for C₄-C₉ quantification. Liquid samples were analyzed with a Hewlett-Packard 5890 GC equipped with a 60 m DB-5 capillary column. The reactor was also equipped with a tube that extended below the liquid level which permitted catalyst slurry samples to be withdrawn periodically.

Catalysts were pretreated with carbon monoxide or activated with synthesis gas with a hydrogen:carbon monoxide ratio of 0.7 or 0.1. In general, the activation gas flow

was started at ambient conditions, the necessary reactor pressure was set and the reactor was ramped to the desired temperature at 2 K min^{-1} . After reaching the activation temperature, the conditions were maintained for 24 h. Following the activation treatment, the reactor was brought to reaction conditions: hydrogen:carbon monoxide ratio of 0.7, $3.1\text{ NL h}^{-1}\text{g}^{-1}(\text{Fe})$ (NL corresponds to 273 K, 0.10 MPa) 543 K and 1.31 MPa.

Catalyst samples were Soxhlet extracted according to the method of McCartney et al., [17] to remove accumulated wax and then analyzed by X-ray diffraction. Powder X-ray diffraction patterns of the catalysts were obtained using a Philips APD X-ray diffraction spectrometer equipped with a Cu anode and Ni filter operated at 40Kv and 20Ma ($\text{CuK}\alpha=1.5418\text{ \AA}$). Iron phases were identified by comparing diffraction patterns of the catalyst samples with those in the standard powder X-ray diffraction file compiled by the Joint Committee on Powder Diffraction Standards published by the International Center for Diffraction Data.

RESULTS AND DISCUSSION

Catalyst Activation

Early in our efforts to develop an effective activation procedure for precipitated iron catalysts, we found that a 24 h treatment with carbon monoxide at 543 K and 1.31 MPa consistently resulted in highly active and stable catalysts (Figures 2a and 3). Initial carbon monoxide conversion for the 100Fe/3.6Si/0.71K and 100Fe/4.4Si/1.0K catalysts activated in this manner were 92% and 85%, respectively, with corresponding deactivation rates of 4.8% and 1.0% per week, respectively. Hydrocarbon productivities typically were in the range of $160\text{-}170\text{ g m}^{-3}(\text{CO}+\text{H}_2\text{ feed})$ with greater than 80% being C_3 and higher. The reproducibility of this activation procedure has facilitated screening

large numbers of catalysts so that reliable data concerning optimum promoter levels can be determined. Much of this work is directed at developing a process for catalyst preparation that is suitable for scale-up to pilot plant scale.

The use of pure carbon monoxide as an activation gas is acceptable for small laboratory reactors; however, it is cost prohibitive for a pilot plant. As a result, it is economically attractive and operationally more facile to be able to activate catalysts *in situ* with the same synthesis gas as used during the FTS. Activity and selectivity results of our initial efforts using synthesis gas activation are shown in Table 1. Treatment of either 100Fe/3.6Si/0.71K or 100Fe/4.4Si/1.0K catalysts with synthesis gas ($H_2:CO=0.7$) at $3.1\text{ NL h}^{-1}\text{g}^{-1}(\text{Fe})$, 543 K and 1.31 MPa resulted in poor FTS activity. Carbon monoxide conversions were typically below 30% and did not increase appreciably with time on stream. Kölbel and Ralek have reported successful synthesis gas activations with a precipitated Fe/Cu/K catalyst at 0.8-1.5 MPa and at a “formation” temperature 15-30 K above the FTS temperature ($\sim 573\text{ K}$); however, they report that at too high a temperature carbon will form and at too low a temperature the formation will not take place and the catalyst will be inactive [6]. In contrast, we have found that increasing the activation temperature to 573 K while maintaining the pressure at 1.31 MPa has little affect on conversion during synthesis with catalysts activated with synthesis gas.

During the Reichsamt comparative experiments conducted in Germany in 1943, the Kaiser Wilhelm Institute, Brabag and Rheinpreussen all activated their iron catalysts with synthesis gas or water gas at atmospheric or subatmospheric pressure [10]. To explore the possible affect of pressure on synthesis gas activation, both 100Fe/3.6Si/0.71K (Figure 3) and 100Fe/4.4Si/1.0K (Figure 2c) catalysts were treated with synthesis gas ($H_2:CO=0.7$) at $3.1\text{ NL h}^{-1}\text{g}^{-1}(\text{Fe})$, 0.10 MPa and 543 K for 24 h. A

dramatic increase in activity was observed as compared to when the same activation was conducted at 1.31 MPa. For both the 100Fe/3.6Si/0.71K and 100Fe/4.4Si/1.0K catalysts, the initial carbon monoxide conversion was greater than 85% which is comparable to that obtained when pretreating with carbon monoxide at 543 K and 1.31 MPa. In fact, the 100Fe/4.4Si/1.0K catalyst had an initial conversion of 92% and displayed remarkable stability, deactivating at an average rate of only 0.59% per week for over 2700 h. In addition, the 100Fe/4.4Si/1.0K catalyst was also activated with synthesis gas ($\text{H}_2:\text{CO}=0.7$) at 573 K and 0.10 MPa. As was found when activating with synthesis gas at 1.31 MPa, increasing the temperature had little effect on the initial carbon monoxide conversion (Figure 2d); however, the deactivation rate was higher at 1.6% per week.

It is interesting to note that no such pressure dependence was observed with carbon monoxide pretreatment (Figure 2b). Pretreating the 100Fe/4.4Si/1.0K catalyst with carbon monoxide for 24 h at 543 K and 1.31 MPa resulted in an initial conversion slightly lower than when activating at 0.10 MPa; however, after 72 h at synthesis conditions, the conversions were essentially the same in both cases.

Selectivity data at high conversion for the 100Fe/4.4Si/1.0K catalyst activated with carbon monoxide or synthesis gas are presented in Table 2. In general, carbon monoxide activations resulted in the production of less methane and more liquid products than activations with synthesis gas. At comparable conversions, the catalyst activated with carbon monoxide at either 543 K/1.31 MPa or 543 K/0.10 MPa produced up to twice as much $\text{C}_{12}+$ as when activated with synthesis gas at 0.10 MPa. In contrast, Bukur et al. reported similar selectivities for a doubly promoted Fe/Cu/K catalyst that was activated with carbon monoxide or with synthesis gas [5].

The fact that pretreatment with carbon monoxide at either 0.10 or 1.31 MPa results in similar FTS activity suggests that the pressure dependence of synthesis gas activation is due to the presence of hydrogen. To test this possibility, the 100Fe/3.6Si/0.71K catalyst was treated with a synthesis gas low in hydrogen ($H_2:CO=0.1$) for 24 h at $2.1\text{ NL h}^{-1}\text{g}^{-1}(\text{Fe})$, 543 K and 1.31 MPa. The initial carbon monoxide conversion was approximately 65% which is intermediate between activation with pure carbon monoxide and synthesis gas with a hydrogen:carbon monoxide ratio of 0.7. As shown in Figure 4, there is a clear correlation between the partial pressure of hydrogen in the activating gas and the carbon monoxide conversion obtained during the early synthesis period.

Catalyst Characterization

Catalyst slurry samples were removed from the reactor for the series of runs with the 100Fe/3.6Si/0.71K catalyst. X-ray diffraction analysis of the catalyst following pretreatment with CO (Figure 5a) or synthesis gas at 0.10 MPa (Figure 5b) shows the presence of Fe_3O_4 and the carbides $\chi\text{-Fe}_5C_2$ and $\epsilon'\text{-Fe}_{2.2}C$. In addition, X-ray diffraction data for the catalyst activated with hydrogen lean synthesis gas ($H_2:CO=0.1$) (Figure 5c) showed Fe_3O_4 and small amounts of iron carbides. In contrast, X-ray diffraction analysis of the catalyst activated with synthesis gas at 1.31 MPa showed only Fe_3O_4 (Figure 5d).

As discussed above, the carbon monoxide conversion of the 100Fe/3.6Si/0.71K catalyst activated with synthesis gas ($H_2:CO=0.7$) at 1.31 MPa and 543 K never rose above 12%. After 96 h of synthesis, the hydrogen flow was stopped and the catalyst was treated with carbon monoxide under the same operating conditions for 22 h. Following the carbon monoxide treatment, the hydrogen flow was resumed and the

activity of the catalyst was found to rapidly increase (Figure 6). The ultimate activity of catalyst was similar to that obtained for the carbon monoxide pretreated catalyst. X-ray diffraction analysis shows that the catalyst consists of only Fe_3O_4 prior to the carbon monoxide treatment; however, following the carbon monoxide treatment, the catalyst consists of a mixture of Fe_3O_4 , $\chi\text{-Fe}_5\text{C}_2$ and $\epsilon'\text{-Fe}_{2.2}\text{C}$ (Figure 7). These results are consistent with the Fe_3O_4 phase being relatively inactive for FTS while $\chi\text{-Fe}_5\text{C}_2$ and $\epsilon'\text{-Fe}_{2.2}\text{C}$ are necessary for high FTS activity. This does not necessarily imply that $\chi\text{-Fe}_5\text{C}_2$ and $\epsilon'\text{-Fe}_{2.2}\text{C}$ are active phases for FTS, in fact, previous works have shown that there is no correlation between the amount of bulk iron carbide present and the activity of the catalyst [2,3]. It is possible; however, that the presence of a bulk iron carbide is necessary to serve as a support for an active surface species. In considering the above results and discussion, it should be kept in mind that the characterization is based upon XRD; therefore, only bulk phases are detected.

The overall Fischer-Tropsch Synthesis with iron catalysts can be approximated as the sum of the hydrogenation of carbon monoxide to methylene groups and the water-gas shift reaction.

For iron based catalysts, whether the catalyst exists as a carbide or as an oxide depends on the reducing behavior of the atmosphere present in the reactor. During Fischer-Tropsch synthesis, the catalyst is exposed to an atmosphere of hydrogen, carbon monoxide and the reaction products: water and carbon dioxide. It is well known that water and carbon dioxide will oxidize metallic iron and iron carbides to Fe_3O_4 [1,2].

Thermodynamic data on the metallic iron/iron oxide system show that at a $\text{H}_2\text{O}:\text{H}_2$ ratio > 0.03 or a $\text{CO}_2:\text{CO}$ ratio > 2.8 oxidizing conditions exist and Fe_3O_4 is the stable phase compared to metallic iron [18]. Equation 3 can be used to calculate the $\text{H}_2\text{O}:\text{H}_2$ and $\text{CO}_2:\text{CO}$ ratios based on the carbon monoxide and hydrogen conversions. During activation of the 100Fe/3.6Si/0.71K catalyst with synthesis gas at 1.31 MPa, the $\text{H}_2\text{O}:\text{H}_2$ ratio was 0.16 and the $\text{CO}_2:\text{CO}$ ratio was 0.022. The water level clearly was high enough to make Fe_3O_4 the thermodynamically stable phase during the activation which would explain why no iron carbides could be detected by XRD. This conclusion requires that the formation of iron carbides results from an iron species that is lower-valent than is present in Fe_3O_4 . In contrast, synthesis gas activation of the same catalyst at 0.10 MPa had a much lower $\text{H}_2\text{O}:\text{H}_2$ ratio of 0.0070 and a $\text{CO}_2:\text{CO}$ ratio of 0.90. These water and carbon dioxide levels were low enough to enable the catalyst to be reduced to form active iron carbides. It appears that by decreasing the hydrogen partial pressure, reaction 1 is suppressed enough during the activation that active iron carbides can be formed. An alternate method of activation with synthesis gas would be to operate at high linear flow rates (low conversion) to suppress water formation and to rapidly remove it from the reactor as is usually done when activating with pure hydrogen [2,5].

CONCLUSIONS

CO pretreatment of precipitated Fe/Si/K catalysts consistently results in high FTS activity because active carbide phases are readily formed. In the case of syngas activation, there is a relationship between the hydrogen partial pressure in the activation gas and the initial FTS activity. During activation with syngas, the catalyst is exposed to carbon dioxide and water as well as carbon monoxide and hydrogen. It has been found

that during activations with high partial pressures of hydrogen, enough water is formed to prevent the catalyst from being reduced to active iron carbide phases and only relatively inactive Fe_3O_4 is formed. The results of this study indicate that the formation of an iron carbide ($\chi\text{-Fe}_5\text{C}_2$ and/or $\epsilon'\text{-Fe}_{2.2}\text{C}$) is necessary for high FTS activity; however, based on previous Mössbauer spectroscopy experiments, the activity of iron catalysts is not related to the amount of bulk iron carbide present [3]. These results indicate that a layer of surface carbide may be responsible for FTS activity.

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Table 1 Results of Syngas Activations at 1.31 MPa								
Catalyst	100 Fe/3.6 Si/0.71 K						100 Fe/4.4 Si/1.0 K	
Activation Conditions	H ₂ /CO = 0.7, 1.31 MPa, 543K		H ₂ /CO = 0.7, 1.31 MPa, 573K		H ₂ /CO = 0.1, 1.31 MPa, 543K		H ₂ /CO = 0.7, 1.31 MPa, 543K	
Time-on-Stream, h	46	92	46	119	47	139	48	192
Conversion/%								
CO	12	12	15	21	62	60	22	33
H ₂	22	26	21	26	58	54	28	35
CO + H ₂	16	18	18	23	61	57	25	34
H ₂ :CO Usage Ratio	1.3	1.5	0.98	0.87	0.65	0.63	0.89	0.74
CO ₂ Selectivity/mol %	37	43	35	34	46	46	38	43
Hydrocarbon Productivity								
g HC Nm ⁻³ feed gas	27	25	37	51	126	120	52	70
g C ₃ + Nm ⁻³ feed gas	22	20	31	44	108	103	44	59
g HC g ⁻¹ (Fe)h ⁻¹	0.084	0.078	0.11	0.16	0.39	0.37	0.16	0.21
Alkene Selectivity/mol %								
C ₂	58	74	62	67	23	16	75	63
C ₃	92	91	84	89	69	62	83	81
C ₃	83	84	81	84	76	76	86	84

Table 2 FTS Results for Catalysts at High Activity								
Pretreatment	CO/543 K/1.31 MPa		CO/543 K/0.10 MPa		H ₂ :CO = 0.7/543K/0.10 MPa		H ₂ :CO = 0.7/573K/0.10 MPa	
Time-on-Stream/h	336	1992	360	1016	312	2852	312	1836
Space Velocity/NL h ⁻¹ g ⁻¹ (Fe)	3.4	3.4	3.1	3.1	3.1	3.1	3.1	3.1
Conversion/%								
CO	84	74	84	79	87	74	84	68
H ₂	76	65	75	73	77	67	76	67
CO + H ₂	81	70	80	76	83	71	81	67
WGS								
CO ₂ /mol %	46	42	45	44	50	46	47	44
H ₂ :CO Usage	0.63	0.61	0.63	0.65	0.62	0.64	0.62	0.68
K _{app}	14	7.2	16	12	40	30	16	4.4
Productivity								
g HC Nm ⁻³ feed gas	167	159	168	162	162	146	165	140
g C ₃ +Nm ⁻³ feed gas	142	132	142	134	130	110	136	116
g HC g ⁻¹ (Fe)h ⁻¹	0.62	0.58	0.52	0.50	0.50	0.45	0.50	0.42
Selectivity/wt.% (alkene)								
C ₁	8.1	8.7	8.2	8.7	11	15	9.6	8.3
C ₂ -C ₄	26(57)	28(61)	27(57)	29(57)	32(48)	37(53)	30(54)	33(65)
C ₅ -C ₁₁	34(58)	27(66)	36(60)	32(60)	46(54)	34(56)	34(59)	40(68)
C ₁₂ +	32	36	29	31	11	15	26	19

Figure 1. Schematic of the one liter continuous stirred tank reactor system.

Figure 2. Carbon monoxide conversion for 100Fe/4.4Si/1.0K catalyst pretreated for 24 h at with (a) carbon monoxide at 543 K an 1.31 MPa, (b) carbon monoxide at 543 K and 0.10 MPa, (c) synthesis gas ($H_2:CO=0.7$) at 543 K and 0.10 MPa, and (d) synthesis gas ($H_2:CO=0.7$) at 573 K and 0.10 MPa.

Figure 3. Carbon monoxide conversion for 100Fe/3.6Si/0.71K catalyst pretreated for 24 h with (○) carbon monoxide at 543 K and 1.31 MPa and (□) synthesis gas (H_2 :CO=0.7) at 543 K and 0.10 MPa.

Figure 4. Initial carbon monoxide conversion as a function of the partial pressure of hydrogen in the pretreatment gas for the 100Fe/3.6Si/0.71K catalyst.

Figure 5. X-ray diffraction results for 100Fe/3.6Si/0.71K catalyst following 24 h pretreatment with (a) carbon monoxide at 543 K and 1.31 MPa, (b) synthesis gas (H₂:CO=0.7) at 543 K and 0.10 MPa, (c) synthesis gas (H₂:CO=0.1) at 543 K and 1.31 MPa, and (d) synthesis gas (H₂:CO=0.7) at 573 K and 1.31 MPa.

Figure 6. Carbon monoxide conversion for 100Fe/3.6Si/0.71K catalyst (○) activated with synthesis gas at 543 K and 1.31 MPa, followed by a carbon monoxide treatment at 543 K and 1.31 MPa after 96 hr of synthesis and (□) pretreated with carbon monoxide for 24 h at 543 K and 1.31 MPa.

Figure 7. X-ray diffraction results for the 100Fe/3.6Si/0.71K catalyst (a) after 96 hr of exposure to synthesis gas at 543 K and 1.31 MPa and (b) followed by a 22 h exposure to carbon monoxide at 543 K and 1.31 MPa.

3.1.5 Attrition, Activity and Selectivity Characteristics of

Supported Iron Fischer-Tropsch Catalysts

Introduction

Iron catalysts undergo a series of phase changes during activation and use in the Fischer-Tropsch synthesis (FTS) (1,2) which cause the volume of catalyst particles to change. These volume changes can cause stresses to develop within individual particles and within agglomerations of catalyst particles which may ultimately cause attrition. The following description utilizes the bulk properties for iron oxide and iron carbide compounds (3-7).

Using the densities listed in Table 1, the volume changes that occur upon activation of an iron catalyst that starts as Fe_2O_3 are shown in Table 2. The initial reduction of Fe_2O_3 to Fe_3O_4 results in a small (2%) decrease in volume and should not induce much stress upon individual catalyst particles nor upon catalyst agglomerates. The next potential step in the reduction, if it occurs, and to date there is no definitive evidence that FeO does form in significant quantities, leads to a 18.9% volume decrease. The conversion to Fe_3C results in a further decrease in volume by 35%, and a similar decrease if Fe_5C_2 is formed. Thus, overall the activation process results in a decrease in the volume of the individual catalyst particle; this decrease in volume may or may not be transferred to the catalyst agglomerate.

During use, some fraction of the iron carbide is converted to Fe_3O_4 . The conversion of Fe_3C to Fe_3O_4 results in an increase in volume of 91%, and a similar increase for Fe_5C_2 . The reoxidation step therefore has the potential to induce severe strains on the individual catalyst particle and upon the catalyst agglomerate. Thus,

there is potential for the reoxidation step to provide the stress to cause the formation of catalyst fines during operation with the iron catalyst.

Catalyst attrition is a major problem in the operation of slurry phase FT reactors using iron-based catalysts (8, 9). During slurry phase FTS with bubble column reactors, catalysts are generally separated from accumulated reactor wax by either internal filtration or an external settling system which circulates catalyst back to the reactor. Catalyst fines produced by attrition may cause filters to plug and are difficult to separate by settling. The problem of attrition is even more pronounced when bench scale continuous stirred tank reactors (CSTR) are used. The impeller of the CSTR greatly increases the rate of attrition which makes it very difficult to test catalysts which produce a large amount of wax. Precipitated iron catalysts with low wax yields ($C_{12+} < 30$ wt%) have been operated in a CSTR for over 3000 hours in our laboratory. We have found that a $0.5\ \mu\text{m}$ sintered metal filter can remove accumulated reactor wax at a faster rate than it is produced despite catalyst attrition. On the contrary, high wax producing catalysts ($C_{12+} > 60$ wt%) usually cannot be run for longer than 200 to 500 hours (depending on catalyst loading) because the high rate of wax production overwhelms the filters if catalyst fines are present. We have also observed that cobalt catalysts supported on alumina can be operated for extended time even in a high wax producing mode. Scanning electron microscopy of these supported cobalt catalysts showed that attrition was minimal. As a result we decided to test the attrition of supported iron catalysts.

A logical route to the development of a robust FTS catalyst, that can be easily separated from reactor wax, is to employ an attrition resistant support. In general, supported iron catalysts have been considered to be inferior to precipitated iron

catalysts because of strong interactions between iron and the most commonly used supports: alumina and silica (1). To neutralize the acidity of silica and alumina, a large amount of alkali promoter (potassium) must be used to achieve reasonable alkene selectivity and low methane yield. Unfortunately a consequence of using a high level of potassium is that stability is generally poor (1). In addition, a loss of FTS activity may occur if iron reacts with the support to form an inactive species such as iron silicates or $\text{Fe}_x\text{Al}_{3-x}\text{O}_4$ mixed spinels. The reaction of alumina with iron can be prevented by using an aluminate as a support. Toledo et al. have studied the dehydrogenation of 1-butene with iron supported on zinc aluminate and with $\text{ZnFe}_x\text{Al}_{2-x}\text{O}_4$ mixed spinels (10). They found that the supported catalyst was the most active because iron was located in octahedral vacancies on the surface of the ZnAl_2O_4 support and did not migrate into the bulk of the support to form $\text{ZnFe}_x\text{Al}_{2-x}\text{O}_4$ species. As part of our effort to develop a robust FTS catalyst, we have prepared a series of catalysts containing 20 weight percent iron on silica, magnesium silicate, alumina and magnesium aluminate. Reported herein are the activity, selectivity and attrition properties of these catalysts used in the slurry phase FTS with a CSTR.

Experimental

Catalyst Preparation

Four supports were impregnated with $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and KNO_3 . The supports used were silica (Grace), alumina (Discovery Chemicals), magnesium silicate (Fisher) and magnesium aluminate. The silica, alumina and magnesium aluminate supports were screened to 60-325 mesh and the magnesium silicate was used as received, 60-100 mesh. Silica, alumina and magnesium silicate were activated at 600°C for 4 hours. Magnesium aluminate was prepared by coprecipitating Mg-Al

hydroxides from $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (1:2 molar ratio) followed by calcination at 400°C for 16 hours and 800°C for an additional 16 hours.

The typical impregnation procedure was as follows. The support (86 g) was heated to 100°C while $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (125 g), $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (3.96 g) and KNO_3 (3.61 g) were melted in an oil bath at 70°C. The melt was slowly added to the support with good mixing. The impregnated support was then calcined at 300°C for 2 hours. The impregnation and calcination procedures were repeated resulting in a catalyst with approximately 21-23 wt% Fe. X-ray diffraction showed the crystalline phase to be $\alpha\text{-Fe}_2\text{O}_3$ for all four catalysts (Figure 1). Nominal compositions and BET data for the supports and catalysts are shown in Table 3.

FTS conditions

Approximately 40 g of catalyst and 290 g of Ethylflo 164 oil (C_{30}) were loaded into one liter stirred autoclave reactors. The slurry was treated with hydrogen at 120 L h^{-1} (referenced to 0°C, 0.10 Mpa) at ambient pressure and the temperature was increased to 270°C at 120°C h^{-1} . Hydrogen reduction was carried out for 24 h and then the temperature was lowered to 250°C. The pressure was increased to 1.31 MPa and a catalyst sample was taken. Carbon monoxide flow was started and the hydrogen flow gradually decreased until the total flow rate was 3.1 SL $\text{h}^{-1}\text{g-Fe}^{-1}$ and the H_2/CO ratio was 0.7. Additional catalysts samples were withdrawn at ~100 h and at the end of the runs. Catalyst samples were Soxhlet extracted to remove accumulated wax and were analyzed by scanning electron microscopy (SEM).

Results and Discussion

Carbon monoxide conversion for each supported catalyst is shown in Figure 2. The 100Fe/6.0Cu/8.1K/250Al₂O₃ and 100Fe/6.0Cu/8.0K/260MgAl₂O₄ catalysts had the

highest conversions. Both went through a long induction period in which the conversion increased from ~40% to 60%. A reactor upset occurred during the 100Fe/6.0Cu/8.1K/250Al₂O₃ run in which the hydrogen flow was cut off for 2-8 hours; however, within 72 hours the conversion had recovered. The 100Fe/6.0Cu/8.1K/250SiO₂ and 100Fe/6.0Cu/8.1K/260MgO·7.5SiO₂ catalysts had maximum carbon monoxide conversions of 32% and 7%, respectively and had poor stability. Hydrocarbon production rates are compared to a precipitated iron catalyst containing similar potassium and copper (100Fe/3Cu/8K/5SiO₂) in Figures 3 and 4. The 100Fe/6.0Cu/8.1K/250Al₂O₃ and 100Fe/6.0Cu/8.0K/260MgAl₂O₄ catalysts both had maximum values >0.35 g h⁻¹g-Fe⁻¹ while the 100Fe/6.0Cu/8.1K/250SiO₂ and 100Fe/6.0Cu/8.1K/260MgOxSiO₂ catalysts were somewhat lower at 0.2 and 0.05 g h⁻¹g-Fe⁻¹, respectively. The low activity of the magnesium silicate supported catalyst is probably due to sulfur poisoning; elemental analysis of the magnesium silicate showed 0.3 weight percent sulfur. The precipitate 100Fe/3Cu/8K/5SiO₂ catalyst had a hydrocarbon production rate over 0.5 g h⁻¹g-Fe⁻¹, so the best supported catalyst had FTS activity roughly 75% that of the precipitated catalyst on a iron mass basis. In terms of catalyst mass (Figure 4), the precipitated catalyst was much more active than the supported catalysts.

The induction period seen with the alumina and magnesium aluminate supported catalysts is typical of catalysts that are not reduced adequately during the activation procedure. Thermogravimetric analysis of the four catalysts is shown in Figure 5. Reduction in hydrogen showed two steps corresponding to: (1) $\alpha\text{-Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4$ and (2) $\text{Fe}_3\text{O}_4 \rightarrow \text{Fe}$. The first step (278-329°C) was exothermic while the second (483-510°C) was slightly endothermic. The presence of magnesium lowered the first

reduction step temperature; however, no effect was seen on the second step. Both reduction steps occurred at lower temperature for silica supported catalysts than alumina supported catalysts. Based on these data an activation temperature higher than 270°C might improve the activity.

Methane, alkene and 1-alkene selectivities have been compared to the precipitated 100Fe/6Cu/8K/6SiO₂ catalyst. Methane selectivity (Figure 6) as a function of time on stream increased in the following order for the different supports: MgAl₂O₄ (<5%) < Al₂O₃ (5-6%) < SiO₂ (>8%) < MgO-3.75SiO₂ (9-15%); however, the best supported catalyst had significantly higher methane yield than precipitated catalyst (~3%). Alkene selectivity as a function of carbon number for the SiO₂, Al₂O₃ and MgAl₂O₄ supported catalysts is shown in Figure 7. Alkene selectivity was similar for all supported catalysts except the MgAl₂O₄ supported catalyst had much higher ethylene selectivity than all other catalysts. The ratio of 1-alkene to total alkene as a function of carbon number is shown in Figure 8. The SiO₂ supported catalyst produced slightly more internal alkenes than the Al₂O₃ and MgAl₂O₄ supported catalysts indicating that SiO₂ catalyzes alkene isomerization. The precipitated catalyst had higher alkene and 1-alkene selectivity than any of the supported catalysts and in general, the alkene and 1-alkene selectivity decreased with increasing carbon number much more rapidly for the supported catalysts than for the precipitated catalyst. Product distributions for the SiO₂, Al₂O₃ and MgAl₂O₄ supported catalysts are compared to the precipitated catalyst in Table 4. In general, the supported catalysts produced a lighter product than the precipitated catalyst. The C₁₂+ selectivity decreased in the order: precipitated (65 wt.%) > MgAl₂O₄ (54%) > Al₂O₃ (42%) > SiO₂ (34%). Overall, the selectivity and activity of the MgAl₂O₄ supported catalyst is the most similar to the precipitated catalysts.

The main purpose for running these catalysts was to develop a catalyst resistant to attrition in a continuous stirred tank reactor. Scanning electron micrographs of the four supported catalysts before FTS and after FTS are shown in Figures 9 and 10. All catalysts had particle sizes ranging from 250 to 60 μm before FTS. The MgO-3.75SiO_2 supported catalyst showed no signs of attrition; particle size and shape were the same before and after FTS. The SiO_2 supported catalyst showed little signs of attrition; the particle size remained unchanged; however, the sharp edges of the particles evident before FTS were smoothed by the end of FTS. The Al_2O_3 and MgAl_2O_4 supported catalysts were not as attrition resistant as the SiO_2 and MgO-3.75SiO_2 supported catalysts; both catalysts had fractured into smaller particles. After 312 hours of FTS the Al_2O_3 supported catalyst consisted of particles between 30 and 100 μm . The MgAl_2O_4 supported catalyst broke up into less than 30 μm particles after 264 hours of FTS; however, this attrition is not nearly as severe as encountered with precipitated iron catalysts. Despite the attrition seen with the MgAl_2O_4 supported catalyst, wax-catalyst separation was still possible.

It is clear from these data that alumina and MgAl_2O_4 supported catalysts have superior activity and selectivity than SiO_2 and MgO-3.75SiO_2 supported catalysts. The best activity and selectivity was obtained with the MgAl_2O_4 supported catalyst; however, it was substantially inferior to a comparably promoted precipitated iron catalyst. All of the supported catalysts studied showed much better attrition characteristics than precipitated iron catalysts; the SiO_2 and MgO-3.75SiO_2 supported catalysts showed very little attrition even in the harsh environment of a CSTR.

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Table 1
Densities of Iron Oxides and Carbides which may be Present During Activation and Fischer-Tropsch Synthesis

Compound	Density	Vol/g	Equivalent Vol/g Fe
FeO ^a	5.97 g/cm ³	0.1675 cm ³ /g	0.2155 cm ³ /g Fe
α -Fe ₂ O ₃ ^b	5.27 g/cm ³	0.1898 cm ³ /g	0.2714 cm ³ /g Fe
Fe ₃ O ₄ ^c	5.20 g/cm ³	0.1923 cm ³ /g	0.2658 cm ³ /g Fe
Fe ₃ C ^d	7.684 g/cm ³	0.1302 cm ³ /g	0.1395 cm ³ /g Fe
Fe ₅ C ₂ ^e	7.672 g/cm ³	0.1303 cm ³ /g	0.1416 cm ³ /g Fe

- a. X-ray diffraction data (39-1088).
b. *Natl. Bur. Std. Monogr.*, **25**, 1837 (1981).
c. *Natl. Bur. Std. Monogr.*, **25**, 531 (1967).
d. *Natl. Bur. Std. Monogr.*, **25**, 2172 (1985).
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Table 2 Oxidation Reduction Steps which may Occur During Activation and Subsequent Oxidation of Iron Fischer-Tropsch Catalysts		
Compound	Volume, cm ³ /g Fe	Volume Change, cm ³ /g Fe (%)
Fe ₂ O ₃	0.2714	
↓	↓	
Fe ₃ O ₄	0.2658	+0.0056 (-2.06%)
↓	↓	
FeO	0.2155	-0.0503 (-18.9%)
↓	↓	
Fe ₃ C	0.1395	-0.0076 (-35.3%)
↓	↓	
Fe ₃ O ₄	0.2658	+0.1263 (+90.5%)
Fe ₅ C ₂	0.1416	-0.0739 (-34.3%)
↓	↓	
Fe ₃ O ₄	0.2658	+0.1242 (+87.7%)

Table 3 BET Surface Area and Pore Volume Data for SiO_2 , $\text{MgO} \cdot 3.75\text{SiO}_2$, Al_2O_3 and MgAl_2O_4 Supports and 100Fe/6.0Cu/8.1K/260MgAl ₂ O ₄ , 100Fe/6.0Cu/8.1K/250Al ₂ O ₃ , 100Fe/6.0Cu/8.1K/260MgO•3.75SiO ₂ and 100Fe/6.0Cu/8.1K/250SiO ₂ Catalysts		
	surface area (m ² g ⁻¹)	pore volume (cm ³ g ⁻¹)
silica	284	1.15
magnesium silicate	231	0.54
alumina	196	0.43
magnesium aluminate	71	0.37
100Fe/6.0Cu/8.1K/250SiO ₂	127	0.53
100Fe/6.0Cu/8.1K/260MgO•xSiO ₂	57	0.22
100Fe/6.0Cu/8.1K/250Al ₂ O ₃	78	0.19
100Fe/6.0Cu/8.1K/260MgAl ₂ O ₄	43	0.16

Table 4 Comparison of FT Activity and Selectivity of Supported Iron Catalysts and Similarly Promoted Precipitated Iron Catalyst				
	Supported Catalysts (100Fe/6Cu/8K/250support)			Precipitated
	SiO ₂	Al ₂ O ₃	MgAl ₂ O ₄	100Fe/3Cu/8K/5SiO ₂
Co conversion (mol%)	25	61	62	88
Hydrocarbon rate (g h ⁻¹ g-Fe ⁻¹)	0.17	0.36	0.37	0.51
Water-gas shift $RQ = \frac{[CO_2][H_2]}{[CO][H_2O]}$	3	13	18	25
CO ₂ selectivity (C%)	43	48	48	49
H ₂ /CO usage ratio	0.66	0.54	0.54	0.58
Hydrocarbon selectivity (wt.%)				
C ₁	9.0	6.0	4.4	3.6
C ₂ -C ₄ (alkene)	21 (73)	18 (73)	13 (79)	12 (82)
C ₅ -C ₁₁ (alkene)	36 (72)	34 (69)	28 (69)	19 (81)
C ₁₂ ⁺	34	42	54	65

Figure 1. X-ray diffractograms of calcined (a) 100Fe/6.0Cu/8.1K/260MgAl₂O₄, (b) 100Fe/6.0Cu/8.1K/250Al₂O₃, (c) 100Fe/6.0Cu/8.1K/260MgO·3.75SiO₂ and (d) 100Fe/6.0Cu/8.1K/250SiO₂.

Figure 2. Carbon monoxide conversion as a function of time on stream for (○) 100Fe/6.0Cu/8.1K/250SiO₂, (□) 100Fe/6.0Cu/8.1K/260MgO·3.75SiO₂, (◇) 100Fe/6.0Cu/8.1K/250Al₂O₃ and (Δ) 100Fe/6.0Cu/8.1K/260MgAl₂O₄.

Figure 3. Hydrocarbon production rate on an iron mass basis as a function of time on stream for (○) 100Fe/6.0Cu/8.1K/250SiO₂, (□) 100Fe/6.0Cu/8.1K/260MgO·3.75SiO₂, (◇) 100Fe/6.0Cu/8.1K/250Al₂O₃ (Δ) 100Fe/6.0Cu/8.1K/260MgAl₂O₄ and (●) precipitated 100Fe/6Cu/8K/6SiO₂.

Figure 4. Hydrocarbon production rate on a catalyst mass basis as a function of time on stream for (○) 100Fe/6.0Cu/8.1K/250SiO₂, (□) 100Fe/6.0Cu/8.1K/260MgO·3.75SiO₂, (◇) 100Fe/6.0Cu/8.1K/250Al₂O₃ (Δ) 100Fe/6.0Cu/8.1K/260MgAl₂O₄ and (●) precipitated 100Fe/6Cu/8K/6SiO₂.

Figure 5. Thermogravimetric analysis with hydrogen of (.....) 100Fe/6.0Cu/8.1K/250SiO₂, (—) 100Fe/6.0Cu/8.1K/260MgO·3.75SiO₂, (-----) 100Fe/6.0Cu/8.1K/250Al₂O₃ (— — —) 100Fe/6.0Cu/8.1K/260MgAl₂O₄.

Figure 6. Methane selectivity on an atomic basis of carbon converted to hydrocarbon. (○) 100Fe/6.0Cu/8.1K/250SiO₂, (□) 100Fe/6.0Cu/8.1K/260MgO·3.75SiO₂, (◇) 100Fe/6.0Cu/8.1K/250Al₂O₃ (Δ) 100Fe/6.0Cu/8.1K/260MgAl₂O₄ and (●) precipitated 100Fe/6Cu/8K/6SiO₂.

Figure 7. Alkene selectivity as a function of carbon number for (○) 100Fe/6.0Cu/8.1K/250SiO₂, (◇) 100Fe/6.0Cu/8.1K/250Al₂O₃ (Δ) 100Fe/6.0Cu/8.1K/260MgAl₂O₄ and (●) precipitated 100Fe/6Cu/8K/6SiO₂.

Figure 8. 1-alkene selectivity as a function of carbon number for (○) 100Fe/6.0Cu/8.1K/250SiO₂, (◇) 100Fe/6.0Cu/8.1K/250Al₂O₃ (Δ) 100Fe/6.0Cu/8.1K/260MgAl₂O₄ and (●) precipitated 100Fe/6Cu/8K/6SiO₂.

100Fe/6Cu/8K/250SiO₂

Fresh, untreated catalyst

100Fe/6Cu/8K/260(MgO·3.75SiO₂)

Fresh, untreated catalyst

Figure 9. Scanning electron micrographs of the 100Fe/6.0Cu/8.1K/250SiO₂ and 100Fe/6.0Cu/8.1K/260MgO·3.75SiO₂ catalysts before and after FTS.

100Fe/6Cu/8K/250Al₂O₃

Fresh, untreated catalyst

100Fe/6Cu/8K/260MgAl₂O₄

Fresh, untreated catalyst

Figure 10. Scanning electron micrographs of the 100Fe/6.0Cu/8.1K/250Al₂O₃ and 100Fe/6.0Cu/8.1K/260MgAl₂O₄ catalysts before and after FTS.

3.1.6 Additional Research

3.1.6.1 Define Attrition Resistance

The powder sample of RJO-181 (30 wt.% $\text{Fe}_2\text{O}_3/\text{SiO}_2$) was used for microhardness test. Cold molds using epoxy hardeners were used to prepare the specimens. After imbedding the particles in the epoxy, they were allowed to harden. Then the epoxy molds were polished. Several particles were photographed in the optical microscope. Using a MICROMET-4 hardness tester, the microhardness measurements were made. The specimen was mounted onto the hardness tester, and a load of 25 gm was used to make the Vicker's indentation on the particles, which are 10 to 50 microns in size. The indentations were so large that they covered the entire particles. Hence, a load of 10 gm (the minimum load available) was used to make the indentations on several individual particles embedded in the epoxy mold. After making the indentations the specimen was mounted on the optical microscope and the diagonal distances of the indentations were measured. The average value of about 50 indentations was taken for measuring the Vicker's hardness, which was calculated to be 40 kg/mm^2 . According to the ASTM standards, this number indicates that the material under investigation is very soft. The value of 40 is not accurate, as the hard epoxy under the particles can also take part of the load. This introduces additional uncertainty to the calculated value. For comparison, the hardness values for several materials are plotted in Figure 1. It can therefore be concluded that the iron oxide catalyst particles are very soft.

HARDNESS **kpsi**

Figure 1. A comparison of the hardness of a Fe₂O₃/SiO₂ catalyst to other materials.

3.1.6.2 Effect of Carbon Deposition

Iron catalysts that have high FTS activity contain bulk iron carbide and large amounts of excess carbon. Pretreatment of the 100Fe/3.6Si/0.71K catalyst with CO at 270°C and 13 atm for 24 hr yields a highly active catalyst and yet produces about twice as much carbon as needed for the formation of Fe_5C_2 . It is of interest to determine the role of this carbon in the FTS and determine its morphology.

The 100Fe/3.6Si/0.71K catalyst was subjected to syngas ($\text{H}_2/\text{CO}=0.7$) activation at 270°C and 13 atm. After 93 hr of synthesis, during which the CO conversion never rose above 12%, H_2 flow was stopped and the catalyst was treated with CO for 22 h. Following the CO treatment the synthesis was restarted. As can be seen in Figure 1, the CO conversion rose very rapidly and reached the same level as when the catalyst is initially activated with CO. X-ray diffraction analysis of catalyst samples withdrawn before and after treating the catalyst with CO show that syngas activation converted the catalyst to Fe_3O_4 and the CO treatment partially reduced the Fe_3O_4 to $\chi\text{-Fe}_5\text{C}_2$ and $\epsilon'\text{-Fe}_{2.2}\text{C}$. Mössbauer spectroscopy results showing the phase transformation is shown in Figure 2. Catalyst samples from this run were submitted to Sandia for high-resolution TEM analysis. High resolution TEM of this catalyst series offers the possibility of showing the location of the iron carbide in relation to the Fe_3O_4 and the structure of the free carbon which forms from CO activation.

Figure 1. Comparison of the CO conversion vs. Time-on-stream for the 100Fe/3.6Si/0.71K catalyst. □- activated with CO at 270°C, 13 atm for 24 hr and ○- activated with $H_2/CO = 0.7$ at 270°C and 13 atm followed by a 22 hr treatment with CO at 270°C and 13 atm. Synthesis conditions: $H_2/CO = 0.7$ at 13 atm and 270°C.

Figure 2. Mössbauer spectroscopy results for the 100Fe/3.6Si/0.71K catalyst activated with $H_2/CO = 0.7$ at 270°C and 13 atm followed by a 22 hr treatment with CO at 270°C and 13 atm. Synthesis conditions: $H_2/CO = 0.7$ at 13 atm and 270°C. ○- superparamagnetic phase, □- Fe_3O_4 and ◇- iron carbide.

3.2.0 Task 3. Catalyst Structure and Characterization

3.2.1 Fischer-Tropsch Iron Catalysts: Characterization by Electron

Microscopy

INTRODUCTION

The Fischer-Tropsch conversion process for producing hydrocarbons from synthesis gas using iron oxide catalysts is well known.¹ In this process synthesis gas (mixture of CO and H₂) is converted over various catalysts to yield a range of hydrocarbon products, which may be refined into synthetic fuels. Catalysts such as iron, cobalt, ruthenium and nickel in their oxide forms, are commonly used for this FT process. Different catalysts yield different product distributions under similar reaction conditions. Schultz *et al.*² hypothesized that Fe₃O₄ (magnetite form) has no synthesis activity and the degree of oxidation of iron to magnetite has limitations on the maximum activity of the catalyst. However, Dwyer *et al.*³ showed that higher yields could be obtained over the preoxidized iron foils than the reduced iron foils.

When the iron oxide catalysts are used for the Fischer-Tropsch synthesis, several forms of iron oxides and iron carbides are formed.⁴⁻⁷ These include iron oxides (hematite and magnetite) and iron carbides, which are known to exist in five or six different forms, namely, ϵ -Fe₂C, ϵ' -Fe_{2.2}C, χ -Fe_{2.5}C, Fe₃C, FeC, Fe₇C₃, etc. The fact that how these phases are formed and at what stage of the reaction pathway, is still subject to debate. Both the formation of these phases during reaction conditions, and their relationship to the activity/selectivity of the catalysts are interesting phenomena. In this investigation, we have attempted to determine the phases formed in a typical iron oxide catalyst prepared in-house through a precipitation process, using X-ray diffraction and high resolution electron microscopy.

EXPERIMENTAL

Iron oxide catalysts were prepared by a precipitation process containing 4.4 wt.% SiO_2 and 3.6% K_2O (balance Fe_2O_3). SiO_2 and K_2O were added as promoters. This catalyst was subjected to Fischer-Tropsch synthesis in a slurry phase reactor, and the samples were withdrawn at different time intervals.

An appropriate amount of catalyst was mixed with C_3 oil to obtain a 10% slurry in a slurry phase reactor. Then this slurry was pretreated in flowing carbon monoxide at 270°C for about 27 hours at atmospheric pressure in order to activate the catalyst. After activation, a portion of the slurry sample was withdrawn from the reactor through a dip-tube. Catalyst sample was separated from the slurry (oil) by Soxhlet extraction using THF.

After this step, the pressure in the reactor was raised to 75 psig and the passage of synthesis gases was returned to carry out the reaction in the slurry phase. While the reaction was in progress, product gases were analyzed to estimate the conversion levels with time.

Catalyst samples in slurry were withdrawn at regular intervals with the dip-tube. The samples thus withdrawn were imbedded in wax. Catalyst particles were separated from the wax using o-xylene as solvent in a Soxhlet extraction unit. The catalyst separated and cleaned from the wax was then used for characterization studies.

Transmission Electron Microscopy

Several samples were selected for electron microscopy work. For this, a Hitachi HF2000, equipped with a field emission gun, analytical electron microscope was used. The operating voltage was 200 kV. The field emission gun employs a single crystal emitter with a very fine point that generates a beam with 100-1000 times the brightness

of the standard thermionic emitter with a much finer ultimate diameter. The field emission electron beam has a much lower energy spread (i.e., higher coherency) than the thermionic emitter beam, thus allowing us to obtain improved high resolution imaging. The microscope has an image resolution of 0.24 nm point-to-point in a standard imaging mode. The microscope was also equipped with a windowless X-ray detector (PGT) thus allowing us to obtain X-ray analysis from regions as small as 1 nm in diameter.

Also, a JEOL 4000EX, a high resolution electron microscope was used at 400 kV. The 0.17 nm point-to-point resolution of this microscope allows us to obtain lattice images from the crystalline particles.

Scanning Electron Microscopy

Scanning electron microscopy was carried out at 20 kV using a Hitachi S-2700 scanning electron microscope, equipped with a LaB₆ filament and a thin window X-ray PGT detector for elemental analysis. All the powder samples were coated with a conductive layer of gold prior to analysis.

X-ray Diffraction

A Rigaku X-ray diffractometer was used at 40 kV, 20 mA (CuK α radiation) with a pyrolytic graphite monochromator in the diffracted beam path. Data were collected using a step width of 0.02° with a count time of 5 sec/step.

RESULTS AND DISCUSSION

RJO-137B

The first sample analyzed was the sample just after CO pretreatment for about 27 hours and prior to the introduction of synthesis gas. This sample has a surface area of about 120 m²/g with a pore volume of 0.22 cc/g. The surface area and pore volume

data for the catalysts analyzed are given in Table 1. The X-ray diffraction showed that this sample is in Fe_3O_4 form. The X-ray diffraction patterns of the samples, shown in Figure 1, clearly depict all the Fe_3O_4 reflections. The JEPDS File #19-629 was overlaid in this figure to indicate the positions of Fe_3O_4 cubic reflections.

Lattice fringe images from two particles obtained from this sample are presented in Figure 2. The particle at the top shows 2.97 Å lattice fringes which correspond to Fe_3O_4 [220] lattice spacings. The particle at the bottom (Figure 2) depicts 4.85 Å lattice fringes corresponding to [111] planes of Fe_3O_4 . Note that these particles do not have any surrounding films. However, the particle shown in Figure 3, has a film of about 4.2 nm width. The graphitic carbon film has a lattice spacing of ~3.4 Å, which corresponds to [002] lattices of graphitic carbon. EDS patterns using a 10 Å probe were obtained from both the surrounding film and from the center of the particle. These are shown in Figure 4. The spectra give additional evidence that the surrounding film is graphitic carbon.

RJO-137D

This sample was withdrawn from the reactor after 28 hours-on-stream. The X-ray diffraction pattern from this sample shown in Figure 1(b), indicates that this sample after 28 hours on stream mostly consists of Fe_3O_4 . An Fe_3O_4 particle with a surrounding graphitic film is shown in Figure 5(a). EDS data obtained from the film showed only carbon and the data obtained from the center showed more Fe and O, and trace amounts of Al. This Al comes from both the film as well as from the center (see Figure 6), and may be an impurity. The beam damage of the specimen can be seen in Figure 5(b), where the irradiation of electron beam caused a hole of about 2.5 nm in diameter.

A typical particle with lattice fringes with its corresponding fourier transform are shown in Figure 7. The FFT can be indexed as diffraction pattern⁸ and enables us to analyze the crystal structure of the particle in question. In Figure 7 the FFT obtained from an area of 256 x 256 pixels in the micrograph is in quite agreement with the diffraction pattern of Fe_3O_4 particle oriented in [211] direction with respect to the beam.

Several efforts made so far to get in the structural information from the fine structure of very small particles from electron diffraction patterns have indicated that there are still some difficulties.⁹ For very thin specimens, Cowley¹⁰ proved that the electron wave may be considered to travel straight through the specimen undergoing only a phase change proportional to the electrostatic potential in the specimen. The recent developments of electron optics and acquisition of images using CCD cameras make it easy to identify the fine structures of ultrafine particles¹¹⁻²⁰. It has been proven that the optical diffraction patterns and Fast Fourier Transform (FFT) patterns of a micrograph of atomic resolution taken under optimum conditions are equivalent to the selected area electron diffraction patterns. Even when the specimen is not very thin and dynamic scattering cannot be disregarded, the diffraction spots formed by the FFT represent the spacing of the lattice plane.²⁰

RJO-137H

This sample was withdrawn after 124 hours-on-stream. The XRD pattern from this sample is presented in Figure 1(c) and exhibits all peaks corresponding to Fe_3O_4 (magnetite) phase. An Fe_3O_4 particle with a surrounding film of graphitic carbon is shown in Figure 8. In addition to this, particles of rectangular shape were observed. Typical rectangular shaped particles are presented in Figure 9. EDS pattern obtained

from one of these rectangular particles (Figure 10) exhibits Fe, Al, O. Note that the rectangular particles could not be seen for the previous samples.

RJO-137M

This sample was withdrawn from the reactor after 461 hours-on-stream. The catalyst still showed about 90% conversion of the reactants. The XRD pattern obtained from this sample is presented in Figure 1(d) and shows some iron carbide peaks. Since the strongest carbide peaks and an Fe_3O_4 (400) peak fall in the region of $2\theta = 40-46$, this region is shown magnified in Figure 11. In this figure the peaks are fitted to Voigt function with the coefficient determination (r^2) above 0.9. In all the XRD traces given in Figure 11, the observed Fe_3O_4 (400) reflection is displaced from the JCPDS file, probably due to the presence of silica and potassium in the sample. The addition of silica to Fe_3O_4 has been found to alter the lattice parameters and this correspondingly causes a shift in 2θ positions. However, in the trace of RJO-137M sample (Figure 11) the appearance of two additional peaks to the left of Fe_3O_4 (400) reflection corresponding to ϵ' -carbide can be seen. These two peaks are evidently absent in the first three samples.

A scanning electron micrograph from this sample presented in Figure 12 indicates that this sample consists of spherical agglomerates of 30-50 μm diameter. A high resolution electron micrograph from this sample is presented in Figure 12 wherein the lattice fringes of [111], [220] and [311] planes can be seen. Several long rectangular particles were also observed which were Fe_3O_4 from lattice fringe measurement.

The XRD pattern for the last sample presents evidence for the presence of trace amounts of carbide. Since this carbide may be in so small a quantity, the TEM examination could not observe carbide particles.

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Table 1			
Catalyst	Pore Diameter, Å	Pore Volume, cm ³ /g	Surface Area (m ² /g)
RJO-137B	140	0.25	70
RJO-137D	170	0.32	77
RJO-137H	250	0.48	77
RJO-137M	200	0.43	87

Figure 1. X-ray diffraction patterns from the catalysts (a) RJO-137B, (b) RJO-137D, (c) RJO-137H and (d) RJO-137M.

Figure 2. Lattice fringe images from 2.97 Å and 4.85 Å lattices corresponding to [220] and [111] planes of Fe_3O_4 .

Figure 3. A Fe_3O_4 particle with a film of graphitic carbon. The film thickness is about 42 Å.

Figure 4. EDS pattern using a 1 nm probe from (a) the film and (b) the center of the particle.

Figure 5. (a) A particle with graphitic carbon film. (b) Same particle after irradiation of 1 nm probe beam for 75 sec. Beam damage of the specimen can be seen.

Figure 6. EDS pattern obtained from (a) the outer film and (b) the center of the particle.

Figure 7. (a) Lattice fringe image from an Fe_3O_4 particle, (b) corresponding FFT pattern showing the Fe_3O_4 zone axis [211].

Figure 8. Fe_3O_4 particle with graphitic carbon film of 35 Å width.

Figure 9. Typical rectangular particles from the sample RJO-137H.

Figure 10. EDS pattern from a rectangular particle.

Figure 11. XRD patterns of a series of catalysts withdrawn from the CSTR reactor.

Figure 12. Scanning electron micrograph of RJO-130M showing spherical agglomerates of 30-50 μm diameter.

3.2.2 Fischer-Tropsch Synthesis. Electron Microdiffraction Study of Ultrafine Iron

Oxide Catalysts

ABSTRACT

An ultrafine (3.0 mm, 300 m²/g) iron oxide sample has been activated in carbon monoxide and then utilized for the conversion of syngas ($H_2/CO = 0.7$) at 270°C and 170 psig (1.17 MPa). The sample, after activation for 24 hrs. in CO and exposure for 2 hrs. to syngas, was shown from TEM microdiffraction data to be composed primarily of iron carbides (mainly Fe_3C). As exposure to syngas continued, carbide particles were converted to Fe_3O_4 and $Fe_{2.2}C$ phases. The iron oxide and iron carbide phases appear to have a similar particle size distribution. The TEM data for identification of iron phases (carbide and oxide) agree with earlier Mössbauer characterization data.

INTRODUCTION

Iron-based catalysts are widely utilized for the Fischer-Tropsch Synthesis (FTS) (1). It has unique properties compared to other potential catalysts; these include activity for the water-gas-shift reaction and the potential to form a stable carbide under synthesis conditions (2). During activation and synthesis, the gas composition in contact with the catalyst has the potential to exhibit either reducing or oxidizing properties. Thus, a variety of iron oxide/carbide phases may be encountered during the activation/synthesis process.

For example, starting with metallic iron, formed by the reduction of an oxide precursor, a mixture of α -Fe, iron carbides and Fe_3O_4 may be present during synthesis (3). Furthermore, the composition may change during synthesis (3). On the other hand, only iron carbide phases may form under other conditions of activation; a fraction of these iron carbide phases may undergo conversion to Fe_3O_4 during synthesis (4).

In addition to the formation of iron carbide, excess carbon may be deposited during the activation procedure. The data from reference 5, plotted in Figure 1, provide an illustration of the relationship between the amount of excess carbon (free carbon, the carbon in excess of that liberated by dissolving iron carbide in acid). In this example, the extent of excess carbon was defined by controlling the activation temperature. The impact of the free carbon on the operation of the catalyst is defined, in this case, as the number of days that the catalyst exhibits greater than 80% CO conversion. The activity, based on this definition, exhibits a maximum in the region where the amount of free carbon is at its maximum value.

Huang et al. (4,6) found only Fe_3O_4 by XRD analysis at the point of maximum activity. However, when syngas was utilized for pretreatment, only Fe_3O_4 was detected and the catalyst exhibited low activity. Huang et al. (4,6) therefore assumed that an iron carbide phase must be present on the surface of an active catalyst and this surface phase is responsible for the catalytic activity.

The composition of the gases used during the pretreatment and/or reaction conditions with an iron catalyst can play a major role in the chemical composition and the phases of the compound present in the catalytic material (7). In some reactors, the catalyst may actually be present in several forms at any given time. For example, in a plug flow reactor the catalyst at the front (top) of the reactor is exposed to a reducing atmosphere whereas the catalyst at the back (bottom) of the reactor will experience an oxidizing atmosphere for operations at high conversion (8). Likewise, the gas composition and temperature of pretreatment may play an important role in the iron compounds that are present. For example, for a reduced catalyst, slight changes in the

H₂/CO ratio and the temperature used for pretreatment can lead to either Häag carbide or cementite (Fe₃C) (9).

Schroff et al. (10) have recently presented data for the activation of a precipitated iron oxide catalyst. These authors indicate that the activity correlates well with the extent of conversion of the iron oxide(s) into the carbide phase. They also report that an amorphous carbon film forms on the carbide particles during synthesis. Amorphous or even graphite-like phases of carbon may be present on small metal particles that have not been exposed to synthesis gas and/or conditions (11,12). Thus, a carbon overlayer appears to be a common feature of these metal carbide systems. The large iron oxide crystals that make up the catalyst utilized by Shroff et al. (10) indicate that it should not be considered as a typical high surface area precipitated iron oxide catalyst.

In the study by Shroff et al. (10) the assignment of the iron oxide/carbide phases depend upon lattice spacing measurements; this was true for both XRD and electron microscopic evidence. The lattice parameter data for several expected iron carbide phases and Fe₃O₄ are given in Table 1. These lattice parameters were obtained from JCPDS (Joint Committee on Powder Diffraction Standards) powder diffraction files and these file numbers are also given in Table 1. In Figure 2, only the region of Fe₃O₄ (400) profile is highlighted. The d-spacings for the (400) phase is 2.099 Å. The d-spacings given in reference (10) for magnetite and Fe_xC phases are given in Table 2. The (400) planes of Fe₃O₄ (magnetite) are separated by 2.099 Å. The percent error in the observation of Fe₃O₄ (311) planes (Table 2), varies from -5.2% to +0.434%. Applying a nominal ± 5% error to the measurements for the (400) planes of Fe₃O₄ would place it in the range of 1.994-2.204 Å, also shown in Figure 2. Hence, the observation of 2.0, 2.2,

2.05 or 2.17 Å lattices might equally as well been assigned to Fe_3O_4 as to the carbide phases. While the 2.1 Å region was used for this illustration, similar considerations apply for most other regions of possible lattice spacings.

Furthermore, it was claimed that the Fe_3O_4 [400] planes are overlapped by the peaks of carbides in XRD patterns (Figures 4, 5 and 6 in reference 10). In Figure 2, it can be seen that the Δd between the Fe_3O_4 [400] planes and the ϵ' - $\text{Fe}_{2.2}\text{C}$ [101] planes is only 0.037 Å. Assignment of Fe_xC phases to the planes reported in reference 10 with d-spacings that are so similar must be viewed with caution.

In the present investigation, the Fe_2O_3 catalyst consisted of ultrafine particles (≤ 3 nm; 300 m²/g surface area). Samples of the catalyst were withdrawn at intervals during activation and the initial synthesis period. The structural characterization was carried out using electron microdiffraction technique, since this technique is suitable for obtaining structural information from small individual particles. Furthermore, the Fe_3O_4 and iron carbide phases can be distinguished using this technique because of the different crystal structures of these materials (Table 1).

EXPERIMENTAL METHODS

Two grams of Fe_2O_3 (Mach, Inc.) were loaded into a continuous stirred tank reactor (CSTR) using tetralin as the solvent. Then carbon monoxide at 100 psig was passed through the reactor which was heated to 260°C during one hour and was held at 260°C for the remainder of 24 hours. A mixture of $\text{CO}/\text{H}_2 = 1$ at 100 psig was then passed through the reactor and slurry samples were withdrawn through a tube that extended below the liquid level at 2, 10, 24, 36, 48 and 72 hours of exposure to CO/H_2 synthesis gas. Thus, the hours given refer to the length of time the sample was exposed to synthesis gas following a 24 hour pretreatment with CO.

Preparation of a sample for TEM analysis involved adding a few drops of the suspension of catalyst in tetralin plus reactor wax to ethanol and then placing the sample in an ultrasonic bath to develop a fine dispersion. A drop of the final suspension was placed on a carbon coated 200 mesh copper grid. After the ethanol evaporated, a thin layer of particles remained on the carbon film that is suitable for examination in the electron microscope.

Prior to the introduction of the Scanning Transmission Electron Microscope (STEM) technique, the lens configuration used for diffraction studies was limited by the spherical aberration of the objective lens, and this allows diffraction patterns to be obtained only from regions larger than 500nm. This limitation can be bypassed by means of microdiffraction, which has the advantage of forming diffraction patterns from regions as small as 2nm. Microdiffraction provides the means to reduce the total diffraction-forming volume and, in turn, increases the contribution from the very small regions (as small as 2nm) of interest. The result is a diffraction pattern with an improved signal-to-noise ratio. The instrument used for this study provides means to obtain diffraction patterns from regions of 2nm, 5nm and 10nm in diameter. Thus, this technique is especially suitable for obtaining diffraction patterns from individual particles of these sizes.

TEM examination was performed using a Hitachi H800 NA microscope at an operating voltage of 200 kV. Microdiffraction and EDX analysis were carried out in the nanoprobe mode, using an incident beam of 2 nm or 5 nm in diameter. This microscope is equipped with a silicon-lithium diode X-ray detector (Link Analytical Limited) and a multi-channel analyzer (Tracor 500). The X-rays emitted from the

specimen upon electron irradiation were collected in the range 0.1 - 20 keV for 60 seconds.

RESULTS

The vendor identified the as-received sample as $\gamma\text{-Fe}_2\text{O}_3$ based on electron diffraction pattern. A typical electron micrograph from this as-received powder is shown in Figure 3. The electron microdiffraction pattern, obtained from a 5 nm region, in the inset of Figure 3 exhibits only two diffuse rings. $\gamma\text{-Fe}_2\text{O}_3$ has a simple cubic structure; hence, reflections from all the planes are possible. The distance from the center to the rings or to the diffraction spots is indicative of the lattice spacing of particular [hkl] planes. Diffraction rings appear for polycrystalline materials as well but these would be sharp and distinct with the continuous array of reciprocal-lattice points which are concentric spheres in reciprocal space indicating random orientation. However, these rings will be diffuse and not sharp for amorphous materials where a lack of crystal structure is evident, or for materials containing nanosized ultrafine particles. The diffuseness and variations in intensity profiles result from inelastic scattering phenomena.

The ratio of the distances, d , from the center to the midpoint of each of the two consecutive rings in Figure 3 is 1.625. This could correspond to $d_1/d_2 = 2.52/1.55 = 1.6258$ as $d_{311} = 2.52 \text{ \AA}$ and $d_{520} = 1.55 \text{ \AA}$. This indicates that the first diffuse ring could be due to the [311] planes of the simple cubic structure of $\gamma\text{-Fe}_2\text{O}_3$, while the second ring would be due to the [520] planes. The intensity calculations show that the [311] planes have the highest intensity while the [520] planes have intensity $< 1\%$ relative to the [311] plane. Hence, it is unlikely that the second ring is from the [520] planes. Therefore, based on this electron microdiffraction pattern, we believe that this ultrafine

material may be considered to be amorphous as far as either electron or X-ray diffraction is concerned.

An electron micrograph was obtained for the two hour sample and the particle size distribution histograms obtained from measuring hundreds of particles of each of the catalyst samples are shown in Figure 4. It can be discerned that the major fraction of particles for the 2 hour sample are in the neighborhood of 5 nm in size. As the particles were extremely small, an electron probe of 2nm in diameter was used for obtaining microdiffraction patterns. A typical microdiffraction pattern obtained from an individual particle shows that this particle is body centered orthorhombic Fe_3C phase which is oriented in the [110] direction with respect to the incident beam. The microdiffraction pattern shows that this particle is body centered orthorhombic Fe_3C phase which is oriented in the [110] direction with respect to the incident beam. Microdiffraction patterns obtained from other particles also exhibited patterns for the Fe_3C phase. However, these fine particles consist of a very limited number of planes which results in a limited number of diffraction spots in the diffraction pattern.

For each sample, the sizes of 100-200 particles from different regions of the samples were measured and the particle size distributions for each sample are given in Figure 5. The major fraction of the particle size distributions (peak distribution) are plotted against time in Figure 6 and the particle sizes appear to follow an S-shape growth pattern; however, this conclusion of an S-shaped pattern is based only on the size of the 72 hour sample. If the 72 hour sample is ignored, the growth is then one of a rapid initial growth followed by a period of constant particle size. The limited amount of catalyst that could be handled in the reactor limited the number of samples that could

be collected during the experiment; hence, more data would be required to decide which growth pattern is followed.

A bright field image was obtained from the ten hour sample and two types of particles can be seen for this sample (Figure 7). One kind of particles appears transparent (lighter) and another kind appears to be black and dense. Tilting the specimen by about 4° , did not change or modify the image of the light and dark particles. Even after tilting the specimen, the light and dark particles retained the same shape and contrast. Hence, attempts were made to distinguish between these two types of particles using the microdiffraction technique. Several microdiffraction patterns using a 5 nm probe were obtained from both types of particles in this sample. As the particles are larger, a greater number of diffraction spots were obtained than was the case for the 2 hour sample. The diffraction patterns obtained from the dark, dense particles show that these particles are carbide phases (Fe_3C or $\text{Fe}_{2.2}\text{C}$). A typical microdiffraction pattern obtained from a dark particle of Fe_3C is presented in Figure 8(a). On the other hand, the lighter particles exhibit the pattern expected for the Fe_3O_4 phase (magnetite); a typical microdiffraction pattern obtained from a single transparent particle is presented in Figure 8(b). Also a few dark particles exhibit the $\text{Fe}_{2.2}\text{C}$ phase; a typical microdiffraction pattern from one of these particles is presented in Figure 8(c). Microdiffraction patterns obtained from about 25-30 particles consistently showed that the dark particles were a crystalline iron carbide phase and the light particles were of the Fe_3O_4 phase.

The iron carbides have different phases with corresponding lattice parameters from those of Fe_3O_4 and these are tabulated in Table 1. In the X-ray diffraction patterns, the (400) profile of Fe_3O_4 is overlapped by one profile of $\epsilon\text{-Fe}_{2.2}\text{C}$ (see Figure

9). The d-spacings of Fe_3O_4 and other carbide phases are illustrated in Figure 2. The difference in d-spacings between Fe_3O_4 and iron carbides can be easily distinguished by microdiffraction because this difference causes different locations for the diffraction spots, other conditions such as camera length remaining the same. For example, the diffraction spots in $\{110\}$ diffraction pattern of Fe_3O_4 will be located differently from those of $\text{Fe}_{2.2}\text{C}$ $\{100\}$ pattern. Solving these diffraction patterns will clearly indicate the phase of particle and the orientation. In this way, all the diffraction patterns were solved and the results showed consistently that the dark/dense particles are iron carbide and light particles are Fe_3O_4 .

Two factors influence the location of the diffraction spots such as shown in figure 8a-c: the crystal structure and the lattice spacing of the particular plane that is oriented to the electron beam to satisfy the Bragg diffraction condition. Fe_3O_4 has a cubic structure whereas the iron carbide structures of interest are either monoclinic or orthorhombic. The number and spatial arrangement of the diffraction spots about the central electron beam will be uniquely determined by the crystal structure. Thus, since Fe_3O_4 has a cubic structure the diffraction spots will appear in a geometric arrangement that uniquely identifies this phase and thereby eliminates from consideration the iron carbide phases given in Table 1. This is not the case for the iron carbide phases since two or more phases have the same crystal structure (Table 1). Thus, the identification of an iron carbide phase depends upon matching the distance of the spots from the spot representing the incoming electron beam and, since this will depend upon the lattice spacing, this identification suffers the same deficiency as the identification of crystal phase by X-ray diffraction. thus, the identification of the Fe_3C and $\text{Fe}_{2.2}\text{C}$ in

Figure 8 is not unique but represents a fitting of theory and the diffraction spots that is consistent with the crystal structure and the diffracting plane given in Figure 8.

A micrograph obtained from the 48-hour sample again showed two kinds of particle morphology. Microdiffraction patterns obtained from the darker particles using a 5 nm electron probe identified iron carbide phases, whereas the lighter particles exhibited Fe_3O_4 phase.

A typical micrograph obtained from the 72-hour sample shows that the particles have grown to about 30 nm in size during 72 hours of syngas conversion, and many particles exhibit a "core/shell" structure (Figure 10). Using a 5 nm probe, electron diffraction patterns were obtained from the core, which exhibited patterns characteristic of iron carbide phases. A typical microdiffraction pattern obtained from the core of a particle is presented in Figure 11 and it exhibits a typical pattern for Fe_3C in [111] orientation. Electron microdiffraction patterns could not be obtained from the region that comprise the shell. Microdiffraction patterns obtained from the less dense transparent particles showed the Fe_3O_4 phase.

The population of light and dark particles are plotted in Figure 12 for the 24 and 72 hour samples. Whereas the carbide particles (i.e., dark/dense particles) are more prevalent in the 24 hour sample, the oxide particles (i.e., light particles) are more prevalent in the 72 hour sample. It appears that the water and/or carbon dioxide produced during the FT synthesis causes oxidation of the carbide which results in the formation of iron oxide. A typical particle size histogram is presented in Figure 13 for the 24 hour sample; this shows the surprising result that there is no significant difference in size distribution between the carbide and oxide particles.

DISCUSSION

The present data, combined with those obtained by Huang et al. (4,6), show that a large fraction (0.8 or greater) of the ultrafine iron oxide is converted to iron carbide (Fe_3C) following 24 hours of pretreatment in CO at 260°C. However, this carbide is not stable under synthesis conditions and a large fraction of it is gradually transformed to an iron oxide (Fe_3O_4).

The data of the current study ($\blacktriangle$) show less Fe_3O_4 than was obtained for the same time of exposure to syngas during the earlier study using Mössbauer data to identify iron compounds (Figure 14; $\blacksquare$), reference 4). Thus, different methods were used to obtain the percentage of Fe_3O_4 in these two studies. In fact, it is gratifying that the TEM data ($\blacktriangle$), which identifies only the fraction of iron in particles large enough to visually identify, agrees so well with the compositions obtained from Mössbauer data, which identifies all of the iron present in the sample.

There is a significant increase of the average particle size during carbiding by CO during 24 hours at 260°C. Following introduction of the synthesis gas there is a period of about 20 hours where particle growth occurs with nearly a 10-fold increase in the particle diameter (1,000-fold volume increase). This volume increase obtained from TEM data corresponds to a significant decrease in the geometrical surface area of the catalyst from about 300 m^2/g to about 30 m^2/g , and this decrease is verified by the surface areas obtained from the BET method.

A comparison of the data in Figure 13 for the oxide (lighter) and carbide (darker) particles show that the two forms have essentially the same size distribution. This is surprising since the oxide form was not present in a significant amount following activation (0 hour sample), and must therefore be formed from the carbide particles.

This could be the result of a very dynamic system in which a particle undergoes transformations between the carbide and oxide forms. It could also result from a gradual growth of the carbide particles and their subsequent irreversible oxidation to Fe_3O_4 . The data do not permit a distinction between these two possibilities or other possibilities.

It is realized that the appearance of the lighter and darker particles could be caused by variations in diffraction contrast between otherwise identical particles. If diffraction contrast is responsible for this appearance, particles will "twinkle" between lighter and darker spots when they are tilted in and out of strong diffraction conditions. However, it seems unlikely that two samples (samples after 10 and 48 hours of synthesis) would have orientations so that one sample has about two times as many of the darker, and half as much of the lighter, particles than the other sample. Furthermore, the same trend for the oxide fraction was obtained from the TEM and the Mössbauer data and this adds credence to the assignment of the lighter and darker particles to oxide and carbide form, respectively. Likewise, it is preferred to obtain the crystal symmetry and unit cell measurements from patterns that are taken close to the major zone axes. This is a concern but, since several, if not all, of the microdiffraction patterns were obtained for the preferred orientation we should have obtained both iron oxide and iron carbide patterns for the lighter and the darker particle groupings. In contrast, this was not the case. In spite of these limitations, the observation that the lighter and darker particles have a similar size distribution requires the iron oxide and iron carbide particles to have the same size distribution. This is an important observation because it indicates that there is not a preferred size for these two iron

compounds and that the iron carbide particle transforms to a similar sized iron oxide particle.

Following a period of synthesis, particles with a solid core surrounded by a shell of less dense materials were observed. One could assign the composition of these particles by analogy with the results reported by Shroff et al. (10); that is, the core would be an iron carbide and the shell could be a carbon overlayer. This observation may also be due to sample preparation for the TEM measurements. One could assume that the suspension contained both small (submicron) and larger (in the 5-30 nm) particles. As the solvent evaporates, the larger particles will retain solvent; thus, these solid particles can be viewed as being surrounded by a solvent "drop" that contains many smaller particles. The final evaporation would deposit a ring of these small particles around the larger particles. This latter view is, in a sense, analogous to the ring of dust particles that are formed when water drops evaporate on a wax surface.

The 24-hour CO pretreatment results in the formation of about two times as much carbon dioxide as would be needed to form $\text{Fe}_{2.2}\text{C}$; thus, it appears that the 24-hour CO activation must deposit "free carbon" on and/or in the iron carbide particles. However, since hydrogen is not present during the 24-hour activation, this carbon cannot be present as some adsorbed hydrocarbon material.

The TEM examination combined with microdiffraction provides a valuable technique for characterization of Fischer-Tropsch catalysts. Under suitable conditions a reasonable quantitative estimation of crystal phases can be determined, as in the present study.

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Table 1					
Lattice Parameter Data for Different Iron Carbides					
			Lattice Parameters (Å)		
Name	Structure	PDF Card #	a	b	c
Fe ₃ O ₄	Cubic	19-629	8.396		
χ-Fe _{2.5} C	Monoclinic	36-1248	11.563	4.573	5.058
ε-Fe ₂ C	Orthorhombic	26-782	4.704	4.295	2.830
ε ¹ -Fe _{2.2} C	Monoclinic	17-897	2.794	2.794	4.360
Fe ₃ C	Orthorhombic	35-772	5.0910	6.7434	4.526
FeC	Orthorhombic	3-411	4.30	2.50	6.70

Table 2					
Lattice Spacings (Å)		Phase	Planes	Fig. # in Ref. 10	% Error
True Value	Observed in Ref. 10				
3.684	3.7	$\alpha\text{-Fe}_2\text{O}_3$	[012]	13	+ 0.434
2.532	2.4	Fe_3O_4	[311]	14(a)	- 5.2
2.532	2.4	Fe_3O_4	[311]	14(c)	- 5.2
2.532	2.5	Fe_3O_4	[311]	14(d)	- 1.26
2.532	2.450	Fe_3O_4	[311]	15(a)	- 3.239
2.532	2.50	Fe_3O_4	[311]	15(b)	- 1.26
2.532	2.4	Fe_3O_4	[311]	15(c)	- 5.2
2.532	2.46	Fe_3O_4	[311]	16(a)	- 2.84
2.532	2.4	Fe_3O_4	[311]	16(b)	- 5.2
2.532	2.5	Fe_3O_4	[311]	16(c)	- 1.26
	2.2	Fe_xC		14(c)	
	2.01	Fe_xC		15(a)	
	2.0	Fe_xC		15(a)	
	2.05	Fe_xC		15(b)	
	2.0	Fe_xC		15(c)	
	2.17	Fe_xC		16(a)	
	2.10	Fe_xC		16(b)	
	2.0	Fe_xC		16(c)

Figure 1. Dependence of the "free carbon" (see text for definition) and the catalyst activity/stability upon the activation temperature (plot of data from reference 5).

Figure 2. Region of the d-spacing that contains the most intensive peak(s) for various d-spacing for iron carbide phases compared to position $\pm 5\%$ for error for the [400] line for Fe_3O_4 .

Figure 3. A TEM picture of ultrafine Fe_2O_3 particles of ≤ 3 nm. The inset is the microdiffraction pattern obtained from an aggregate using a 2 nm electron probe, which shows diffuse rings.

Figure 4. Electron micrograph showing a uniform distribution of particles for the 2 hr. sample.

Figure 5. Particle size distribution histogram obtained from TEM for catalysts withdrawn at increasing synthesis times.

Figure 6. Average particle size versus time in the reactor.

Figure 7. A bright field image obtained from the 10 hr. sample.

Figure 8. Electron microdiffraction patterns using a 5 nm electron beam from the 10 hour sample. (a) pattern from a dark/dense particle, showing Fe_3C particle in $[110]$ orientation. (b) pattern from a lighter particle, showing Fe_3O_4 phase in $[100]_{\text{fcc}}$ orientation, and (c) pattern from another dark/dense particle showing $\text{Fe}_{2.2}\text{C}$ phase oriented in $[100]$ direction.

Figure 9. Relative intensity for XRD peaks for Fe_3O_4 and iron carbides for a range of d-spacings.

Figure 10. An electron micrograph from 72 hr sample depicting the core/shell type morphology.

Figure 11. Electron microdiffraction pattern obtained from the core showing Fe_3C phase in $[111]$ orientation. (a) Experimentally obtained pattern, and (b) (O) theoretically generated reflections for $[111]$ orientation of Fe_3C phase and (Δ) experimentally obtained reflections.

Figure 12. The average population of light and dark particles for the (a) 24 hr. sample and (b) 72 hr. sample.

Figure 13. Particle size distribution for light and dark particles for the 24 hr. sample.

Figure 14. Comparison of the percentage of iron oxide from Figure 11 (▲) with the percentage of iron oxide reported by Huang et al. (8) for Mössbauer data from a similar study (■).

3.2.3 MÖSSBAUER STUDY OF IRON FISCHER-TROPSCH CATALYSTS DURING PRETREATMENT AND SYNTHESIS

ABSTRACT

Mössbauer data indicate that pretreating an iron Fischer-Tropsch catalyst containing Cu, K and Kaolin with syngas for 24 hours at 270°C and 12.9 atm. produces a material that has essentially all of the iron in the form of Fe_3O_4 ; on the other hand, following a similar pretreatment except CO is substituted for the syngas produces a material that contains more than 80% of the iron in the form of $\chi\text{-Fe}_{2.2}\text{C}$ and the remainder as Fe_3O_4 . The CO pretreated catalyst exhibits a high activity, whereas the syngas pretreated sample has a low activity. Moreover, the CO pretreated sample converts during 50 hours of synthesis to a mixture that contains more Fe_3O_4 (40%) and less $\chi\text{-Fe}_{2.2}\text{C}$ (60%) whereas the syngas pretreated sample contains about 80% $\chi\text{-Fe}_{2.2}\text{C}$ after 50 hours of exposure to synthesis gas. Thus, both catalysts underwent significant changes in the bulk composition without a parallel change in CO conversion. Another catalyst formulation, containing more Cu, much less K, and no binder, showed significantly different activity for syngas conversion following the CO and the syngas activation even though they had a similar bulk phase compositions, with the CO pretreated sample being more active. A catalyst, initially pretreated with syngas and exhibiting low activity, showed evidence for only Fe_3O_4 ; this low activity material, following a 24 hour treatment in CO, exhibited a dramatic increase in catalytic activity and the formation of a significant fraction of the carbide phase. The bulk analysis of phase composition is informative about changes in the bulk composition of iron catalysts but these changes do not directly track catalytic activity in many cases.

INTRODUCTION

Iron catalysts have been used extensively for the Fischer-Tropsch Synthesis (FTS) and are currently the catalysts utilized in the commercial operations at Sasol (1). The iron catalyst permits the production of olefinic products when operated in either the low or high alpha mode (2). The iron catalyst, unlike the cobalt and ruthenium catalysts, forms a carbide under the normal reaction conditions employed in its use. Thus, the composition of the iron catalyst is one aspect that must be elucidated in order to develop a complete understanding of the FTS mechanism (e.g., 3).

In general, pretreatment of an iron catalyst can be accomplished using one of three techniques: CO followed by synthesis gas, H_2 followed by synthesis gas and startup in synthesis gas (e.g., 4-6). Much of the early work was accomplished starting with fused or sintered catalysts and these could only be made active by first reducing to elemental iron in a hydrogen atmosphere (7). Exposure to synthesis gas converted the iron in part or essentially to the carbide. Pretreatment in CO resulted first in the reduction to Fe_3O_4 and then more slowly to carbides (e.g., 8-10). Pretreating in synthesis gas is more complicated because of the competition between synthesis and carbiding as well as the formation of water that retards the reduction/carbiding steps. Much of the early German work utilized atmospheric or lower pressure start-up pressures when synthesis gas was used (6). It has been claimed that a pretreatment in CO produces an active catalyst that does not require a complex start-up program and is essentially independent of the catalyst composition; however, the start-up procedure used with either synthesis gas or reduction with H_2 followed by synthesis gas appears to depend upon the catalyst formulation (8). In a commercial operation, a synthesis gas

stream is readily available; however, while a pure hydrogen stream may be available it is unlikely that a pure CO stream will be available.

Much of the early characterization of the phases of iron present in FTS catalysts utilized techniques such as X-ray and magnetization; however, these were difficult to make quantitative (7). Mössbauer spectroscopy, because of its sensitivity for iron and its quantitative nature, provides a convenient technique for the characterization of iron FTS catalysts and the changes in composition that they undergo during synthesis. The utilization of a continuous stirred tank reactor (CSTR) permits all of the catalyst charge to be exposed to the same gas composition and, with appropriate experimental technique, to withdraw catalyst samples for characterization at intervals during the pretreatment and synthesis operations. These techniques have been employed in the work that is reported in this communication.

Two of the catalysts utilized in this study were prepared for use in a screening study designed to provide data for the selection of a catalyst for ultimate use in the bubble column reactor at LaPorte, Texas. These two catalysts were prepared by United Catalyst, Inc. according to compositions provided them. The catalyst was formed into spherical particles nominally of about 40-60 micron diameter using a spray drying technique. The third catalyst was formulated at the CAER so that one batch contained copper and the other did not; these batches were prepared for studies to define the role of copper in determining the phases present in the catalyst. At the same time, activity data was obtained so that an attempt could be made to define the role of catalyst phase in determining the catalyst activity.

EXPERIMENTAL

Three catalyst samples were employed. Two catalysts (UCI 1185-57 containing kaolin and UCI 1185-149-2) were prepared by United Catalysts, Inc. according to specifications set by a consortium in preparation for a run at LaPorte, Texas. The precipitated iron oxide catalyst (prepared at CAER) was prepared by continuous precipitation from aqueous solutions of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and concentrated NH_4OH at pH 10. The precipitate was thoroughly washed with distilled-deionized H_2O and dried at 120°C .

For a typical test at the CAER, catalyst slurry consisting of 72.7 g of precipitated catalyst and 290 g of C_{30} oil (or rather solvents) were mixed inside a 1 L autoclave operated as a continuous stirred tank reactor. The precipitated catalyst slurry was heated to 270°C at $1.5 - 2.0^\circ\text{C}/\text{min}$. under a flow of CO ($2.0 \text{ nL/hr-g}(\text{Fe})$). CO pretreatment continued at 270°C for 22 to 24 hours. Following pretreatment, hydrogen flow was started to give a H_2/CO ratio of 0.7 with a flow rate of $3.4 \text{ nL/hr-g}(\text{Fe})$. Catalyst slurry samples were removed ($\sim 10\text{-}15 \text{ g}$) from the reactor at various times of the pretreatment and synthesis. CO and H_2 conversions were determined by analyzing the exit gas stream with a Carle gas analyzer. Catalyst slurry samples were Soxhlet extracted using refluxing toluene or *o*-xylene to remove accumulated hydrocarbons.

For a typical test conducted at PETC with a CO pretreatment, conditions were slightly different than at CAER. 36.5 g of precipitated catalyst and 370 g of wax were loaded as a 9 wt.% slurry inside a 1 L autoclave. The slurry was heated under a flow of helium at 175 psig to 150°C and stirred at 1000 rpm. Then heating was continued at $1^\circ\text{C}/\text{min}$. under a flow of CO ($1.4 \text{ nL/hr-g}(\text{Fe})$) to 270°C . CO pretreatment continued at 270°C and 175 psig for 22 to 24 hours. Following pretreatment, synthesis gas with a

H₂/CO ratio of 0.7 was introduced at a rate of 2.4 nL/hr-g(Fe). The synthesis was carried out at 270°C and 175 psig. Catalyst slurry samples (~ 1-3 g) were removed from the reactor. The wax kept the catalyst from oxidizing in air during handling.

For the syngas activation conducted at PETC, the catalyst/wax slurry was heated in flowing helium at 150 psig to 200°C. Then syngas was introduced at 1.8 nL/hr-g(Fe), with an additional 0.6 nL/hr-g(Fe) of helium. The temperature was raised to 280°C and held for 14 hours, again at 150 psig. Following pretreatment, synthesis gas with a H₂/CO ratio of 0.7 was introduced at a flowrate of 2.4 nL/hr-g(Fe). The pressure was raised to 175 psig and the temperature lowered to 270°C.

The Mössbauer experiments were carried out using a constant acceleration spectrometer. The radioactive source consisted of 50-100 mCi of ⁵⁷Co in a Pd matrix. The samples were in powder form and were loaded into Plexiglass compression holders presenting a thin aspect to the gamma ray beam. All spectra were analyzed by a least-squares fitting procedure which models the spectra with a series of Lorentzian peaks. The percentages of the total sample iron contained in each iron-bearing phase identified are determined from the relevant peak areas.

RESULTS

64%Fe₂O₃/5%CuO/1%K₂O/30% Kaolin (UCI-1185-57)

Batches of this catalyst were activated in syngas and in CO. For the CO pretreatment, the catalyst temperature was ramped from 200 to 270°C at 1.5°C/min under CO at 13 atm; it was maintained at 270°C in a CO flow of 2.0 NL/hr.-gFe during the remainder of a 24 hour period. During this pretreatment the iron oxide in the catalyst was first reduced to Fe₃O₄ and then converted to iron carbide. At the end of the 24 hour pretreatment, the catalyst contained about 90% χ -Fe₅C₂ with the remainder

of the iron being present in a superparamagnetic form (figure 1). Low temperature (12 K) Mössbauer measurements on one of the samples of withdrawn catalyst showed that the superparamagnetic (spm) phase was Fe_3O_4 , and not the carbide which can also be present in a spm phase. During synthesis the amount of $\chi\text{-Fe}_5\text{C}_2$ decreased to about 60% during 30 hours and remained at about this level (figure 1). The CO pretreated catalyst exhibited a conversion ($\text{H}_2 + \text{CO}$) in the 70-80% range during 150 hours of synthesis (figure 2).

A portion of the catalyst was pretreated in synthesis gas. This was accomplished by heating the slurry to 200°C in He and then switching to synthesis gas ($\text{H}_2/\text{CO} = 0.67$) at 150°C after which the sample was heated to 280°C at a rate of 7.0°C/min. After holding the catalyst at 280°C in a flow of synthesis gas for 12 hours, the pressure was increased to 20 atm and the temperature was lowered to 265°C. These conditions for the pretreatment (activation) and synthesis were chosen to correspond to the conditions used for Run 2 at the LaPorte, Texas slurry bubble reactor demonstration plant. The catalyst was rapidly converted to magnetite and then the magnetite was slowly converted to iron carbides. At the end of the pretreatment (activation) period, about 40% of the iron was present as a mixture of $\chi\text{-Fe}_5\text{C}_2$ and $\epsilon'\text{-Fe}_{2.2}\text{C}$ (figure 3). During 24 hours of synthesis, the catalyst composition changed so that it contained almost 80% $\chi\text{-Fe}_5\text{C}_2$ and $\epsilon'\text{-Fe}_{2.2}\text{C}$.

As can be seen in figure 2, the conversion of syngas was increasing during the pretreatment period, and had attained about 60%. During this period the amount of carbide was increasing and attained a level of about 40%. Almost immediately after the change of conditions to those used for the synthesis, the conversion dropped to the 20-30% level. At this low conversion level the formation of carbide continued to exceed

that of the CO pretreated catalyst at an equivalent time on stream. The different levels of carbide present during the synthesis is considered to be controlled primarily by the level of conversion of the syngas, and not by the different pretreatments. A high level of ($H_2 + CO$) conversion produces CO_2 and H_2O , which are oxidizing gases. On the other hand, for low ($H_2 + CO$) conversions, the catalyst is exposed to a reducing atmosphere.

57.2%Fe/9.3%Cu/0.05%K

This catalyst differs from the one described above since it does not contain the Kaolin binder (support), contains almost twice as much copper and only about one-twentieth as much potassium. The catalyst was pretreated in CO under the conditions normally employed at the CAER (1.4 NL/hr.-gFe of CO at 13 atm, 270°C, 22 hr). The composition of the catalyst underwent a decrease in the amount of superparamagnetic magnetite present as well as a decrease in the amount of magnetically ordered magnetite. During synthesis the amount of χ - Fe_5C_2 increased from the 30-40% level to about 70% (Table 1). At the same time there was a decrease in the amount of superparamagnetic magnetite, and then the Fe_3O_4 ; apparently the superparamagnetic material is converted to the carbide more rapidly than the magnetically ordered Fe_3O_4 is. During synthesis time, the conversion dropped from about 90% to the 50% level. This drop is typical with this type of heavy wax used as startup solvent, as discussed below.

The catalyst pretreated in synthesis gas had a poor activity, with the conversion in the 5-20% range (Table 2). At the end of the 14 hour activation period the catalyst contained 36% χ - Fe_5C_2 . After 26 hours of synthesis the amount of χ - Fe_5C_2 had

increased to 84% and this increased to 91% after 49 hours. This test was conducted in a light wax, n -octacosane.

Pretreatment of this catalyst in CO was conducted in two solvents: for comparison, purified n -octacosane and the residue of a vacuum distillation of an Allied-Signal wax (comprised of predominantly C_{40+}) were used. Similar results were obtained in both solvents. In the C_{28} wax, the catalyst contained 86% χ - Fe_5C_2 following the 22 hour pretreatment in CO and this phase declined to about 55% during 160 hours of synthesis (Table 3). During the synthesis the χ - Fe_5C_2 appears to be converted predominately to the superparamagnetic material rather than magnetically ordered Fe_3O_4 . It appears that the fraction of iron present in the χ - Fe_5C_2 phase was slightly lower in the heavy solvent than in the lower molecular weight wax (64 versus 86%) (Tables 3 and 4). During the synthesis the carbide phase decreases with a corresponding increase in the superparamagnetic material. In both solvents a small fraction (0.06-0.12) of ϵ - $Fe_{2.2}C$ is formed during the initial period of the CO pretreatment, but this phase is not observed following about 10 hours of pretreatment.

The activity of the catalyst is similar in the two solvents during the first 100 hours; however, the conversion is slightly lower in the higher boiling wax and declines more quickly after 100 hours on stream.

100 Fe/3.6 Si/0.71 K

This catalyst was initially pretreated in synthesis gas and then used for synthesis. Following a period of synthesis the catalyst was subjected to a pretreatment in CO, and this was followed by a period of synthesis. The CO pretreatment caused a dramatic increase in the synthesis gas conversion; details of this as well as the impact of pressure of the synthesis gas used during pretreatment on the activity are reported in

detail elsewhere (11). The catalyst was exposed to synthesis gas ($H_2/CO = 0.67$) at $270^\circ C$, 13 atm., and a flow of 3.1 NL/hr.-gFe. After six hours the catalyst contained 25% magnetically ordered Fe_3O_4 and 75% superparamagnetic phase (Table 5). During the next 87 hours, the amount of the superparamagnetic phase decreased below the detectable limit, and the sample was essentially 100% magnetically ordered Fe_3O_4 . During this period the synthesis gas conversion was in the range of 9-12%. A surface layer (or partial layer) of χ - Fe_5C_2 or spm χ - Fe_5C_2 may be present, but undetected by the Mössbauer measurements, and this was responsible for the small syngas conversion that was observed.

Following the 93 hours exposure to synthesis gas, the hydrogen flow was stopped so that the sample was exposed to only CO at 270° and 13 atm. during a 22 hour period. At the end of this 22 hour period the catalyst contained 58% magnetically ordered Fe_3O_4 , 9% of the superparamagnetic phase and 33% χ - Fe_5C_2 . Shortly after hydrogen was reintroduced so that the catalyst was again exposed to the synthesis gas, the conversion increased to 25% and within 4 hours (119.5 hours total) had attained a conversion level of 59%. Within 77 hours following the CO only treatment, the syngas conversion was 88% and remained at or above 80% during the 500 hours of the test. There was little change in the composition of the catalyst following the treatment with CO. Thus, the CO treatment caused the conversion of about one-third of the iron to the carbide form and this resulted in an increase in the conversion to greater than 80%. It is therefore apparent that the nearly 100 hour exposure to synthesis gas did not impact the catalyst so as to inhibit the subsequent activation by CO. Furthermore, the subsequent CO pretreatment produced a catalytic material that had an activity that was essentially the same as if the catalyst had been pretreated initially with CO. Other runs

with different portions of this catalyst batch show that the conversion level will remain low even if synthesis gas flow had been continued for hundreds of hours without the CO pretreatment; furthermore, the amount of carbide would slowly increase at longer times on stream.

Another portion of the catalyst was pretreated in syngas under identical conditions as used above except that the total pressure was held at 1 atm for a 24 hour period before increasing to the synthesis conditions (13 atm, 270°C, 3.1 NL/hr.-gFe, $H_2/CO = 0.67$), and the results are given in Table 6. After the 24 hour period at atmospheric pressure, the catalyst was composed of 41% $\chi\text{-Fe}_5\text{C}_2$, 27% superparamagnetic phase and 32% magnetically ordered Fe_3O_4 . After 24 hours at 13 atm pressure, the conversion was 82%. The conversion declined slowly to 69% during the 384 hour run. It is therefore apparent that the low pressure treatment with synthesis gas led to the formation of a significant quantity of carbide whereas this was not the case when the treatment was carried out at 13 atm. In addition, the presence of iron carbide lead to a catalyst with high activity whereas the catalyst that did not contain a detectable amount of carbide had low activity.

As a means of evaluating the role of copper upon the activation, the 100Fe/3.6Si/0.71K catalyst was impregnated with sufficient aqueous copper nitrate to give 2.6 atomic % Cu relative to Fe. This catalyst was then utilized for the synthesis (13 atm, $H_2/CO = 0.67$, 270°C and 3.1 NL/hr-gFe) without prior activation. After 4.3 hours, the sample consisted of 19% superparamagnetic phase (carbide and/or oxide) and 81% magnetically ordered Fe_3O_4 (table 7). Continuing the reaction resulted in a decrease in the superparamagnetic phase with an increase in the magnetically ordered Fe_3O_4 . At 114 hours of synthesis the superparamagnetic phase corresponded to only

3% and there was 15% χ -Fe₅C₂; the carbide phase increased to 20% after 215 hours on stream. The conversion of synthesis gas was higher when copper was present than when it was absent; this is true whether a carbide phase is present or not. Thus after 19 hours in syngas the Cu containing material produced 26% conversion whereas the same catalyst without Cu produced only about 10% conversion. The conversion continued to increase with time on stream when Cu was present but this did not appear to be the case when Cu was not present. After 215 hours on stream, the activity of the Cu-containing catalyst had increased to provide about 50% syngas conversion.

DISCUSSION

For the Kaolin containing catalyst only the χ -Fe₅C₂ carbide phase was observed. However, when the same catalyst was pretreated with synthesis gas, both χ -Fe₅C₂ and ϵ -Fe_{2.2}C were observed; however, these carbides are observed when the conversion was low. Furthermore, the CO pretreatment leads to a high fraction of the carbide phase and to high catalytic activity. With increasing time on stream the amount of the carbide phase decreases while the conversion remains essentially constant. Thus, the catalyst undergoes changes in chemical composition while the catalyst activity and selectivity (11) both remain essentially constant. On the other hand, treating the catalyst in synthesis gas at 13 atm leads to a material which produces low synthesis gas conversion. Under these low conversion conditions, the fraction of iron present as a carbide phase gradually increases to exceed that of the CO pretreated sample.

An iron catalyst containing much less potassium (0.05%) and no support produced a significant amount of carbide for both the CO and syngas pretreatment. However, the activity of the catalyst pretreated with CO was significantly greater than the one pretreated in syngas. The activities for the material pretreated by the two ways

were quite different when the catalysts contained the same amount of carbide. Thus, when about 40% of the iron was present as a carbide, the CO pretreated sample provided 84% syngas conversion (at 84 hours on stream) whereas the syngas sample produced a conversion that was very low (<5% at 14 hours on stream). As the carbide fraction of the CO pretreated sample increased with time on stream the synthesis gas conversion decreased. Thus, it is necessary for some carbide to be present to have a catalyst with a high activity; however, it is evident that the activity of the material cannot be predicted solely from the fraction of iron that is present as the carbide.

In general, the CO pretreated samples have a high activity and a high fraction of the iron present as the carbide phase; with increasing time on stream the fraction of iron carbide decreases. The fraction of iron present as the carbide following the CO pretreatment appears to depend upon the composition of the catalyst. However, if the relative fraction of iron carbide that is converted to the oxide with time on stream is considered; the iron carbide fraction of each catalyst was converted to the oxide at about the same rate with time on stream (figure 4). There is a rapid conversion of the carbide to the oxide as the sample is initially exposed to the synthesis gas; however, after about 40 hours the fraction of carbide remaining (about 0.6 of the initial amount) attains a pseudo steady state. It must be kept in mind that the general scheme illustrated in figure 4 applies only to those catalysts that have a high activity, and is not intended to apply to all possible experimental conditions. The data in figure 4 include a catalyst that has been pretreated with synthesis gas at 1 atm; therefore, the low pressure activation in synthesis gas appears to resemble an activation in CO.

In general, when a catalyst activation produces both an active catalyst and a high fraction of iron carbide, there will be a conversion of the carbide to the oxide and

the attainment of a pseudo steady state composition. A material whose pretreatment produces a catalyst with a low activity and a low fraction of iron carbide will undergo carbiding with time on stream to approach nearly complete carbide formation. Much of the characterization data in the literature has been generated using experimental conditions that correspond to low conversion conditions (reducing atmosphere). Consequently, the fact that these materials exhibit complete, or nearly complete, carbide phase is considered to be more dependent upon the low conversion conditions than upon the catalyst.

In summary, it appears that the presence of some fraction of iron carbide is necessary for a material to exhibit a high (>80%) conversion; however, the presence of carbide is not a sufficient condition for high activity. Furthermore, the current data is in agreement with the observation that the catalytic activity and selectivity will remain essentially constant while the catalyst undergoes significant chemical and/or phase changes. It is therefore not possible to predict the catalyst performance based upon the bulk analysis of the catalyst. However, when the bulk analysis of the catalyst, at the end of the activation step shows no carbide present, the catalyst performance can be predicted to be poor.

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Table 1				
Catalyst: UCI 1185-149-2 (57.2 Fe/9.3 Cu/0.05 K) Activated in CO at 270°C, 175 psig, 22 hr, 1.4 nL/hr-g(Fe) FT Synthesis Conditions: H ₂ /CO = 0.70, 270°C, 175 psig, 2.4 nL/hr-g(Fe) 9% Catalyst Loading in Distilled Allied-Signal Heavy Wax of 370 g				
Sample	$\chi\text{-Fe}_5\text{C}_2$	Fe_3O_4	SPM	(H ₂ + CO), Conversion %*
FT Run TOS = 84 hrs	40	37	23	84.0
FT Run TOS = 235 hrs	60	30	10	67.7
FT Run TOS = 305 hrs	68	27	5	51.2
* FT synthesis runs were carried out at PETC.				

Table 2				
Catalyst: UCI 1185-149-2 (57.2 Fe/9.3 Cu/0.05 K) Activated in H ₂ /CO/HE at 270°C, 175 psig, 22 hr, 1.8 nL syngas/hr-g(Fe) FT Synthesis Conditions: H ₂ /CO = 0.70, 270°C, 175 psig, 2.4 nL/hr-g(Fe) 9% Catalyst Loading in C-28 Light Wax of 370 g				
Sample	χ -Fe ₅ C ₂	Fe ₃ O ₄	SPM Phase	(H ₂ + CO), Conversion %*
Activated for 14 hrs	36	48	16	---
FT Run TOS = 26 hrs	84	14	2	16
FT Run TOS = 49 hrs	91	7	2	6
* FT synthesis runs were carried out at PETC.				

Table 3					
FT Synthesis in Light Wax					
Catalyst: UCI 1185-149-3 (57.2 Fe/9.3 Cu/0.05 K)					
Activated in CO at 270°C, 175 psig, 22 hr, 1.4 nL/hr-g(Fe)					
Synthesis Conditions: H ₂ /CO = 0.70, 270°C, 175 psig, 2.4 nL/hr-g(Fe)					
9% Catalyst Loading in C28, n-octacosane, Light Wax of 370 g					
Sample	χ -Fe ₅ C ₂	Fe ₃ O ₄	SPM Phase	ϵ -Fe _{22,2} C	(H ₂ + CO), Conversion %
Activated for 2 hrs	---	82	6	12	---
Activated for 18 hrs	77	21	2	---	---
Activated for 22 hrs	86	12	2	---	---
FT Run TOS = 19.5 hrs	58	15	27	---	89
FT Run TOS = 43 hrs	56	16	28	---	91
FT Run TOS = 90 hrs	65	20	15	---	91
FT Run TOS = 160 hrs	56	21	23	---	91

Table 4					
FT Synthesis in Heavy Wax					
Catalyst: UCI 1185-149-3 (57.2 Fe/9.3 Cu/0.05 K)					
Activated in CO at 270°C, 175 psig, 22 hr, 1.4 nL/hr-g(Fe)					
Synthesis Conditions: H ₂ /CO = 0.70, 270°C, 175 psig, 2.4 nL/hr-g(Fe)					
9% Catalyst Loading in Distilled Allied-Signal Wax of 370 g					
Sample	χ -Fe ₅ C ₂	Fe ₃ O ₄	SPM Phase	ϵ -Fe _{22.2} C	(H ₂ + CO), Conversion %*
Activated for 2 hrs	---	88	6	6	---
Activated for 9.5 hrs	54	37	9	---	---
Activated for 22 hrs	64	27	9	---	---
FT Run TOS = 24 hrs	42	30	28	---	81
FT Run TOS = 47.5 hrs	39	34	27	---	87
FT Run TOS = 94.5 hrs	37	40	23	---	86
*The SPM phase is likely to be α -FeOOH as revealed by low temperature measurements on UCI 1185-149-3 catalyst subjected to CO activation and 24 hrs of FT synthesis.					

Table 5				
Activation Carried out at High Pressure (12 atm)				
Catalyst: 100 Fe/3.6 Si/0.71 K (atomic % relative to Fe)				
Initial Activation in Syngas at 12 atm, 270°C, H ₂ /CO = 0.7, S.V. = 3.4 nL/hr-g(Fe)				
Synthesis Conditions: 270°C, 175 psig, 3.4 nL/hr-g(Fe), H ₂ /CO = 0.7				
Catalyst	SPM Phase	Fe ₃ O ₄	χ-Fe ₅ C ₂	Conversion %
Syngas: TOS = 6.33 hrs	75	25	---	9.2
Syngas: TOS = 24.0 hrs	31	69	---	9.7
Syngas: TOS = 46.0 hrs	11	89	---	11.5
Syngas: TOS = 93.0 hrs	---	100	---	12.2
CO: TOS = 115 hrs	9	58	33	
Syngas: TOS = 119.5 hrs	15	60	25	59
Syngas: TOS = 192.5 hrs	18	63	19	88
Syngas: TOS = 313 hrs	13	67	20	86
Syngas: TOS = 456.0 hrs	11	63	26	81

Table 6				
Pretreatment Carried out at Low Pressure (1 atm)				
Catalyst: 100 Fe/3.6 Si/0.71 K (atomic % relative to Fe)				
Activation Conditions: 270°C, 1 atm, H ₂ /CO = 0.7, S.V. = 3.4 nL/hr-g(Fe), 24 hrs				
Synthesis Conditions: 270°C, 13 atm, S.V. = 3.4 nL/hr-g(Fe), H ₂ /CO = 0.7				
Sample	χ -Fe ₅ C ₂	Fe ₃ O ₄	SPM Phase	(H ₂ + CO) Conversion %
Activated for 24 hrs	41	32	27	---
FT Run TOS = 24 hrs	36	40	24	82.0
FT Run TOS = 48 hrs	31	47	22	83.0
FT Run TOS = 95 hrs	33	48	19	79
FT Run TOS = 218 hrs	26	50	24	75
FT Run TOS = 384 hrs	20	60	20	69

Table 7

Pretreatment Carried out at High Pressure (12 atm)

Catalyst: 100 Fe/3.6 Si/2.6 Cu/0.71 K (atomic % relative to Fe)

Initial Activation in Syngas at 12 atm, 270°C, $H_2/CO = 0.7$, S.V. = 3.4 nL/hr-g(Fe)

Synthesis Conditions: 270°C, 175 psig, 3.4 nL/hr-g(Fe), $H_2/CO = 0.7$

Catalyst	SPM Phase	Fe_3O_4	$\chi\text{-}Fe_5C_2$	Conversion %
TOS = 4.33 hrs	19	81	---	26
TOS = 21.0 hrs	10	90	---	26
TOS = 45.0 hrs	14	86	---	32
TOS = 113.7 hrs	3	82	15	43
TOS = 214.5 hrs	4	76	20	51

Figure 1. Iron phase distribution in the catalyst UCI 1185-57 versus TOS (a) during activation in CO, and (b) during FT synthesis.

Figure 2. (H₂ + CO) conversion dependence on pretreatment.

Figure 3. Iron phase distribution in the catalyst UCI 1185-57 versus TOS (a) during activation in syngas, and (b) during FT synthesis.

Figure 4. The fraction of the initial carbide remaining after increasing time on stream (▲, UCI 1185-149 (syngas, Table 4); ●, UCI 1185-149 (CO, Table 3); ■, 100 Fe/3.6 Si/0.71 K (syngas, 1 atm, Table 6).

3.2.4. Scanning Electron Microscopy Study of Co-precipitated Iron Oxide

Catalysts

ABSTRACT

Iron oxide Fischer-Tropsch catalysts were prepared using a sol-gel method to incorporate varying amounts of silica (SiO_2) and a constant amount of potassium oxide (K_2O) promoters. The sol-gel slurries containing different Fe/Si ratios were dried using a spray dryer. The spray-dried materials were calcined at 300°C prior to the use as catalysts for the Fischer-Tropsch reaction. Scanning electron microscopy (SEM), combined with energy dispersive X-ray spectroscopy (EDS) and elemental dot mapping (EDM) techniques, was utilized to characterize the structural morphology for these promoted iron oxide catalysts. The results indicate that the promoters (SiO_2 , K_2O) are evenly distributed throughout the catalysts, and no agglomerated regions of iron, silica or potassium could be observed. Thus, the sol-gel preparation, followed by spray drying produces industrial catalysts of fine particle morphology and a uniform distribution of the promoters.

INTRODUCTION

The Fischer-Tropsch process has attracted a great deal of attention in terms of catalytic activity and selectivity to produce higher carbon number hydrocarbons by reacting carbon monoxide and hydrogen at high pressures in the presence of catalysts (Fischer and Tropsch (1923)). Shortly after the initial discovery, Fischer and Tropsch developed more active catalysts for indirect liquefaction. The product distribution resulting from the Fischer-Tropsch synthesis (FTS) varies widely depending upon the catalysts, the temperature and pressure of reaction, pretreatment conditions, etc. It is always desirable to improve the selectivity while maintaining the activity intact. One

approach to achieving this task is the addition of promoters such as oxides of K, Mn, Ti, Mo, Ni, and Co, etc. It was observed that most of these promoted catalysts exhibit an increase in selectivity to higher hydrocarbons (Barrault, *et al.* (1988); Ledford, *et al.* (1987); Takhashi, *et al.* (1988); Baker and Clark (1987)). For example, the addition of thoria as a promoter to cobalt-kieselguhr catalysts resulted in an enhanced yield of C_5^+ hydrocarbons (Storch, *et al.* (1951)). Even a small amount of thoria promoter (~0.4 wt.%) addition to Co/ZSM-5 causes a remarkable increase in the conversion, shift activity, and C_5^+ selectivity (Rao, *et al.* (1985)). Thoria added as a promoter to a precipitated iron oxide catalyst appears to decrease wax selectivity (Dry (1981)). It is generally believed that the factors such as dispersion effects of rare earth oxides (Ledford, *et al.* (1987); Rao, *et al.* (1985); Dry (1981); Anderson (1956); Mok, *et al.* (1983)), the redox properties (Barrault, *et al.* (1988); Takhashi, *et al.* (1988)), and the basic properties of rare earth oxides and (Takhashi, *et al.* (1988); Rao, *et al.* (1985)), greatly influence the activity and selectivity.

The FTS reaction is very exothermic and handling the heat generated during the synthesis has presented significant problems in developing processes for the synthesis. One approach to handling the excess heat of reaction is to utilize a slurry reactor. In order to utilize this approach, it is necessary to effect catalyst/wax separation. As heavy wax builds up in the reactor during synthesis, the liquid level will rise. To maintain a constant liquid level in the reactor, slurry must be withdrawn, catalyst and wax separation effected, and the catalyst is returned to the reactor. For effecting a uniform slurry in the reactor and for many solid separation techniques, it is advantageous to have the catalyst with a spherical shape with a narrow size distribution. One way to obtain this type of catalyst is to utilize spray drying to develop

spherical catalyst particles with a narrow size distribution. This technique has been utilized in this study.

Iron oxide and oxyhydroxide catalysts can be synthesized following various preparation methods. The current investigation describes the preparation and characterization by electron microscopy of the iron oxyhydroxide catalysts promoted by silicon and potassium.

EXPERIMENTAL METHODS

(a) Catalyst Preparation

A 15 kg batch of the catalyst was made by a continuous precipitation technique. The slurry (containing 5 at.% silicon based on Si and Fe content corresponding to 3.8 wt.% SiO₂) was divided into three portions, as outlined in Figure 1. The first portion was directly spray-dried. The product was then dried at 100°C for 27 hours. This dried sample was designated as **RLS5.0Si-I**.

The second portion of the catalyst sample was mixed with a slurry containing sufficient potassium silicate (K₂SiO₃) to add 0.5 wt.% potassium and hydrolyzed tetraethylorthosilicate (TEOS) in an amount to provide a total of 7.5 wt.% SiO₂ in the finished catalyst. This slurry was then spray-dried. While spray-drying this sample, it was found that the initial product was too damp because of a high feed rate; hence the feed rate was reduced and a drier product was then obtained, as shown in Figure 1. Both the damp and drier products were then dried at 100°C for 27 hours. The damp product and the drier products were consequently designated as **RLS5.0Si-II-A** and **RLS5.0Si-II-B**, respectively.

The third portion of the catalyst was treated the same way as the second except the amount of TEOS was sufficient to produce 12.2 wt.% SiO₂. This sample was

designated as **RLS5.0Si-III**. Portions of the spray-dried products were, after drying at 100°C for 27 hours, calcined at 200°C for 15 hours or at 300°C for 23 hours.

(b) Description of the Spray Dryer

The drying chamber consists of a ten foot tall cylinder with a diameter of four and one-half feet and has a two foot conical section attached to the bottom of the cylinder. Hot gases at 600-650°F (combustion by-products from a gas burner) are blown by a fan into the top of the chamber and exit the bottom of the chamber, while the catalyst slurry is pumped through an atomizer nozzle at the bottom of the chamber (the nozzle is inserted through the conical section at the bottom of the chamber). The catalyst travels vertically upwards (countercurrent flow) with enough velocity so that it almost hits the top of the chamber, then it is entrained in the hot gas in a downward motion (cocurrent flow) towards the bottom of the chamber. This countercocurrent flow yields an effective chamber height of about 20 feet. Attached to the bottom of the chamber (i.e., the bottom of the conical section) is a collection device for capturing the dried catalyst. Exhaust gases exit the bottom of the chamber and are sent to a cyclone for removal of catalyst fines and then the exhaust gases pass through filters and are vented to the atmosphere.

(c) Scanning Electron Microscopy

A Hitachi S-2700 scanning electron microscope was used with a spatial resolution of about 3.5 nm. Secondary electron images, qualitative energy dispersive X-ray spectra as well as elemental distribution maps, were obtained from the catalysts under investigation. This scanning electron microscope was outfitted with a Princeton Gamma Tech IMIX-II Omega SLS (Sealed Light Element Spectrometer), which is a

Si(Li) detector utilizing an ultra-thin window, sensitive to all elements with an atomic number of boron and higher.

The spray—dried powders were spread on a flat aluminum holder and this was coated with carbon to minimize charging effects. The carbon-coated specimens were then mounted into the microscope for analysis.

RESULTS AND DISCUSSION

Electron micrographs were obtained from powder specimens of the catalysts under investigation at various magnifications. An electron micrograph obtained from catalyst RLS5.0Si-I depicts several agglomeration of particles (Figure 2). Under high magnification, each agglomeration is shown to consist of many small particles. If the powders were ultrasonically dispersed in an organic compound such as acetone or alcohol before the specimen preparation, the agglomerates were no longer present, and only small particles appeared in the microscopic examination. Hence, the specimen preparation for microscopy is very important, and it should not be allowed to distort the true morphology of the specimens. All the electron micrographs presented in this investigation were prepared from the as-dried powders without any ultrasonic treatment.

An energy dispersive X-ray spectrum obtained from one agglomerate is presented in Figure 3. X-ray lines corresponding to $\text{FeK}\alpha$, $\text{K}\beta$, and $\text{L}\alpha$ are observed. In addition to Fe lines, a Si $\text{K}\alpha$ line also appeared exhibiting a minor fraction of SiO_2 . The intensity ratio of $\text{FeK}\alpha$ to $\text{SiK}\alpha$ is 8.67. This sample contains about 5 at.% silicon relative to Si and Fe contents in the starting slurry (see Figure 1).

Samples RLS5.0Si-IIA and RLS5.0Si-IIB were obtained from the second portion of the starting slurry to which 0.5 wt.% K and 4 wt.% SiO_2 were added prior to spray-

drying. A scanning electron micrograph obtained from sample RLS5.0-Si-IIA is shown in Figure 4. The morphological features are quite similar to those of the previous sample. An EDS spectrum obtained from this sample (Figure 5), shows a minor fraction of potassium in addition to the Fe and Si K α x-ray lines. Examination of sample RLS5.0Si-IIB revealed similar morphological features. Elemental dot maps from one of these two catalysts are shown (Figures 6), along with the image from the region where the dot map data were collected. The maps show that the potassium and silica promoters are distributed very uniformly in the catalyst. X-rays emanating from each element present in the illuminated area were collected for a timed interval.

A scanning electron micrograph of catalyst RLS5.0Si-III, dried at 100°C, (Figure 7), shows that the agglomerate size is greatly reduced compared to the samples described above. Several EDS spectra obtained from this catalyst at different locations indicated the presence of Fe, Si, K, and O. An elemental dot map obtained from the dried sample of RLS5.0Si-III clearly showed the potassium and silicon promoters to be uniformly distributed on the catalyst surface. Similar morphological features were observed for the sample RLS5.0Si-III, dried at 300°C.

The characteristic morphological features from these spray-dried catalysts were examined at various locations of the samples and at various magnifications. It was observed that the agglomerates consisted of very small particles. The sizes of the agglomerates were measured and plotted for the series of catalysts dried at 100°C (Figure 8(a)), and those at 300°C (Figure 8(b)). The sizes of these agglomerates range up to about 100 microns.

The relationship between the mean agglomerate size and the silica content is presented in Figure 9. The two samples with the lowest silica contents have

agglomerate sizes that are essentially the same as an iron sample prepared by the same procedure that did not contain silica, and the maximum in the size distribution occurs for agglomerates in the 40-60 μm range. With increasing silica content the agglomerate size decreases. Thus, the agglomerate size for the 7.5 wt.% silica sample is smaller than the one containing 3.8 wt.% SiO_2 . The sample containing 12.2 wt.% SiO_2 has a particle size centered at 20-40 μm . A similar sample that contained 30 wt.% SiO_2 had a particle size centered at about 10 μm . Thus, the agglomerate size of the material dried at 100°C depends upon the silica content with the size decreasing with increasing SiO_2 content as shown in Figure 9. All slurry drying runs were conducted using similar slurry compositions, temperatures, slurry and atomizing gas feed rates, and drying gas rates. It appears that the silica present either on the surface of the individual particles and/or incorporated in the bulk of the material that ultimately form the agglomerates permits the formation of smaller drops during the atomization process. If this was not the case, it would be necessary for the initial droplets to further divide during the drying process, and this does not seem to be likely.

Calcination at 300°C produces a surprising result. For the two samples with the lowest silica content there is some increase in agglomerate size following calcination, but it is very slight. For both of these samples the maximum for the agglomerate size is in the range of 40-60 μm as it was in these samples that had been only dried at 100°C. However, the agglomerate size for the catalyst containing 12.2 wt.% SiO_2 had increased appreciably to show a maximum in the 40-60 μm range, whereas the dried sample exhibited a maximum in the 20-40 μm range. It therefore appears that silica enhances agglomerate size growth during the calcination process.

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Figure 1. Synthesis routes showing the schematics of the procedure followed for making a 15 kg batch of promoted iron oxide catalysts.

Figure 2. Scanning electron micrograph from the sample RLS5.0-Si-I, dried at 100°C for 27 hours.

Figure 3

Figure 3. Energy dispersive X-ray spectrum from an agglomerate shown in Figure 2.

Figure 4. Scanning electron micrographs from RLS5.0-Si-IIA, dried at 100°C for 27 hours.

Figure 5. Energy dispersive X-ray spectrum from the sample RLS5.0Si-IIA, showing Fe, Si, K, O lines. These lines are indicated in the figure.

Figure 6. Elemental dot maps for the catalyst RLS5.0Si-IIA dried at 100°C. The last square is the image from which the dot map data were collected.

Figure 7. Electron micrographs from the catalyst RLS5.0Si-III, dried at 100°C.

Figure 8. Size distribution for the agglomerates for the three catalysts (a) 100°C and (b) 300°C.

Figure 9. Agglomerate size (in microns) of iron oxide catalysts dried at 100°C containing varying amounts of SiO₂.

3.2.5 PROMOTED IRON FISCHER-TROPSCH CATALYSTS. CHARACTERIZATION BY THERMAL ANALYSIS

ABSTRACT

The effects of metal and alkali promoters on precipitated iron oxide Fischer-Tropsch catalyst precursors are examined using thermal gravimetry (TG) and differential thermal analysis (DTA). A distinct exotherm corresponding to what appears to be the transformation from FeOOH to Fe_2O_3 is observed for unpromoted and promoted iron oxides where the promoter's ionic radius is less than approximately $0.7\text{\AA}$. The heat released during the exotherm is similar for unpromoted and promoted iron oxides corresponding to this size range. For promoters having ionic radii larger than $0.7\text{\AA}$, the exotherm occurs over a broad temperature range. Silica exhibits a unique propensity to stabilize against this transition, and appears to be present as two species. Increased loadings of Si cause a shift from the sharp, narrow temperature range exotherm to the broad transition observed for promoters with larger ionic radii.

INTRODUCTION

Iron catalysts find significant application in the ammonia synthesis [1] and Fischer-Tropsch synthesis [2]. In both of these applications the iron catalyst is promoted, and usually multiply promoted. Structural promoters, such as SiO_2 and Al_2O_3 , are added primarily to improve or maintain surface area, and thereby to extend the life of the catalyst. Alkali or alkaline-earth promoters are added to improve activity, selectivity and/or catalyst life. In many instances, the catalyst is prepared by precipitation of the iron as a hydrous oxide, oxyhydroxide or hydroxide. Promoters may be incorporated during the precipitation step, during the washing step or by impregnation following the washing step. The impregnation may be done prior to

adding the catalyst to the reactor, following a pretreatment, or added *in-situ* prior to or during the conversion.

One or more precondition steps are usually necessary before using the material for a catalytic reaction. This is true even for the unusual case where the precipitated Fischer-Tropsch catalyst is heated to the reaction temperature in the synthesis gas. Much more frequently, the dried material will be subjected to one or more heat treatments prior to or during the preconditioning process.

It has been observed that the surface area of promoted iron oxide catalysts varies with the size of the metal promoter [3]. Those promoters with an ionic radius smaller than iron produce a calcined material with a surface area higher than iron oxide while materials that contain a promoter with an ionic size larger than iron have a lower surface area than iron oxide. Since calcination is a common step in the preparation of most iron catalysts in both experimental laboratory and commercial scale synthesis, it is of interest to learn how a variety of promoters impact the thermal events that occur as the catalyst precursor is subjected to thermal treatments. The present paper is concerned with defining the impact of a variety of promoters on the weight loss, thermal events and the extent of heat liberated in the thermal events.

EXPERIMENTAL

Unpromoted iron hydroxide (or oxyhydroxide) was prepared by the precipitation of Fe^{III} nitrate (1M) by the addition of the amount of ammonium hydroxide that was calculated to produce a pH=8. The resulting dark brown precipitate was then filtered and washed four times with distilled deionized water prior to drying in flowing air at 100°C for 24 hours. Metal oxide promoted samples were prepared under similar conditions using a 15.6M ammonium hydroxide solution to effect precipitation from a

solution of iron nitrate and, in most cases, the appropriate metal nitrate (Table 1 indicates those instances when other salts were employed). In several cases the pH slightly exceeded 8.5. The silica promoted iron was coprecipitated from iron nitrate and silica gel, prepared from the hydrolysis of tetraethyl orthosilicate. Promoter loadings were 6% by weight based on the stable oxide following calcination in air. (The 6 wt.% refers to the nominal loading; in several instances (especially Al, Si and Zr) the material from several repeat preparations were in good (± 0.3 wt.%) agreement with the expected value.) Some physical properties of these samples are summarized in Table 1. Potassium and calcium were added to the 6% Al_2O_3 and 6% SiO_2 promoted samples by incipient wetness using solutions of potassium nitrate or calcium nitrate. Alkali loadings were 2%, 4% and 6% by weight. Another set of doubly promoted samples were prepared by sequential incipient wetness corresponding to 2% K, 2% Ca; 4% K, 4% Ca and 6% K, 6% Ca on the 6% Al and the 6% Si promoted iron oxides. All samples were dried in flowing air at 100°C for 12 hours and portions of each alkali or alkaline-earth promoted sample were calcined in air at 300°C for 6 hours in order to examine the effects of temperature. The results reported herein were obtained in batch precipitators. For the unpromoted and the Si and Al containing catalysts, the preparations have been scaled to the preparation by continuous precipitation of 2 to 10 kg samples. In one instance (Si/Fe + Si = 4.4) the procedure was scaled up to prepare a 70 kg batch. The surface areas of the materials from the larger scale preparation were similar to those of the smaller scale [4].

Differential thermal analysis (DTA) and thermogravimetry (TG) were performed using a Seiko SSC/5200 instrument. Typical sample size was 20-30 mg with aluminum oxide used as a reference. Each sample was heated in a He atmosphere from 25°C to

900°C at a rate of 20°C per minute and held for 10 minutes before cooling. A tin standard was analyzed under identical conditions in order to calculate the heat evolved during the exotherms observed for iron and promoted iron samples. These data are listed in Table 1.

X-ray diffraction patterns were obtained using a Phillips model 3100 instrument fitted with a CuK α radiation source.

RESULTS

The weight loss and differential thermal analysis curves for the iron-based samples indicate that essentially all of the weight loss for the unpromoted iron oxide (the sample will be referred to as though it was an oxide although it is realized that the initial material may be amorphous to X-rays or is a crystalline form of FeOOH) is that expected for the dehydration of a hydrous material rather than that of a salt hydrate such as, for example, CaSO₄•H₂O. There is a gradual weight loss upon heating to about 400°C; above this temperature there is essentially no weight loss (Figure 1). The weight loss corresponds to 10.5% of the initial sample suggesting a transformation from FeOOH to Fe₂O₃ (theoretical weight loss of 10.14%). During the period of the weight loss, the endothermic event is consistent with the gradual loss of water. However, following the dehydration period, an exothermic event occurs that is centered at 442°C. This event has been observed in other systems and has been termed a "glow phenomenon;" this usually occurs through a sintering of small particles to produce larger particles with a lower surface area [5,6]. The exotherm for the unpromoted iron oxide corresponds to 4.0 kCal (16.7 kJ)/mole of Fe₂O₃, a value in agreement with that expected to be associated with the loss of surface area. A sample of the unpromoted iron oxide was "amorphous" to X-rays following heating to 300°C to correspond to the

TGA but was converted to crystalline $\alpha\text{-Fe}_2\text{O}_3$ during heating for 4 hrs. at 400°C. The heat produced during the exotherm was determined by calibrating the instrument for the peak area of the heat of fusion corresponding to a tin standard measured under identical temperature program conditions. For the samples such as shown in Figure 1 or 2, the instrument program establishes a baseline that is determined by the broad "apparent peak" and there is little uncertainty in doing this. As the temperature for the exotherm peak increases and the peak decreases in intensity, both the position and magnitude of the exotherm becomes increasingly uncertain.

All of the samples listed in Table 1 exhibited weight loss curves that were similar to the unpromoted sample in that essentially all of the weight loss occurred prior to the exothermic event. Furthermore, the temperature-weight loss curve for all of the materials exhibited a similar shape, and all samples attained a constant weight at about the same temperature (less than 400°C as shown in Figure 1). No indication of a weight loss was observed that could be associated with the conversion of a supported hydrous oxide such as, for example, hydrous chromium oxide. No correlation was found between weight loss and temperature of the exotherm or ionic radius of the promoter metal.

When the ionic radius of the metal promoter was much larger than that of iron, the exotherm tended to become less distinct. For the chromium promoter (ionic radius of 0.69Å versus 0.64Å for iron) there is a distinct exothermic thermal event at 480°C (Figure 2). The results with magnesium and tungsten promoters, with ionic radii slightly larger than iron, were very similar to those shown in Figure 2 for chromium. However, for the samples promoted by the four metals with the largest ionic radii shown in Table 1 (Zr, Ca, Th, and Ba), there was no prominent, distinct exothermic event. The trace in

Figure 3 is typical of the type of DTA curves obtained for the materials promoted by the metals with the four largest ionic radii.

It appears that the temperature of the exotherm remains approximately constant and then declines as the ionic radius of the metal promoter approaches that of iron (Figure 4, Table 1). The exotherm temperature then increases as the ionic radius of the promoter increases beyond that of iron; the material promoted with magnesium appears, however, to exhibit a much higher exotherm temperature than anticipated by the trend established with the ionic radii. Repeat runs show that the heat liberated for the Mg promoted material is reproducible. The exotherm temperatures for the promoters with the largest radii are difficult or impossible to identify, due to the absence of a sharp peak.

The heat liberated during the exothermic event was about the same for the unpromoted iron oxide and for many of the promoted materials (23-26 cal/g; 96-109 J/g) (Figure 5). Less heat was liberated during the exothermic event for the two samples promoted with metals with the lowest ionic radii than for iron oxide. For the four materials promoted with the metals having the largest ionic radii, the heat liberated could not be estimated due to the poor definition of the exothermic event. It appears likely that the inability to observe the exothermic event with the materials promoted with the metals with the four largest ionic radii was due to the fact that the crystallization occurred over a broad temperature region in contrast to the materials that showed the transformation in a distinct, narrow temperature region.

A series of Si and Al promoted materials were prepared to contain 2, 6 and 12 atomic% of the metal oxide promoter. It appears that the weight loss during heating to 900°C is essentially the same for the unpromoted material and the ones containing

various promoter loadings. However, in both instances the materials that contained only 2 atomic% promoter lost less (20-30%) weight than the unpromoted material. It is not apparent why this should be the case. The temperature of the exothermic event increases with increasing loading of the promoter for both Si and Al; however, each succeeding addition, on an equivalent weight basis, is less effective in increasing the temperature of the exotherm (Figure 6). The data shown in Figure 6 make it apparent that of the two promoters, Si is more effective in increasing the exotherm temperature; furthermore, it appears that Al approaches a limiting effect at the 6 atomic% loading but that further increases in Si content should continue to cause significant increases in the temperature of the exotherm. The heat liberated during the distinct, narrow temperature range exotherm increases with the addition of the Al promoter and then declines slightly so that the heat released by the material containing 11 atomic% Al is about the same as that of the unpromoted iron oxide (Figure 7). The heat released declines as Si is incorporated in the iron oxide. At the same time, silicon is especially effective in retaining the iron oxide in an amorphous state [3], and this is the likely reason for the low value of the exotherm for the silicon promoted material. The amorphous structure is retained for the material containing 12% SiO₂ even following calcination in air at 500°C for four hours; presumably the fraction of Si that stabilizes the amorphous phase of iron oxide behaves much as that of, for example, thorium so that the crystallization occurs over a broad temperature range and the exotherm is not observed. On the other hand, some of the Si must be present in a form that increases the temperature of the exothermic event and transforms over a narrow temperature range. The decrease in the heat liberated with increasing Si content indicates that fraction of the added Si that is incorporated to produce the distinct, narrow temperature

range exothermic event decreases as the Si loading increases. The decrease in the heat liberated for the 3 atomic% Si sample indicates that 84% of the added Si is of the form that contributes to the higher-temperature, narrow-range exothermic event; this is 56% for the material with 6 atomic% Si and decreases to less than 10% for the material containing 12 atomic % Si. Based upon the heat liberated during the sharp exothermic event for the material promoted with silicon and for the unpromoted iron oxide, it is estimated that about 15% of the silicon is present in the form that leads to the distinct, narrow temperature region exothermic event.

Alkali promoters are utilized in Fischer-Tropsch catalysts in addition to silica, alumina, etc. The data (Figure 8) indicate that the addition of 2 or 6 atomic% K to the silica or alumina promoted materials cause only a slight increase in the exotherm temperature. However, in most cases, the addition of alkali causes a dramatic decrease in the heat liberated during the narrow temperature-range exotherm event (Figure 9). In the case of the alumina promoted material, the addition of potassium always causes a dramatic decrease in the heat liberated during the well-defined exothermic event even though the temperature at which this event occurs does not change significantly. Thus, it appears that the added alkali interacts with the alumina promoter. Furthermore, the fact that the heat liberated decreases with increased K indicates that a fraction of the AlO_2^- that would interact with iron oxide in the absence of K^+ , has been altered by interacting with K^+ . The trend in the decrease of heat liberated indicates that the iron oxide-alumina- K^+ interaction varies over a wide range in order to spread the exothermic event over a wide temperature range.

The situation with silica differs from that of alumina. It appears that the alkali has much less impact upon the amount of heat liberated in the well-defined region. This is

consistent with the view that the silica, unlike alumina, is present in a range of species even in the absence of K^+ .

The promoter has little or no impact upon Fischer-Tropsch catalytic activity during early time-on-stream. The impact of the promoter therefore is more important for determining activity retention (Figure 10) and, not shown, product selectivity. Thus, the addition of a promoter with a larger ionic radius (K^+) than Fe^{3+} leads to a more rapid decline in activity than for the catalyst containing only iron. On the other hand, adding a promoter with a smaller cation radius (Si^{4+}) than Fe^{3+} leads to a catalyst that retains activity for a longer time than the iron only catalyst. However, when both Si and K are present there must be a significant interaction with iron and/or the two added components that is not present when either promoter is present alone. Thus, the retention of activity is much better when both Si^{4+} and K^+ are present. In fact, samples prepared similar to the one that contains both Si^{4+} and K^+ have been utilized for up to 4,000 hours with a decline in CO conversion in the range of only 0.5 to 1.0% per week. Thus, the promoter influence on activity retention is an important factor but, because of the complex interactions, is beyond the scope of this manuscript.

DISCUSSION

The presence of a promoter dramatically alters the thermal conversions of a precipitated iron oxide catalyst precursor. In general, the presence of the promoter causes an increase in the temperature at which the exotherm occurs from that of the unpromoted iron oxide. As the mismatch of ionic radius between the promoter and iron ion increases, so does the temperature at which the exothermic event occurs. Presumably the fraction of the promoter that is effective in increasing the exotherm temperature is that which is present on the surface of the precipitated hydrous iron

oxide particles. If this is the case, then the fraction of the promoter that is on the surface increases as the ionic radius of the added metal ion becomes larger than that of iron. It is becoming increasingly apparent that the addition of anions, such as SO_4^{2-} , MoO_4^- , WO_4^- , etc., to the surface of a hydrous metal oxide inhibits the loss of surface area and the occurrence of the "glow phenomenon," or events that are similar to the glow phenomena [7-9]. However, it does not appear that all of the promoters having an ionic radius larger than iron would be present on the surface as an oxygen containing anion cluster. For example, it is likely that Ca^{2+} and Ba^{2+} would not be present on the surface as an anion cluster but rather as the cation. It therefore appears that these larger cations may also function by causing the anion clusters to interact with iron oxide to form a surface cluster that resembles $\text{Ca}_3(\text{FeO}_3)_2$ or CaFeO_2 .

All of the promoters employed in the study having an ionic radius smaller than 0.7Å interact in such a way that a distinct, narrow-range exothermic event occurs during the heating of the catalyst precursor. The heat released during this exothermic event is similar for nearly all of these promoters, and is very close to that of the unpromoted iron oxide. Therefore, the transformation responsible for the exotherm is a common one for the unpromoted and most or all of this grouping of promoted iron oxide catalyst precursors. The promoter does not cause an event to occur which is distinct from that observed in the unpromoted material, but rather provides a barrier that must be overcome for the event to occur. For the promoters with an ionic radius larger than about 0.7Å, the exotherm is difficult to observe, presumably because the transformations leading to the exothermic event occur over a wide range of temperatures. This implies that the promoters having larger ionic radii do not form a

specific compound but form instead a nearly continuous range of structures whose interactions between the iron oxide and the promoter varies almost continuously.

One could anticipate that Si and Al promoters should produce similar effects and that the thermal transformations of catalyst precursors containing either of these promoters should be similar. That expectation clearly does not coincide with the experimental observations. Both promoters do cause an increase in the temperature at which the exothermic event occurs; however, the Si promoter is more effective in doing this than is the Al promoter. The Al promoter causes an initial increase in the heat liberated during the exothermic event, but the heat liberated by a material containing 6 atomic% Al is about the same heat as the unpromoted iron sample. By analogy with other promoters, such as SO_4^{2-} , this implies that Al is present as the AlO_2^- anion at the conditions of the iron precipitation, and that this anionic species coats the surface of the iron oxide particles. However, it appears that silica is functioning in two roles. A portion of the silica causes an effect resembling the promoters with larger ionic radii by spreading the exothermic event over a wide range of temperatures not measurable by the experimental technique used in the present study. Another portion of the silica appears to behave as would be expected for a material with its ionic radius, causing the exothermic event to occur over a narrow temperature range. Thus, it appears that as the Si loading in the catalyst precursor is increased, an increasingly smaller fraction of the Si acts as the SiO_2^- anion to produce the narrow temperature range exotherm. Concurrently, an increasingly larger fraction appears to be present in a form that functions as a cation which could stabilize against the transformation by inducing the formation and bonding with a structure such as FeO_2^+ . This view of these two promoters suggests that Al should cover a larger fraction of the surface of the iron oxide

catalyst than a similar amount of Si would. The activity of the iron catalyst promoted with Al and carbided with CO begins to decrease as the Al loading reaches about 5 atomic%. On the other hand, the activity of the Si promoted catalyst does not decrease even as the Si loading is increased to 15 atomic%. These activity measurements [10] are consistent with the view that silica does not cover the surface of the iron oxide and the iron carbide catalyst resulting from the carbiding procedure, as effectively as the Al promoter does. One explanation for this is that the fraction of the Si promoter that functions as the cation species is a positively charged silica polymer, Si_xO_y^+ . Another would be the incorporation of Si in the bulk structure of the iron oxide.

CONCLUSIONS

The impact of added promoters upon the temperature at which an exothermic event (crystallization) occurs has been shown to depend upon the ionic radius of the promoter. Thus, the exotherm temperature decreases with increasing ionic radius. However, the heat liberated during this exothermic event does not appear to be related to the ionic size. While both Si and Al promoters increase the exotherm temperature, the heat liberated is nearly constant with increasing Al content but decreases with increasing Si content. These changes should occur during catalyst calcination and/or activation and, since promoters impact catalyst performance, may be crucial in scale-up for commercial production. However, it appears that, while the promoter impacts activity retention, it may have little impact upon the initial activity. When two promoters are incorporated, the beneficial effect of activity retention is enhanced more than is due to either promoter alone. The reason for this synergistic effect is not apparent.

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Table 1

Exotherm Temperature and Heat Evolved During Crystallization of Iron Catalysts
Containing 6 wt.% of Various Metal Oxide Promoters

<u>Promoter</u>	<u>Precursor</u>	<u>Ion</u>	<u>Ionic Radius (Å)</u>	<u>ΔH (cal g⁻¹)</u>	<u>Temperature of exotherm (°C)</u>
B	Boric Acid	B ³⁺	0.20	18.33	575
Si	Tetraethyl orthosilane	Si ⁴⁺	0.41	3.62	620
Al	Aluminum ^{III} nitrate	Al ³⁺	0.50	26.05	572
Mn	Manganese ^{II} nitrate	Mn ²⁺	0.54	25.10	537
V	Ammonium metavanadate	V ⁵⁺	0.59	23.16	522
M	Ammonium heptamolybdate	Mo ⁶⁺	0.62	23.16	491
None	---	Fe ³⁺	0.64	25.10	442
Mg	Magnesium nitrate	Mg ²⁺	0.65	23.16	573
WO	Ammonium metatungstate	W ⁶⁺	0.68	23.16	512
Cr	Chromium ^{III} nitrate	Cr ³⁺	0.69	30.21	480
Zr	Zirconium oxynitrate	Zr ⁴⁺	0.79	--	(broad)
Ca	Calcium nitrate	Ca ²⁺	0.99	--	~616 (broad)
Th	Thorium nitrate	Th ⁴⁺	0.99	--	~541 (broad)
Ba	Barium nitrate	Ba ²⁺	1.35	--	~585 (broad)

Figure 1. Thermal gravimetric (TG) and differential thermal analysis (DTA) curves for the unpromoted iron oxide sample.

Figure 2. Thermal gravimetric (TG) and differential thermal analysis (DTA) curves for the 6% chromium oxide promoted iron oxide.

Figure 3. Thermal gravimetric (TG) and differential thermal analysis (DTA) curves for the 6% barium oxide promoted iron oxide.

Figure 4. Exotherm temperature for unpromoted and promoted (6% metal oxide) iron oxides.

Figure 5. Heat liberated during the exotherm for unpromoted and promoted (6 wt.% metal oxide) iron oxides.

Figure 6. Exotherm temperature for Si and Al promoted iron oxides.

Figure 7. Heat liberated during exothermic event for Si and Al promoted iron oxides.

Figure 8. Exotherm temperature for K and Si or Al doubly promoted iron oxides.

Figure 9. Heat liberated during the exothermic event for K and Si or Al doubly promoted iron oxides.

Figure 10. CO conversion with time-on-stream for catalyst containing: $\circ$, only iron; $\square$, iron + 0.72 K; $\diamond$, iron + 3.6 Si; $\triangle$, iron + 3.6 Si and 0.71 K.

3.3.0 Task 4. Catalyst Testing

3.3.1 Deactivation of Iron-based Catalysts for Slurry-Phase Fischer-

Tropsch Synthesis

ABSTRACT

Deactivation rates and aged catalyst properties have been investigated as a function of time on stream for iron-based Fischer-Tropsch catalysts in the presence/absence of potassium and/or silicon. There is a synergism in activity maintenance with the addition of both potassium and silicon to an iron catalyst. The addition of silicon appears to stabilize the surface area of the catalyst. Catalysts containing only iron or added silicon with or without potassium consist mainly of iron oxide at the end of the run. However, iron carbides are the dominant phase of the iron catalyst with added potassium alone. Catalyst surface areas increase slightly during synthesis. The bulk phase of the catalyst does not correlate to the catalyst activity. The partial pressure of water in the reactor is lower for potassium-containing catalysts and is not a reliable predictor of catalyst deactivation rate.

INTRODUCTION

The Fischer-Tropsch Synthesis (FTS) converts synthesis gas (a mixture of CO and H₂) to hydrocarbons. Iron-based catalysts lose activity with time on stream (TOS). The rate of deactivation is dependent on the presence/absence of promoters such as potassium and/or binders such as silica [1,2]. Several possible causes of catalyst deactivation have been postulated [3]: (i) Sintering, (ii) Carbon deposition, and, (iii) Phase transformations. With respect to phase transformations, there is considerable disagreement whether the active phase for the FTS is iron oxide or carbide [4,5]. In

addition, certain reactor conditions, such as a high partial pressure of water, are known to cause a decline in activity [6].

There were two major objectives of this study. Firstly, the effects of the addition of potassium and/or silicon on catalyst deactivation rates and changes in catalyst properties with TOS were investigated. Secondly, the possible causes of catalyst deactivation were examined by following aged catalyst properties and reactor conditions as a function of TOS for each catalyst. The FTS was carried out in a continuous-flow stirred slurry reactor to ensure uniformity in catalyst aging and reactor conditions throughout the reactor. The aged catalyst properties examined as a function of TOS were total surface areas, carbon deposits and phase transformations.

EXPERIMENTAL

Four precipitated iron-based catalysts were used. The first catalyst consisted of only iron. The other catalysts contained either added potassium, added silicon or both. The catalysts were designated in terms of the atomic ratios as: 100Fe, 100Fe/3.6Si, 100Fe/0.71K and 100Fe/3.6Si/0.71K. The catalysts were prepared by continuous precipitation from iron (III) nitrate and concentrated ammonium hydroxide. For silica-containing catalysts, a colloidal suspension of tetraethyl ortho silicate was mixed with the iron nitrate solution prior to precipitation. Potassium was added to the catalysts in the form of potassium tertiary butoxide during the loading of the FTS reactor.

The FTS was carried out in a 1 liter continuous flow stirred tank slurry reactor. The vapor phase products exiting the reactor passed through two traps in series. The first trap was maintained at 100°C while the second was maintained at 0°C. The second trap served to condense almost all of the water present in the product stream. Further details of the reaction system and product analysis (both on- and off-line) have been

reported previously [7]. A known amount (~ 70 g) of the catalyst was charged to the reactor along with 300 g of a hydrocarbon oil supplied by Ethyl Corp. (carbon number range of about C₂₅ - C₃₀). The catalyst was pretreated with a continuous flow of CO at 2.0 NL/hr-gFe at 270°C, 175 psig for 24 hours. Subsequently, the FTS was carried out at 270°C, 175 psig with a synthesis gas having an H₂/CO ratio of 0.7 at a flowrate of 3.4 NL/hr-gFe. Both during pretreatment and synthesis, small amounts of catalysts (0.1 to 0.2 g per sample) were removed from the reactor at various TOS. The aged catalyst samples were Soxhlet-extracted with xylene prior to analysis. These aged catalyst samples were examined to determine BET surface areas, elemental carbon and hydrogen contents and bulk catalytic phases.

Elemental carbon and hydrogen contents were determined using a Leco CHN analyzer wherein the catalyst sample was placed in a furnace at 1350°C under flowing oxygen. All of the carbon and hydrogen in the sample was converted to CO₂ and water respectively which were then measured. Bulk catalyst phases were determined by two methods: X-ray diffraction (XRD) and Mossbauer spectroscopy (MS). X-ray diffraction patterns were obtained using a Phillips APD X-ray diffraction spectrometer equipped with a Cu anode and a Ni filter operated at 40 kV and 20 mA (CuK α =1.5418 Å). Mossbauer spectra of the catalyst samples were obtained with a constant acceleration spectrometer using a radioactive source consisting of 50 to 100 mCi of ⁵⁷Co in a Pd matrix.

RESULTS AND DISCUSSION

The conversion of synthesis gas is a measure of the FTS activity of a catalyst. The catalysts studied show varying rates of decline in synthesis gas conversion with TOS (Figure 1). Note that the conversions for different catalysts are compared at the

same synthesis gas space velocity which is defined as normal liters of synthesis gas per gram of iron in the reactor. The addition of silica alone (100Fe/3.6Si) slows the decline in FTS activity as compared to a catalyst containing only iron (100Fe). In contrast, the addition of potassium alone increases the deactivation rate as compared to a catalyst containing only iron (100Fe). The catalyst containing both silica and potassium (100Fe/3.6Si/0.71K) exhibits the lowest deactivation rate. Hence, there is a synergism in the maintenance of FTS activity with the addition of both silica and potassium.

The surface areas of the catalysts are substantially decreased during pretreatment (Figure 2). During synthesis, however, the surface area of the catalysts increases slightly. It is postulated that this slight increase may be due to the deposition of porous carbon on the catalyst surface. Catalysts containing silica exhibit higher surface areas on preparation, and during pretreatment and synthesis. Hence, silica appears to stabilize the surface area of the catalysts. Since the total surface area increases during synthesis, the presence/absence of sintering during FTS cannot be deduced from BET surface area measurements.

The catalyst sample is exposed to air for a short time during XRD and MS. However, using similar procedures Mossbauer spectra have been previously obtained showing 97% of the iron in a catalyst as iron carbide and substantial (36%) amounts of metallic iron in another catalyst [8]. Hence, re-oxidation of catalyst phases during XRD and MS is negligible. The results from XRD indicate the following events occurring during pretreatment and synthesis: The catalyst as charged into the reactor is in the form of an oxide and/or an oxyhydroxide. During pretreatment in CO, the catalyst is rapidly converted to Fe_3O_4 which is subsequently partially converted in a slow step to a

mixture of carbides (Fe_5C_2 and $\text{Fe}_{2.2}\text{C}$) as shown in Figure 3. During synthesis, the relative amounts of carbide and oxide change dependent on the catalyst composition. For the catalyst containing only potassium, the catalyst at the end of the run consists of mainly carbides (Figure 3) while for the other catalysts the oxide is the dominant phase at the end of the run (example of 100Fe given in Figure 3). These qualitative observations are consistent with quantitative results obtained by MS. Since the catalyst containing potassium alone has the highest deactivation rate, it is tempting to conclude that the iron oxide is the active phase, or at least more active than the carbide, for the FTS. However this is not true as the bulk composition of the catalyst, as shown below, does not correlate to the catalyst activity. Figure 4 shows quantitative results of the bulk composition of the catalyst obtained by MS as a function of TOS for the catalyst with the lowest deactivation rate (100Fe/3.6Si/0.71K). The results are similar to those for the catalyst containing only iron but are different from those obtained for the catalyst containing iron and potassium but no silicon. The bulk composition of the catalyst changes greatly with TOS. At small TOS, iron carbide is the dominant phase while at long TOS the catalyst consists predominantly (80%) of iron oxide. Note, however, that synthesis gas conversion for this catalyst varied only slightly (between 80 and 90%) with TOS. Hence, the particular active phase of the catalyst (oxide or carbide) cannot be deduced from bulk catalyst compositions.

The carbon measured as a result of high temperature oxidation can be due to either CH_x species on the catalyst surface, or the oxidation of iron carbides, or the oxidation of carbon deposits. The contribution of CH_x species can be estimated by elemental analysis of hydrogen and assuming the value of x to be 2. The remaining carbon measured on the catalysts (Figure 5) ranged from 10 to 30 wt.%. Note that if all

the iron in the catalyst were converted to carbide the carbon amount would be 8 to 9 wt.% assuming the iron carbides are Fe_5C_2 and $\text{Fe}_{2.2}\text{C}$ as shown by XRD and MS. Hence, substantial amounts of carbon deposits were present on the catalyst surface. The addition of potassium to the catalyst containing only iron (100Fe/0.71K) increased the amount of carbon measured as well as its rate of increase. However, this may have been due to the high amount of carbide formed on this catalyst during synthesis as shown by XRD and MS. The catalyst with the lowest deactivation rate (100Fe/3.6Si/0.71K) contained substantial amounts of carbon at the end of the run even though its activity was quite stable. Recall that this catalyst consisted mainly of iron oxide so that the carbon measured consisted mainly of carbon deposits. Hence, the amount of carbon deposits on the catalysts does not correlate with the rate of deactivation.

As stated previously, almost all of the water present in the product stream is condensed in a trap downstream of the reactor maintained at 0°C. It is further assumed that the uncondensed gases leaving the trap are saturated with water. The partial pressure of water is then calculated by measuring the total flow rate of the uncondensed gases and the composition of the other products and unconverted reactants. This procedure yields oxygen component balances of greater than 96%. The value of the partial pressure of water in the reactor depends on the presence/absence of potassium promoter (Figure 6). The partial pressure of water is low for catalysts containing potassium and decreases slightly with TOS. In contrast, the partial pressure of water is higher for catalysts without potassium and increases with TOS. Low water partial pressures for potassium-containing catalysts may be due to the higher rates of the water gas shift (WGS) reaction observed over these catalysts. A high partial

pressure of water is known to deactivate the catalyst [6]. However, the results shown in Figure 6 indicate that the value of the partial pressure of water does not correlate to the rate of catalyst deactivation. For instance, both the catalyst with the highest and lowest deactivation rates (100Fe/0.71K and 100Fe/3.6Si/0.71K respectively) exhibit similar partial pressures of water.

It has been postulated that changes in the amount of iron oxide on the catalyst surface (as opposed to the bulk followed by XRD and MS) can be followed by a comparison of the ratios of the rates of the FTS to that of the WGS with TOS [9]. It is postulated [9] that iron oxide is more active than iron carbides for the WGS than for the FTS and hence, a decrease in the ratio of the rate of the FTS to the rate of the WGS indicates an increase in the amount of iron oxide on the catalyst surface. However, none of the catalysts examined in this study show a decline in the reaction rate ratio with TOS (Figure 7). For catalysts containing potassium, the reaction rate ratio changes negligibly with TOS, while the reaction rate ratio actually increases with TOS for the catalysts without potassium. Further, the increase in the reaction rate ratio with TOS for catalysts without potassium may not be due to changes in surface phases. We have earlier shown [10] during kinetic studies that the ratio of the reaction rate of the FTS to that of the WGS increases with residence time (not TOS) or synthesis gas conversion for iron-based catalysts. Hence, the increase in the reaction rate ratio observed for two of the catalysts studied may be a consequence of decreasing synthesis gas conversion (due to deactivation) rather than a change in surface catalyst phases.

CONCLUSION

Increasing and decreasing deactivation rates of iron FTS catalysts are observed upon the addition of potassium and/or silicon respectively. There is a synergism in the

maintenance of activity with the addition of both potassium and silicon leading to a low deactivation rate.

Changes in catalyst properties and reactor conditions with TOS depend upon the presence/absence of potassium and silicon. The addition of silicon appears to stabilize the surface area of the catalyst both on preparation and during pretreatment and synthesis. At the end of pretreatment, all of the catalysts studied consist of a mixture of iron oxide (Fe_3O_4) and iron carbides (Fe_5C_2 and $\text{Fe}_{2.2}\text{C}$). During synthesis, the catalyst containing potassium alone is converted predominantly to iron carbides at the end of the run. The other catalysts, however, decline in the amount of iron carbide and increase in the amount of iron oxide during synthesis. The addition of potassium alone to an iron catalyst substantially increases the amount of carbon (from carbon deposits and carbides) measured by high temperature oxidation of aged catalyst samples. The partial pressure of water in the reactor is low and decreases with TOS for potassium-containing catalysts while it is higher and increases with TOS for the catalysts without potassium.

Possible causes of catalyst deactivation have been investigated in this study. The surface areas of aged catalyst samples increase with TOS during synthesis possibly due to porous carbon deposits. Hence, information from total surface area on sintering as a possible mechanism of deactivation is inconclusive. Measurement of the amount of carbon deposits on the catalysts by high temperature oxidation is complicated due to the contribution from iron carbides. The bulk composition of the catalyst having the lowest deactivation rate changes greatly during synthesis whereas the synthesis gas conversion changes negligibly. This implies that the catalyst bulk composition does not correlate to the rate of activity decline. The value of the partial of

water as well as its variation with TOS are similar for the catalysts with the highest and lowest deactivation rates. Hence, water partial pressure is not a reliable predictor of the catalyst deactivation rate.

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Figure 1. Synthesis gas conversion as a function of time-on-stream.

Figure 2. Catalyst surface areas as a function of time-on-stream (TOS). Negative TOS denote catalyst pretreatment; positive TOS denote Fischer-Tropsch synthesis.

Figure 3. X-ray diffraction results for two catalysts (100Fe and 100Fe/0.71K) during pretreatment and at the end of synthesis ((1) Fe₃O₄, (2) χ-Fe₅C₂, (3) ε-Fe_{2.2}C).

Figure 4. Bulk composition of catalyst: 100Fe/3.6Si/0.71K from Mössbauer spectroscopy as a function of time-on-stream. Negative TOS denote catalyst pretreatment; positive TOS denote Fischer-Tropsch synthesis. S.P. denotes superparamagnetic.

Figure 5. Amount of carbon deposits and carbon in the form of iron carbide as a function of time-on-stream (TOS). Negative TOS denotes catalyst pretreatment; positive TOS denotes Fischer-Tropsch synthesis.

Figure 6. Partial pressure of water as a function of time-on-stream.

Figure 7. Ratio of the reaction rates of the Fischer-Tropsch synthesis to the water-gas shift reaction as a function of time-on-stream.

3.3.2 Fischer-Tropsch Synthesis. Conversion of Alcohols over Iron Oxide and Iron Carbide Catalysts

ABSTRACT

Both iron oxide (Fe_2O_3) and iron carbide catalysts are active for the dehydration of tertiary alcohols; the oxide catalyst is not reduced nor is the carbide oxidized by the steam generated during the dehydration reaction. Secondary alcohols are selectively converted to ketones plus hydrogen by both the iron oxide and carbide catalyst. Fe_2O_3 is reduced to Fe_3O_4 during the conversion of secondary alcohols. Both iron carbide and oxide catalysts dehydrogenate a primary alcohol (C_n) to an aldehyde; however, the aldehyde undergoes a secondary ketonization reaction to produce a symmetrical ketone with $2n-1$ carbons. These results suggest that dehydration of alcohols to produce olefins makes a minor, if any, contribution during Fischer-Tropsch synthesis with an iron catalyst at low pressure conditions.

INTRODUCTION

The conversion of syngas, a mixture of CO and H_2 , was initially believed to occur through the formation of an iron carbide which subsequently underwent hydrogenation to hydrocarbons (1). Later, a mechanism was advanced which involved the formation of an oxygen-containing surface species which underwent a series of combination-dehydration steps, ultimately leading to a primary alcohol or an alkene (2). Isotopic tracer studies by Emmett and co-workers provided data which was considered to provide strong support for the oxygen-containing intermediate (3-11). As sophisticated surface science instrumentation became available, their use showed that the metal surface was covered with carbon but that little, if any, surface oxygen could be detected. Thus, a mechanism involving the dissociation of CO to form C and O

adsorbed on the surface became widely accepted (*for example, 12-15*). In this mechanism, the adsorbed O was hydrogenated to water which rapidly desorbed while the adsorbed C was hydrogenated to form adsorbed CH, CH₂ and CH₃ groups. While any of these groups could be involved in the formation of ethylene and higher hydrocarbons, the methylene groups was considered in most mechanisms to be the surface species which underwent polymerization to produce an Anderson-Schulz-Flory distribution of hydrocarbon products.

In the case of an iron Fischer-Tropsch catalyst, the carbide phase could be formed following activation in either CO alone or with a mixture of CO/H₂ (*16,17*). In addition, any metallic iron formed by hydrogen reduction of the iron oxide catalyst precursor was quickly converted to iron carbides when the activated catalyst was exposed to the synthesis gas (*18*). However, during synthesis the iron carbide was gradually converted to a mixture containing both iron carbides and Fe₃O₄; the extent and rate of formation of the iron oxide phase depended upon the operating conditions such as CO conversion, water-gas-shift activity, promoter levels, and time-on-stream. Thus, the iron in a "working, steady-state" catalyst is present as a mixture of the oxide and carbide phases. However, while an attractive model for the working catalyst was a surface layer of iron carbide supported on a core of Fe₃O₄, data to define the structure of the working catalyst is still lacking (*19*).

Recently, isotopic tracer studies using a variety of alcohols, alkenes and carbon dioxide have produced results for iron catalysts that were consistent with a chain initiating species that contains oxygen (*20-27*). Thus, it is of interest to define the pathways for conversion of various alcohols using iron oxide and iron carbide catalysts and that is the subject of this paper.

EXPERIMENTAL

Catalyst. The iron oxide catalyst was prepared by adding concentrated ammonia to a 1M iron nitrate solution to produce a pH of about 10.5. The solid was collected and washed by repeated dispersion/filtration cycles; at the end of the washing cycles the pH was in the 7-8 range. After drying overnight at 110°C, the material had a BET surface area of 252 m²/g. The material following calcination at 300°C had an X-ray diffraction pattern consistent with α -Fe₂O₃. An iron oxide catalyst that contained 6 wt.% thoria was also prepared using a published procedure (28); this material was also α -Fe₂O₃ following calcination at 300°C.

The iron carbide catalyst was prepared by treating the α -Fe₂O₃ sample for 24 hr. in a flow of CO at 1 atm. and 300°C. Prior to use, the sample was flushed with nitrogen for 30 minutes. To obtain a sample of the carbide catalyst for X-ray analysis, the material was passivated at room temperature by passing nitrogen containing 1% oxygen over the iron carbide for about three days.

Conversions. A plug flow quartz reactor with the catalyst located in the middle was utilized. Glass beads were placed on top of the catalyst bed to serve as a preheater and a thermowell extended into the middle of the catalyst bed. During the run the alcohol was added by a syringe pump at atmospheric pressure without a diluent gas. Liquid samples were collected at appropriate intervals.

The iron oxide catalyst was activated overnight in a flow of air at 300°C prior to a run. To start a run, the air flow was terminated and the catalyst was flushed with dry nitrogen for 30 minutes. The nitrogen flow was stopped and the alcohol flow was then started. The alcohols were purchased from Aldrich and were used without purification.

The liquid samples that were collected at appropriate time intervals were analyzed by g.c. using a DB-5 column.

The iron carbide catalyst was prepared and flushed with nitrogen for about 15 minutes immediately prior to use for the alcohol conversions.

RESULTS

The conversion of 2-octanol at 275°C showed that the iron oxide catalyst was very selective for dehydrogenation but had little dehydration activity (Figure 1). Prior to the run the catalytic material was α -Fe₂O₃ (Figure 2a) but following the run the catalyst contained both α -Fe₂O₃ and Fe₃O₄ (Figure 2b). Thus, the hydrogen produced during alcohol dehydrogenation was effective in reducing the catalyst to Fe₃O₄, and the extent of reduction would presumably depend upon the length of the time that the catalyst was exposed to the flow of alcohol.

The conversion results for the thoria-containing catalyst are very similar to the run with the α -Fe₂O₃/Fe₃O₄ catalyst mixture. While the selectivity for dehydrogenation is slightly lower for the thoria containing catalyst, it has a selectivity and activity that is similar to the iron oxide catalyst (Figure 1). Following 5 hr. use as a catalyst for the conversion of 2-octanol, the X-ray diffraction pattern of this material was similar to that of the α -Fe₂O₃ catalyst that did not contain thoria (Figure 3). However, peaks at $2\theta = 31.9, 45.8$ and 66.8 , corresponding to ThO₂, were evident in the X-ray diffraction pattern for this material in addition to those for a mixture of α -Fe₂O₃/Fe₃O₄ (Figure 2c).

3-Methyl-3-pentanol, a tertiary alcohol which cannot undergo direct dehydrogenation to a ketone, was converted with the α -Fe₂O₃ catalyst. At 230°C, the catalyst was active only for dehydration to produce a mixture of cis- and trans-3-methyl-2-pentenes. Following 5 hr. use as a catalyst, the alcohol flow was terminated, the

catalyst flushed with nitrogen at reaction temperature, and then cooled to room temperature in a nitrogen flow. The X-ray diffraction pattern of the material was identical to that of the initial catalyst (Figure 3), indicating that the conversion of this tertiary alcohol did not effect any reduction of the catalyst, and this is the expected result. The conversion data for 3-methyl-3-pentanol (Figure 4) show that the tertiary alcohol is converted more rapidly than 2-octanol, a secondary alcohol.

3-Methyl-3-pentanol was also converted with an iron carbide catalyst using similar conditions as with the Fe_2O_3 catalyst except for the flow. Since the flow rate was about 1.7 times greater with the iron carbide catalyst, the iron carbide catalyst is about twice as active for 3-methyl-3-pentanol dehydration as the iron oxide catalyst is.

3-Pentanol was run at 230 and 260°C. At these two temperatures, the selectivity for dehydrogenation is almost the same although the conversion at 260°C is higher than that at 230°C. For both of these runs, the catalytic activity for 3-pentanol conversion did not decline significantly during the run (Figure 5). The X-ray diffraction pattern of the catalyst exhibited peaks corresponding to both $\alpha\text{-Fe}_2\text{O}_3$ and Fe_3O_4 following the conversion of 3-pentanol (Figure 3b) These experiments confirm that the reduction of the catalyst occurs due to exposure to the secondary alcohol.

In another run, the $\alpha\text{-Fe}_2\text{O}_3$ was reduced at 270°C for 5 hr. in a flow of hydrogen and then cooled to 230°C in hydrogen flow. A flow of 2-octanol was initiated and the flow of hydrogen was terminated. The catalyst exhibited activity for 2-octanol conversion; however, the selectivity for dehydrogenation was lower (ca. 0.83 vs. 0.96) at 230°C than at 270°C (Figure 4).

The $\alpha\text{-Fe}_2\text{O}_3$ was treated with CO at 260°C for 18 hr. to convert the iron oxide to an iron carbide. Following the treatment with CO the catalyst was flushed with nitrogen,

then a flow of 2-octanol was started and the nitrogen flow was terminated. This iron carbide catalyst had an activity and selectivity for dehydrogenation that exceeds that of the catalyst comprised of a mixture of α -Fe₂O₃ and Fe₃O₄ (Figure 6) and does not lose activity during 8 hrs. Following use as a catalyst for 8 hrs., the sample was flushed with nitrogen and cooled to room temperature. The X-ray diffraction pattern of this sample following use as a catalyst contains peaks that are consistent with both iron carbides and Fe₃O₄ (Figure 7), with the carbide being the dominant component. A chemical analysis of the sample following use as a catalyst showed that it contained 9.0 percent carbon, a value that is consistent with the sample being Fe_{2.2}C (9.67% C).

While secondary alcohols may be formed during the Fischer-Tropsch synthesis, a primary alcohol is the dominant alcohol for each carbon number. Thus, 1-octanol was converted over the iron oxide and the iron carbide catalysts. This alcohol underwent conversion by dehydrogenation to the aldehyde. The conversion increased initially and then remained essentially constant with time. The aldehyde underwent a secondary reaction that involved decarbonylation (and/or decarboxylation) to produce CO/CO₂ and the formation of a 15-carbon number symmetrical ketone. This reaction has been observed frequently during the conversion of primary alcohols with metal oxide catalysts that possess dehydrogenation properties (29). Likewise, the selectivity for 1-octanal decreased as the conversion increased. Initially 40 mole% of the products from the conversion with the catalyst was 1-octanal and the remainder was 8-pentadecanone; after the first hour 1-octanal accounted for only 26-29 mole% of the products, the remainder being 8-pentadecanone. As the activity of the iron carbide increased, the selectivity for 1-octanal decreased from 88 mole% to about 65 mole%. Thus, the iron carbide catalyst exhibited an activity for 1-octanol conversion that was about 3-4 times

that of the iron oxide catalyst and it had a selectivity for 1-octanal that was 2-2.5 times that of the iron oxide catalyst. Neither the iron oxide nor the carbide catalyzed dehydration of 1-octanol since only traces octenes were observed.

DISCUSSION

The catalytic material remains Fe_2O_3 during the conversion of 3-methyl-3-pentanol. This is not surprising since a tertiary alcohol cannot undergo dehydrogenation; rather it is dehydrated to produce an olefin and water.

The iron carbide catalyst does not undergo measurable conversion to the oxide. Likewise, the greater activity of the iron carbide, compared to Fe_2O_3 , suggests that even the surface remains the carbide during the dehydration of 3-methyl-2-pentanol and the generation of water vapor.

On the other hand, Fe_2O_3 is reduced, at least partially, to Fe_3O_4 during the conversion of secondary alcohol. However, the iron oxide is not converted to an iron carbide during the conversion of this alcohol, at least not to an extent so that the carbide phase can be detected by X-ray diffraction (XRD). The sample containing 6 wt.% ThO_2 also underwent conversion to a mixture of Fe_2O_3 and Fe_3O_4 ; in addition, a ThO_2 phase was formed so that it could be detected by XRD. This is surprising since it has been reported that when this amount of thorium is present in an iron catalyst it provided a material that had superior activity for the water-gas shift reaction than a similar material that did not contain thorium (28). It is difficult to understand why thorium should impact the activity for water gas shift if phase separation occurs in a reducing atmosphere.

If Fe_2O_3 is treated in CO to produce iron carbides, the material that remains following conversion of 2-octanol during 8 hrs is predominantly iron carbides. Thus, the

carbide is not converted to the oxide in the presence of the small amount of water produced during the dehydration of 2-octanol, primarily during the early reaction period, to an extent such that the oxide(s) can be detected by XRD.

Except during an initial break-in period, the pure iron oxide and the iron oxide sample containing 6 wt.% ThO₂ were very selective dehydrogenation catalysts for primary and secondary alcohols. Only with the tertiary alcohol, where dehydrogenation is not possible, was the iron oxide catalyst selective for dehydration.

With the secondary alcohol, the iron oxide catalyst was very selective in dehydrogenating the alcohol to the corresponding ketone. Essentially no secondary reaction products were observed.

With the primary alcohol, the iron oxide catalyst was selective for dehydrogenation to the corresponding aldehyde. However, the aldehyde underwent a secondary reaction in which it was converted to a symmetrical secondary ketone plus either CO or CO₂. This reaction is known to occur when primary alcohols are converted over a variety of metal oxide catalysts (29). In this reaction it resembles the ketonization reaction that many metal oxide catalysts effect when starting with an acid. However, the mechanism for these reactions has not been clearly elucidated to date.

The iron carbide catalyst has a selectivity that resembles that of iron oxide but it is about twice as active for the conversion of the secondary alcohols. The higher activity of the iron carbide catalyst implies that either the surface is not oxidized to the oxide during the conversion of the alcohol or the oxycarbide that is formed on the iron carbide surface is more active than the iron oxide surface. The chemical composition of the gas phase is such that the iron is expected to be present in the carbide phase (30). A similar conclusion is reached for the conversion of 1-octanol over the iron oxide and

carbide catalysts. The iron carbide is about 4 times as active for the conversion of 1-octanol as the iron oxide and has only about half the activity for the formation of a symmetrical ketone from the primary dehydrogenation product, 1-octanal.

It has been demonstrated convincingly that alcohols can serve to initiate chain growth during the Fischer-Tropsch reaction (27). Furthermore, when using a promoted iron catalyst, the alcohol incorporates into the Fischer-Tropsch products about 50-100 times greater than the alkene that would be formed from dehydration of the alcohol. The present data indicate that the primary reaction of an alcohol that is formed during the Fischer-Tropsch synthesis is to undergo dehydrogenation to the aldehyde and this is true for both Fe_3O_4 and iron carbide catalysts. The present results indicate that reincorporation of the alcohol into Fischer-Tropsch products is not through an alkene intermediate that is formed by the dehydration of the alcohol. The results are consistent with the Fischer-Tropsch mechanism requiring an initiation step that involves an oxygen-containing species, and not a surface carbon or carbene intermediate.

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Figure 1. The conversion of 2-octanol for the Fe₂O₃ (□) and Fe₂O₃-ThO₂ (○) catalysts and the selectivity for dehydrogenation for the Fe₂O₃ (■) and Fe₂O₃-ThO₂ (●) catalysts [275°C, 1 atm, LHSV = 3.2 h⁻¹].

Figure 2. The X-ray diffraction patterns for: (a) the Fe₂O₃ catalyst (bottom); (b) the Fe₂O₃ catalyst after use for the conversion of 2-octanol (middle), and (c) the thoria containing catalyst after use for the conversion of 2-octanol (top).

Figure 3. The X-ray diffraction pattern for the Fe_2O_3 catalyst following (a) use for the conversion of 3-methyl-3-pentanol (top) and (b) of Fe_2O_3 following use for the conversion of 3-pentanol (bottom).

Figure 4. The conversion (∇) and dehydrogenation selectivity ($\blacklozenge$) for 3-pentanol ($\text{LHSV} = 1.5 \text{ h}^{-1}$) with the Fe_2O_3 catalyst; the conversion ($\blacksquare$) and dehydration selectivity ($\bullet$) for 3-methyl-3-pentanol ($\text{LHSV} = 3.2 \text{ h}^{-1}$) with the Fe_2O_3 catalyst; and the conversion ($\blacktriangledown$) and dehydration selectivity ($\triangle$) for 3-methyl-3-pentanol ($\text{LHSV} = 5.4 \text{ h}^{-1}$) the iron carbide catalyst (230°C , 1 atm).

Figure 5. The conversion (□) and dehydrogenation selectivity (◇) for the Fe_2O_3 catalyst following reduction in hydrogen at 230°C , 1 atm, $\text{LHSV} = 1.5 \text{ h}^{-1}$.

Figure 6. Conversion of 2-octanol with Fe_2O_3 (275°C , 1 atm, $\text{LHSV} = 3.2 \text{ h}^{-1}$) (□) and iron carbide (275°C , 1 atm, $\text{LHSV} = 3.2 \text{ h}^{-1}$) (○) and the dehydrogenation selectivity with Fe_2O_3 (■) and iron carbide (●).

Figure 7. X-ray diffraction scan of the iron carbide catalyst following use for the conversion of 2-octanol at 275°C, 1 atm and LHSV = 3.2 h⁻¹.

Figure 8. The conversion (▽; 275°C, 1 atm, LHSV = 3.3 h⁻¹) of 1-octanol with Fe₂O₃ and iron carbide (○; 275°C, 1 atm, LHSV = 3.3 h⁻¹) and the dehydrogenation selectivity to 1-octanal for Fe₂O₃ (▼) and iron carbide (●). [The low selectivity is due to formation of 8-pentadecanal from 1-octanal by secondary reactions].

3.3.3 A Comparison of Fischer-Tropsch Synthesis in a Slurry Bubble

Column Reactor and a Continuous Stirred Tank Reactor

Abstract

Fischer-Tropsch synthesis (FTS) was studied using a precipitated Fe/K catalyst in a improved short slurry bubble column reactor (SBCR) equipped with a satisfactory reactor-wax separation system and a continuous stirred tank reactor (CSTR) using the same experiment conditions. The catalyst in the SBCR had a lower catalytic activity. Methane and the products of the gas are higher in the CSTR. Some effects may be related to different mixing heat, mass transfer phenomena between two reactors. The C_3+ hydrocarbons ($C_3+H.C.$) with synthesis gas ($CO+H_2$) conversion ratio had similar values.

Introduction

A SBCR is a gas-liquid-solid reactor in which the finely divided solid catalyst is suspended in the liquid by the rising gas bubbles. It offered the following advantages: (a) the ability of the liquid phase to handle the large heats of reaction, (b) low H_2/CO ratio synthesis gas without needing a preliminary water-gas shift step, and (c) relatively low capital and operating cost. A considerable interest has been expressed in using the SBCR to carry out FTS.

FTS takes place in a SBCR where the synthesis gas is converted on catalysts suspended in a liquid as fine particles. The synthesis gas flows as small bubbles through the catalyst suspension. The products are volatile under the synthesis conditions which are removed with unconverted gases, and the liquid products are separated from the suspension. The bubbles in the reactor are produced by the gas distributor located in the bottom of the reactor. As reported by W-D Deckwer, et al. (1),

the higher liquid phase transfer coefficient values were found in short columns, and it can be explained with the increased mass transfer during bubble formation, but the formation of the bubble should be regarded as end effect which will be constant for a given gas distributor. The engineering problem for bubble column reactor that needed to be solved was the catalyst separation from wax.

The improved design of the short bubble column reactor in CAER F-T pilot unit contains a good axial dispersion function and a continuous reactor-wax removal system. This axial dispersion function would cause an increase in gas-liquid backmixing, and would have a great effect on conversion and selectivity. The improved F-T reactor-wax separation system enabled us to increase the flexibility and reduce the manpower requirement for the reactor-wax/slurry separation.

A CSTR is designed to use a powdered catalyst in a slurry. The agitation of the reactor provides optimum isothermal and residence time conditions. A dip-tube fitted inside the reactor provides excellent gas/liquid contact.

The purpose of the present study was to compare certain aspects of the FTS as carried out on the same precipitated Fe/K catalyst in the SBCR and the CSTR using the same experimental conditions. It is expected that there would be some differences in the conversion and selectivities obtained from these reactors, because these reactors differ in the type of mixing and heat and mass transfer phenomena.

Experimental

A schematic diagram of the experimental apparatus is shown in Figure 1 for the SBCR and Figure 2 for the CSTR. The bubble column reactor has 5.08 cm diameter and a 2 m height. The CSTR is 1 liter autoclave. The SBCR was equipped with a gas distributor and a K-ray detector. The gas distributor produce fine gas bubbles in the

liquid phase and the K-ray indicates the catalyst axial suspension inside the reactor. The CSTR was filled initially about 2/3 of the reactor volume and the SBCR filled about 3/4 of the column volume with the slurry that was made of 20 wt% catalyst and the Shell C₃₀ oil. The level of the slurry is dependent on the calculation of gas holdup in the SBCR at the synthesis condition (2). Briefly, the synthesis gas was passed continuously through the reactors, the products gas and liquid, at the top of the reactor pass through a separation section to a hot condenser (230°C), and a cold separator (3°C). A dry flow meter for SBCR and a bubble meter for CSTR was used to measure the exit gas flow rate.

The composition of the exit gas was determined by GC techniques. The condensed liquid phases were sampled at periodic times (12 hours for SBCR and 24 hours for CSTR) and the mass of each sample was obtained. The aqueous phase was analyzed for water and oxygenates using a GC fitted with Porpack Q column. The oil and wax phases sample was combined according to the mass fraction, O-xylene was added as an internal standard, then this sample was analyzed for hydrocarbons by GC with the DB-5 column.

The catalyst particle sizes after synthesis for 309 hours (SBCR) and for 253 hours (CSTR) were obtained by SEM. The SEM was carried out after coating the power samples with carbon, using a Hitachi S-2700 scanning electron microscope at 20 KV. EDS was carried out using a thin window Si-Li diode detector.

The operating conditions for both reactor systems are given in Table 1.

Results and Discussion

Catalyst axial dispersion and mixing

The gas-liquid backmixing plays an important role in the performance of the reactor. The quality of the flow is dependent on the type of gas distributor, properties of the liquid, column size, gas velocities, solid concentration and solid particle (3-5). At low gas velocity (<5 cm/sec.), the bubble rise separately in the liquid or slurry and the homogeneous bubble flow regime prevails (3). The solid dispersion, detected by a K-ray at gas velocity 3 cm/sec, shows that the liquid phase is more likely uniform in the column (Figure 3). However, a trend towards bubble coalescence behavior was also observed in this figure. The agitation in the SBCR by rising gas bubbles and in the CSTR by a magnedrive stirrer operated at 750 rpm, so that the agitation of the CSTR provides excellent mixing.

Conversion

Table 2 lists the data obtained from the both reactor systems at same time-on-stream time. It is shown that the difference in conversion between the two reactors is caused by the difference of heat and mass transfer phenomena and gas resident time in the reactor. The gas hourly space velocity (GHSV) based on the volume of reactor is 379 in the SBCR and 209 in the CSTR. Some possible effects of the reactor type on the catalyst activity may be caused by the GHSV based on the liquid volume is slight different (518 in the SBCR and 504 in the CSTR) and the liquid level is much higher in the SBCR, the synthesis products volatile under the operating conditions are removed slowly with the residual gas in the SBCR, so that some high molecular weight liquid products remain in the reactor, fill catalyst pores, and surround the catalyst particles (6). The H_2O/H_2 ratio is slightly higher in the SBCR. This can produce the iron and iron

carbides present as magnetite (7,8). Therefore, maximum F-T conversion may be influenced by the reaction of iron carbide with H_2O to form Fe_3O_4 , which has no hydrocarbon synthesis activity. A possible explanation of the observed deactivation could be carbon formation as result of the Boudouard reaction. Carbon deposition in the SBCR causes disintegration of catalyst particles to fines. Apparently, carbon nuclei form inside the Fe crystallites and grow to an extent that the particles are broken by the expanding carbon deposit (Figure 5) (9). The mechanically stirring in the CSTR disintegrates the catalyst particles to fines (Figure 6).

Selectivity

The production of methane is slight higher in the CSTR, and the C_3 - C_4 olefin/paraffin ratio is not significantly different in the two systems. The gas production is higher in the CSTR (84.4% and 80.6%), because the water gas shift reaction is stronger in the CSTR. The C_3 + H.C. (g/ M^3 -hr)/CO+ H_2 conversion ratio is almost same in the two systems (1.63 in the SBCR and 1.65 in the CSTR). Figure 7 illustrates the differences in the products distributions for both reactors. The mole fraction of higher molecular weight products is higher in the SBCR, and the plot of the products breaks sharply at about C_{12} . The alpha values based on total hydrocarbons formation for the SBCR, are 0.68 and 0.93, and for the CSTR, are 0.42 and 0.82. After 240 hours on-stream, the carbon number distributions are similar for both reactors (Figure 8).

Summary

The improved design of the CAER short bubble column reactor offers good gas-slurry mixing and excellent catalyst wax separations. The iron concentration in the wax collected after passing the separation system is about 10 ppm. The data presented in this study indicate that the catalyst activity is different between two reactor systems at

same operating conditions, the activity is about 10% higher in the CSTR than in the SBCR, the water-gas shift reaction is weak and the gas percentage of synthesis products is less in the SBCR, the (C_1+C_2) /total hydrocarbons ratio is higher in the SBCR. The SBCR produced more the higher molecular weight products on-stream for synthesis times of less than 240 hours.

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Table 1		
Operating Conditions		
	SBCR(503)	CSTR(LX238)
Catalyst	4.4 Si/K	4.4 Si/K
Cat. loaded wt%	20	20
Cat. Activation at:		
Gases	CO+H ₂	CO+H ₂
H ₂ /CO	0.7	0.7
Gas space velocity (SL/hr-g Fe)	5.3	5.15
Temperature (°C)	270	270
Pressure (atm.)	1	1
Synthesis at:		
H ₂ /CO	0.7	0.7
Gas space velocity (SL/hr-g Fe)	5.3	5.15
Temperature (°C)	270	270
Pressure (MPa)	1.21	1.21
Gas superficial velocity (cm/sec)	3	Stirred speed 750 RPM

Table 2		
Conversion and Selectivity		
	SBCR	CSTR
CO Conversion %	48.63	58.94
H ₂ Conversion %	48.38	54.52
CO+H ₂ Conversion %	48.48	57.03
Products gas (%)	80.63	84.44
(C ₁ +C ₂)/T.H.C. (%)	16.76	15.45
C ₂ /(C ₂ +C ₃) (%)	45.01	48.66
C ₃ /(C ₃ +C ₄) (%)	87.03	87.99
C ₄ /(C ₄ +C ₅) (%)	84.27	84.23
C ₃ +H.C.(g/M ₃ -hr)/CO+H ₂ (%) Conversion	1.63	1.65
H ₂ O/H ₂ Ratio	1.26	1.2
H ₂ /CO Usage	0.69	0.67

Figure 1. Schematic of the FTS slurry bubble column reactor.

Figure 2. Schematic of the CSTR FTS reactor system.

Figure 3. K-ray data for the SBCR indicating uniform catalyst distribution.

Figure 4. Conversion comparisons for the CSTR and SBCR systems.

Fig. 5. SEM Scanning, the sample from the SBCR after synthesis 309 hrs.

Fig. 6. SEM Scanning, the sample from the CSTR after synthesis 253 hrs.

Figure 7. Comparison of the product distributions obtained in the CSTR and SBCR systems.

Figure 8. Comparison of the product distributions obtained in the CSTR and SBCR systems.

3.3.4 Additional Research

3.3.4.1. Verify the Quality of Data Obtained from the CSTRs.

The previously unexplained loss and re-establishment of activity has been found to be due to the lowering of the liquid level in the reactor. The conversion data shown in Figure 1 clearly show the loss of activity when rewax (wax from the reactor) was collected on a daily basis in the first 500 hours of the run. When the sampling of the rewax was stopped the activity recovered to approximately the initial level. Repeating this cycle produced a loss and gain of activity again. From these data, it was suggested that removing the reactor wax lowered the liquid level by physically removing the wax material and thus allowed more of the lighter material including the start-up oil to be removed from the reactor. After most of the start-up oil was removed and the reactor contained a sufficient amount of FTS wax, the reactor liquid level became stabilized and sampling of the reactor wax could be done without affecting the activity.

Figure 1. %CO conversion vs. Time on stream for runs LGX276-279 and LGX283 (4.4at%Al/3.0wt.%Cu/2.5-10.0wt.%K with $T_{\text{syn}} = 230^{\circ}\text{C}$).

3.3.4.2 Comparison of Silica Based Hi-Alpha Catalyst at 230°C and 250°C

With C-30 oil at a 5.0wt% Catalyst Loading

Two series of runs using five catalysts at synthesis temperatures of 250°C and 230°C were performed in the one liter continuously stirred tank reactors (CSTR). When Ethylflo C30 decene trimer was used as the start-up oil, a 5 wt.% catalyst slurry containing 15.3 g and 290 g of oil was used. When PW3000 wax was used, the initial slurry was 3 wt.% catalyst and contained 9.6 g of catalyst and 310 g of wax. For all the runs, the reactor solvent was C-30 oil with a catalyst loading of 5.0wt%. The iron-based catalysts used in these tests had been co-precipitated so that the atomic ratio of silicon to silicon + iron, i.e., $[\text{Si}] / [\text{Si} + \text{Fe}]$, was at 0.044, or 4.4atomic(or mole)%. All the catalyst had been impregnated with copper such that the weight percentage of copper (relative to Fe) was at 3.0wt%Cu. Each of the five catalysts had a different amount of potassium present, specifically, 0.0wt%K, 2.5wt%K, 5.0wt%K, 7.5wt%K, and 10.0wt%K. As was the case for the copper, the potassium wt%'s are also relative to Fe. The list below shows the five catalysts tested and designates the atomic(mole) ratios of Si, Cu, and K, based on 100 atoms(moles) of Fe.

RJO228 (0.0wt%K) 100Fe:4.60Si/2.72Cu/0.00K

RJO229 (2.5wt%K) 100Fe:4.60Si/2.72Cu/3.66K

RJO230 (5.0wt%K) 100Fe:4.60Si/2.72Cu/7.52K

RJO231 (7.5wt%K) 100Fe:4.60Si/2.72Cu/11.58K

RJO232 (10.0wt%K) 100Fe:4.60Si/2.72Cu/15.87K

The first five runs performed were at 250°C and designated LGX236(0.0wt%K), LGX239(2.5wt%K), LGX240(5.0wt%K), LGX241(7.5wt%K), and LGX242(10.0wt%K). A comparison of the %CO conversion versus days on stream is shown in Figure 1. The

second series of runs, specifically LGX235(0.0wt%K), LGX244(2.5wt%K), LGX245(5.0wt%K), LGX246(7.5wt%K), and LGX247(10.0wt%K), was performed at the synthesis temperature of 230°C and the %CO conversion versus days on stream is given in Figure 2.

In general, the catalysts performed better in regards to CO conversion at the synthesis temperature of 250°C. At both temperatures, the catalyst run with the 5.0wt%K loading (RJO230) had the best CO conversion, while also for both temperatures, the 0.0wt%K loaded catalyst (RJO228) runs produced the poorest CO conversions. Again, for both temperatures, the catalysts at 2.5wt%K and 7.5wt%K (RJO229 and RJO231, respectively) produced comparable CO conversions, slightly lower than the CO conversion exhibited by the 5.0wt%K (RJO230) loaded catalyst runs, and the catalyst runs with the 10.0wt%K loadings were the fourth best with respect to the CO conversions, these also at both synthesis temperatures.

Note that for the 230°C synthesis conditions (Figure 2), the CO conversions for the 2.5, 5.0, 7.5, and 10.0wt%K loaded catalysts all fell within a 20% band at the start of the run and improved to a band of 10% or less by the end of the run. This band of CO conversions was also observed for the runs performed at 250°C, but only for the 2.5, 5.0, and 7.5wt%K loaded catalysts. The CO conversions were at ~80% for the 2.5, 5.0, and 7.5wt%K catalysts, while the CO conversion for the 10.0wt%K catalyst had a starting value of only ~50%. This justified another run using the 10.0wt%K catalyst, RJO232, at the synthesis temperature of 250°C. Run LGX250 was performed and the results of the CO conversion are given in Figure 3 and it can be seen that the %CO conversion did improve to values greater than 70%, with the exception in the drop of conversion starting at run hour 168 and reaching a minimum at ~run hour 264, which

was found to be due to a faulty inert gas valve. After corrective action was taken in regards to the valve, it can be seen the CO conversion did rebound and if these results were plotted with the 2.5, 5.0, and 7.5wt%K data, they would all fall into a band even tighter than that found with the 230°C CO conversions (i.e., bandwidth of ~10% CO conversion for the 250°C synthesis conditions).

Thus, in general, based on %CO conversions for these catalysts,

$$T_{\text{syn}} = 250^{\circ}\text{C} > T_{\text{syn}} = 230^{\circ}\text{C}$$

$$5.0\text{wt}\%K > 2.5\text{wt}\%K \cong 7.5\text{wt}\%K > 10.0\text{wt}\%K > 0.0\text{wt}\%K.$$

Figure 1. %CO Conversion vs Days on Stream for Runs LGX239-242 @ 250°C.

Figure 2. %CO Conversion vs Days on Stream for Runs LGX244-247 @ 230°C.

Figure 3. %CO Conversion vs Time on Stream for Run LGX250_{R7} with T_{syn} @ 250°C.

3.3.4.3 Comparison of Reactor Solvents (C-30 oil vs PW_R3000 Wax)

This series of runs involves comparing the performance of a high molecular weight polyethylene wax, Polywax PW_R3000, for use as a reactor solvent, to that of the typically used C-30 oil. For this comparison, the well studied 4.4Si150 cyclone catalyst was used (4.4atomic%Si and 1.0atomic%K, both relative to Fe, i.e., [Si(or K)]/[Si(or K) + Fe]). 32.22g of the catalyst was used in all of the runs, and for the C-30 oil application the catalyst loading was at 10.0wt%, while for the PW_R3000 wax a 11.1wt% catalyst loading was used. This difference in weight% loadings stemmed from attempts to establish equivalent volumes of solvent during the initial loading of the continuously stirred tank reactors (CSTR). These runs were modeled after previous runs that used the C-30 oil as a solvent, which were normally loaded at a 10.0wt% catalyst loading, specifically 32.22g of catalyst along with 290.0g of C-30 start up oil/solvent. With the density of the C-30 oil at ~0.80g/cm³, this yielded a start up solvent volume of 362.5cm³, thus the target volume for the PW_R3000 wax was 362.5cm³. As the PW_R3000 wax is a solid at ambient temperatures, it was heated until it melted, i.e., at ~130°C, at which point the density was determined to be 0.71g/cm³. Thus at 130°C, it requires 257.4g of PW_R3000 wax to obtain a volume of 362.5cm³. Note that the density of the C-30 oil should have been determined at a temperature of 130°C, instead of at ambient temperature (at a later date the densities and specific volumes(cm³/g) of the PW_R3000 and C-30 oil were determined up to 210°C, as well as the densities and specific volumes for the C-28 (octacosane) and the PW_R2000 high molecular weight polyethylene wax, and that algorithms were then developed for the densities and specific volumes as a function of temperature from ambient through 210°C).

Run LGX248 was performed as the baseline case with the C-30 oil and the %CO conversion results are given in Figure 1. The %CO conversion results for the PW_R3000 run, LGX249, are shown in Figure 2. Both reactor solvents produced CO conversions of 80-90%, until gas feed tube pluggages occurred (at ~run hour 550 for the C-30 oil and at ~run hour 460 for the PW_R3000 solvent). These two runs showed the feasibility of using the PW_R3000 polyethylene wax as a reactor solvent. It was then decided to repeat the PW_R3000 run to confirm the reproducibility of the results obtained in run LGX249. Run LGX251 was started and it was observed that the pretreatment pressure had climbed to ~40psig (pretreatment is to be carried out for 24 hours at 0psig), but aborted after two days at synthesis conditions. Thus run LGX252 was initiated, but it too was aborted after three days at synthesis conditions, due to a pressure of ~100psig during the pretreatment period. It was discovered that the reason for the elevated pressures during the pretreatment period was caused by the restriction of the gas out and due to blinding off and/or plugging in the 7 μ -wax filter and the wax line out of the reactor, which functions as a continuous line out for the gas products produced during the FTS reaction. It was found that the restrictions were caused by the condensing and solidifying of the PW_R3000 polywax (melting point at ~130°C) which possibly had been entrained in the gas out of the reactor via the wax line out. To rectify this problem, the wax filter was fitted with a thermocouple and an additional heat tape was installed on the wax line, as well as increasing the amount of insulation on the wax line out (this was also done for the rewax line out to allow for the removal of the reactor liquid products). This allowed for the monitoring and adjustment, if necessary, of the temperature of the 7 μ -wax filter and wax line. After these modifications, run LGX253 was started and the pretreatment period was successfully completed at the desired pressure of 0psig.

Figure 3 gives the %CO conversions for runs LGX251, LGX252, and LGX253 and shows an inverse relationship with %CO conversion and pretreatment pressures. Note that the %CO conversion for run LGX253 agrees rather well to that of the %CO conversion for run LGX249. That is, for run LGX253 the CO conversion starts at ~90% and is maintained at ~85% or greater up through run hour 500. It was thus shown that the PW_R3000 polyethylene wax could be used as a suitable reactor solvent for the FTS synthesis.

Figure 1. %CO Conversion vs Time on Stream [TOS] for Run LGX248_{R1}.

Figure 2. %CO Conversion vs Time on Stream for LGX249_{R2}.

Figure 3. %CO Conversion vs Time on Stream for Runs LGX251-253.

3.3.4.4 Comparison of Alumina and Silica Based High-Alpha Catalyst at 230°C and 250°C

Once it was shown that the Polywax PW_R3000 was a suitable reactor solvent, five Fe-based/silica catalysts and five Fe-based/alumina catalysts were tested at both 250°C and 230°C for their conversion performance in the one liter continuously stirred tank reactors (CSTR). The ten catalysts tested at the two synthesis temperatures are referred to as the hi-alpha catalyst studies. All catalysts were activated with syngas (H₂/CO = 0.7) at 270°C, ambient pressure and a space velocity of 3.11 (STP) h⁻¹ g-Fe for 24 h. The reactor pressure was increased to 1.3 MPa after activation and FT synthesis was started. The alumina and silica series catalysts were both co-precipitated with the iron such that atomic ratios of aluminum(silicon) relative to Fe was 0.044 or, 4.4atomic% Al(Si). All ten catalysts were impregnated with copper so that the copper was present at a 3.0wt%Cu, relative to iron. Both the silica and alumina series Fe-based catalysts had varying amounts of potassium, specifically 0.0wt%K, 2.5wt%K, 5.0wt%K, 7.5wt%K, and 10.0wt%K, relative to Fe. The following list identifies the catalyst and gives an atomic(mole) representation of the Si/Al, Cu, and K, based on 100 atoms/moles of Fe.

Silica Series:

RJO228(0.0wt%K) 100Fe:4.60Si/2.72Cu/0.00K

RJO229(2.5wt%K) 100Fe:4.60Si/2.72Cu/3.66K

RJO230(5.0wt%K) 100Fe:4.60Si/2.72Cu/7.52K

RJO231(7.5wt%K) 100Fe:4.60Si/2.72Cu/11.58K

RJO232(10.0wt%K) 100Fe:4.60Si/2.72Cu/15.87K

Alumina Series:

RJO250(0.0wt%K) 100Fe:4.60Al/2.72Cu/0.00K

RJO251(2.5wt%K) 100Fe:4.60Al/2.72Cu/3.66K

RJO252(5.0wt%K) 100Fe:4.60Al/2.72Cu/7.52K

RJO254(7.5wt%K) 100Fe:4.60Al/2.72Cu/11.58K

RJO255(10.0wt%K) 100Fe:4.60Al/2.72Cu/15.87K

The silica series catalysts at a synthesis temperature of 250°C were tested first and Figure 1 shows the %CO conversion versus time on stream. These runs were designated as LGX254-258 and used the RJO232, RJO231, RJO230, RJO229, and RJO228 catalyst, respectively. The %CO conversion for the silica series at 230°C is presented in Figure 2 (runs LGX259-263 utilizing the RJO232-228, respectively).

For the alumina series at 250°C, the CO conversion is given in Figure 3 (runs LGX267-271 utilizing the RJO250, RJO251, RJO252, RJO254, and RJO255 catalysts, respectively) while Figure 4 shows the %CO conversion for alumina at 230°C (runs LGX276-279 using the RJO251, RJO252, RJO254, and RJO255 catalyst, respectively, and run LGX283 using the RJO252 catalyst). Note that for the 230°C alumina series that the catalyst with 0.0wt%K was not tested and that run LGX283 is a repeat run of LGX277 (the 5.0wt%K catalyst). Also note for runs LGX276, LGX278, and LGX279, at ~run hour 183, a re-pretreatment of the catalysts with only CO gas was performed, which did not appear to help.

In general, the following trends were observed for the %CO conversion,

☞ For Both 230°C and 250°C Synthesis Temperatures

Silica Series Better Than Alumina Series

☞ For Both Alumina and Silica Series

%CO Conversions Better at 250°C than at 230°C

☞ For The Alumina Series

230°C : 2.5wt%K $\approx$ 5.0wt% > 7.5wt%K > 10.0wt%K

250°C : 2.5wt%K >> 5.0wt%K > 7.5wt%K >> 10.0wt%K > 0.0wt%K

☞ For The Silica Series

230°C : 7.5wt%K $\geq$ 5.0wt% $\geq$ 2.5wt%K >> 10.0wt%K > 0.0wt%K

250°C : 2.5wt%K $\geq$ 5.0wt%K $\geq$ 7.5wt%K >> 10.0wt%K > 0.0wt%K

Figure 1. %CO Conversion vs Time on Stream for Runs LGX254-258.

Figure 2. %CO Conversion vs Time on Stream for Runs LGX259-263.

Figure 3. %CO Conversion vs Time on Stream for Runs LGX267-271.

Figure 4. %CO Conversion vs Time on Stream for Runs LGX276-279 & LGX283.

3.3.4.5 High-Aluminas

A series of runs was performed using catalyst that contained varying amounts of alumina as a support. The alumina, Al_2O_3 , varied nominally from ~10wt% to ~53wt% for the four catalysts used in this series of runs and each catalyst had different amounts of Al, Cu, and K. The reactors had a 10.0wt% catalyst loading in the PW_R3000 polyethylene wax reactor solvent and a synthesis temperature of 270°C was used for these runs. The following list identifies the catalyst and gives an atomic(mole) representation of the Al, Cu, and K, based on 100 atoms/moles of Fe.

a. RJO274 (10.15wt% Al_2O_3 & 52.69wt%Fe), 100Fe:21.1Al/2.73Cu/11.8K

b. RJO275 (17.74wt% Al_2O_3 & 46.93wt%Fe), 100Fe:41.4Al/2.72Cu/11.6K

c. RJO276 (37.58wt% Al_2O_3 & 35.19wt%Fe), 100Fe:117Al/2.72Cu/11.6K

d. RJO277 (53.13wt% Al_2O_3 & 23.47wt%Fe), 100Fe:248Al/2.74Cu/11.6K

Figure 1 shows the %CO conversion for runs LGX284, LGX285', LGX286 and LGX287, which used catalysts RJO274, RJO275, RJO276, and RJO277, respectively.

Run LGX284 was aborted after 144 hours on stream due to the inability to withdraw liquid reactor product through the 2μ -rewax filter, which is located inside the reactor and submerged in the catalyst/wax reactor slurry at start up . It is not certain if the 2μ -rewax filter for LGX284 was blinded off from previous runs or if the tubing run from the reactor to the rewax trap (vessel for the collection of liquid reactor product) was plugged, or a combination of both. Modifications to the tubing run from the reactor to the rewax trap have been implemented to allow for a repeat of this run.

Run LGX285' was a repeat run of LGX285, as LGX285 was aborted during the 24 hour pretreatment period due to the reactor pressure rising to ~400psig (as the pretreatment pressures are fixed at a nominal 0psig).

Although there was an inability to remove reactor product via the rewax filter for run LGX284, difficulties in catalyst/wax separation and reactor product removal was not encountered for runs LGX285'-287. In fact, there was no plugging or blinding off of the rewax filters over the course of these runs and the reactor product removed through the rewax filter was visibly free from catalyst contamination. The increased amounts of Al_2O_3 and the lower Fe content associated with these catalysts are thought to be mainly responsible for the ease of reactor product removal through the rewax filter. This, along with the fact that there were problems associated with the mass balance resulted in removal of too much reactor product via the rewax filter for runs LGX285'-287. Specifically, after the completion of these runs, the reactor contents were collected and measured and deficits of 84g, 186g, and 213g from the initial catalyst/ PW_R 3000 wax loading of 344.0g was found for runs LGX285', LGX286, and LGX287, respectively. In effect, this results in higher percentage catalyst loadings for these runs, as well as a reduced residence time in the reactor slurry, but the effect on CO conversion is not well understood.

The previously mentioned problems present some difficulty in attempting to compare this series of runs, but with respect to the data for %CO conversion over time, the best results were obtained using the RJO276 catalyst (run LGX286) as CO conversions were maintained at levels of 70-80%. The CO conversion for runs LGX287(RJO277) and LGX285(RJO275) were comparable to one another for run hours 100-336, but both had CO conversions of 40% at run hour 336 while for run LGX286, the CO conversion was at +70%.

Figure 1. %CO Conversion vs Time on Stream for Runs LGX284-287.

3.3.4.6 Reactor Wax Withdrawal Modifications

In the past, reactor product and catalyst separation has been accomplished using a $\frac{1}{2}\mu$ -grade Mott Metallurgical Corporation sintered stainless steel filter ($\frac{1}{2}$ "OD and $\frac{7}{8}$ " in length for a surface area of 0.0109ft²). This filter was positioned so that when it is installed to the reactor head that it's bottom surface is ~3" down 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 PW_R3000 hi-molecular weight wax as a reactor solvent (LGX249 first PW_R3000 run) 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 referred to as 'rewax'), allowing the reactor to fill up, ultimately resulting in aborting the runs. Potential solutions to this problem have been suggested and/or implemented.

The first of the solutions which has been incorporated, was to lower the filter to insure that it is completely immersed in the wax/catalyst slurry. The thinking here is that with the filter immersed in the slurry, it would be out of the gas/froth space (which may or may not contain smaller ebullated catalyst particles) and would be continually washed by the slurry and eliminate or at least minimize the blinding off of the filter. To accomplish this end, the filter was lowered to an elevation so that it's bottom surface is ~7" below the upper surface of the reactor (specifically, the bottom of the filter is positioned ~ $\frac{1}{4}$ " above the upper surface of the gaspersator blades). At this elevation there is no doubt that the filter is covered by the slurry for the current loadings of PW_R3000 polywax and hi-alpha catalysts. The first run using this lowered filter configuration was LGX263 (100Fe:4.60Si/2.72Cu/0.00K) and as can be seen in Figure

1 (i.e., 'Rewax Flux Density vs Sample Day for Run LGX263') problems were encountered in attempting to remove the rewax for the first 12 sample days. It was found that this inability to remove the rewax during this period was not due to blinding off of the filter, but instead by the line from the reactor head to the rewax trap being heated at a too low of a temperature, specifically lower than the melting point of the reactor product (note that the melting point of the Polywax PW_R3000 is ~130°C at ambient conditions). Once 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 next run utilizing the lowered filter was run LGX266 (100Fe:4.60Si/2.72Cu/7.52K) and from Figure 2, the performance of the filter, as measured by flux density (gpm/ft²), can be seen in general to decrease with time. The implication here is perhaps there is increased blinding of the filter with subsequent rewax letdown periods. As in run LGX263, the rewax product was visibly free of iron, and in fact LGX266-005 and LGX266-007 each were tested for iron content and tested at 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 0.13-0.20gpm/ft², surface area of 0.175ft², and a porosity of 18μ (corresponding to ~16 times the area and an increase of 36 times the porosity of the Mott SS-filter that we were using). With the maximum Δp across the Mott SS-filter at 75psid and the Δp across the Regimesh filter not known, there is difficulty in making a comparison of the performance of the filters, but from liquid flow characteristic graphs supplied with the Mott product catalog, if the μ-grade is increased from ½μ to 20 μ (with Δp and viscosity held constant), the flux density (gpm/ft²) increases ~100-fold. However, if the Δp is varied

and the μ -grade and viscosity held constant, there seems to be a linear relationship with flux density.

After the completion of run LGX266, an attempt was made to test out a 2 μ -grade Mott SS-filter, the second of the modifications to improve the rewax removal. This was accomplished by opening up the reactor once it had cooled to 130°C and replacing the ½ μ -filter with a 2 μ -grade filter. Comparing the liquid flow media charts in the Mott catalog for the ½ μ and 2 μ filters, at equal Δp 's and viscosities (for Δp 's of 100, 60, 10, 6, and 1 psid and viscosities of 500, 100, 20, and 5cP's, as well as for water), the average flux density increased 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 and unfortunately ~300g of reactor contents were removed. The collected reactor product did in fact have catalyst present, but at the time, it was not known if;

- 1) the wax/catalyst leaked through an improperly tightened filter fitting,
- 2) had it passed straight through the 2 μ -grade 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 possibly a combination of the above.

Since the 2 μ -grade filter test was inconclusive for run LGX266, after the completion of run LGX268 (100Fe:4.60Al/2.72Cu/3.66K) which also used a ½ μ -filter, another test of the 2 μ -grade filter was attempted. The results from this series of rewax letdowns was more promising in that the rewax product collected appeared catalyst free and thus was justification for the installation of a 2 μ -grade filter prior to the start of a

run. Subsequent iron based catalyst FTS runs have incorporated the use of the 2μ-grade rewax filter.

The third 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 as to maintain a constant reactor inventory. Simply stated,

$$\text{Reactor Accumulation(g)} = \text{Gas}_{\text{in}}(\text{g}) - \text{Gas}_{\text{out}}(\text{g}) - \text{Trap Products}_{\text{out}}(\text{g}).$$

Two versions of this mass balance were developed. The first just accounts for the mass of the gas out based solely on the Carle Series 400 AGC chromatographic data and is referred to the simplified mass balance, while the second, and certainly more sophisticated, utilizes chromatographic data from the HP-5790 as well as the AGC data (this second mass balance was developed by Scott Lambert and is referred to as Scott's mass balance). Both mass balance methods also account for the liquid and solid products out, i.e., water, oil, wax, and rewax. By adding either reactor accumulation terms to the starting weight of the wax/catalyst, a predicted reactor inventory is determined. Figure 3 shows run LGX267 (100Fe:4.60Al/2.72Cu/0.00K) using Scott's mass balance which predicted that there was ~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 solvent and catalyst in the reactor, which was 318.68g. Figure 4 is for run LGX269 (100Fe:4.60Al/2.72Cu/7.52K), which also had a starting weight of 318.68g. Both the simplified and Scott's mass balances are presented here 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 between the two mass balance methods was at ~40g (346g for the simplified and 386 for Scott's), but the actual measured amount of wax/catalyst in the reactor for this run was at 598g, 55% more than what Scott's mass balance predicts and 73% more than the simplified mass balance prediction. These discrepancies have yet to be resolved. Figure 5 shows the results of the two mass balance methods applied to run LGX270 (100Fe:4.60Al/2.72Cu/11.58K). For this run the predicted reactor contents agree to within ~20g of one another (384.8g for the simplified and 363.2g for Scott's method, within 6% of each other), and both prediction models compare well to the final measured wax/catalyst weight of 310g (24% high for the simplified method and 17% high for Scott's method).

Figures 6 and 7 are plots of the 'Net Reactor Accumulation' (i.e., gain/loss from initial starting weight of 344.0g of catalyst/solvent) for runs LGX284 and LGX285', respectively. For run LGX284 (Figure 6), the simplified mass balance was better (95% of the actual/measured value of +408g) at predicting the reactor accumulation than was Scott's mass balance (121% of actual/measured value). The opposite is true for the net reactor gain/loss for run LGX285' (Figure 7). Scott's method predicted a loss of 35g from the starting weight of 344.0g (within 49g of the actual/measured loss of 84g), while the simplified mass balance predicted a gain of 130g. Referring to Figure 7, it can be seen that the two prediction methods agreed with one another to within ~50g, up through run hour 360, but then they diverged to predicting values in disagreement of 165g for the end of the run. It is unclear as to what caused this divergence when they had agreed so well with one another.

The problems concerning the disagreement with the two methods are presently being addressed, as this is potentially a very useful technique for maintaining and

predicting reactor inventory, as well as predicting the amount of rewx to be removed from the reactor on a daily basis.

A fourth solution has been incorporated in attempts to aid in the removal of the rewx product. In the past, rewx letdown was accomplished by opening the rewx letdown valve while closing the wax letdown valve. With the wax valve closed and the rewx filter submerged, there is no discharge path for the gas (unless the reactor's contents are at a level lower than the rewx filter) to exit the reactor and subsequently the reactor pressure climbs. To eliminate excessive increases in reactor pressure, the wax valve would be periodically cracked to vent excess gas in the reactor. This required constant monitoring of reactor pressure and as a result of pressure variations, the FTS reactions were probably affected. With both the wax and the rewx valves open, an exhaust path for the gas is available, as is a path for the removal of reactor product. Although this letdown procedure does not allow for as large of a Δp across the rewx filter as that which occurs when using the former (with wax valve closed), it has been shown that there was sufficient Δp to let down rewx through the filter. Not only was it possible to remove reactor product using this method, but the rewx collected was , visibly clean, which is also a testament to the use of the 2.0 μ -rewx filter. The only difficulties encountered in using this method has been in the prediction of the amount that can be removed over a given period of time.

To enhance the predictability in removing a desired amount of rewx (as determined from the mass balance techniques) a more recent modification of the rewx letdown procedure incorporates the use of Boyle's law to attempt rewx removal. As the rewx sample bomb can be totally isolated from the reactor system without interruption to reactor operation, and the fact that volume of the rewx receiver is known and that the rewx

sample receiver can be independently charged to any pressure, we should be able to predict at what pressure to charge the empty rewax bomb so as to allow for a volume of rewax to be collected. As the rewax is collected, the bomb pressure should increase until it equilibrates to that of the reactor. The verdict is still out on this method of predicting specific amounts of rewax removal, but appears to be promising.

A final method 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 isolating the bomb 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 and the rewax valve can then be 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, it is felt that there is simply not enough rewax present in the line and filter to perform an adequate backflush as well as the fact that the rewax letdown valve is of the flow control/throttling type of valve and does not allow for an instantaneous surge of higher pressure gas to back flush the rewax material such as a ball valve would offer. 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.

The importance of cleaning the filter cannot be understated, and can be demonstrated by returning to Figure 2 of Section 3.3.7.6, where it is seen that as time progresses, the flux density decreases, requiring longer periods of letdown time to

remove the desired amounts of re wax, which are determined by using either of the reactor mass balance techniques.

Figure 1. Rewax Flux Density vs Sample Day for Run LGX263_{R7}.

Figure 2. Rewax Flux Density vs Sample Day for Run LGX266_{R7}.

Figure 3. Predicted Reactor Inventory vs Time on Stream for RunLGX267_{R1}.

Figure 4. Predicted Reactor Inventory vs Time on Stream for RunLGX269_{R3}.

Figure 5. Predicted Reactor Inventory vs Time on Stream for Run LGX270_{R4}.

Figure 6. Net Reactor Accumulation vs Time on Stream for Run LGX284.

Figure 7. Net Reactor Accumulation vs Time on Stream for Run LGX285'.

3.3.4.7 Technical Assessment of the Fischer-Tropsch Synthesis

1. Executive Summary

A technical assessment of the Fischer-Tropsch synthesis was completed.

2. Abstract

The objective of this research project is to develop the technology for the production of physically robust iron-based Fischer-Tropsch catalysts that have suitable activity, selectivity and stability to be used in the slurry phase synthesis reactor development. The catalysts that are developed shall be suitable for testing in the Advanced Fuels Development Facility at LaPorte, Texas, to produce either low- or high-alpha product distributions. Previous work by the offeror has produced a catalyst formulation that is 1.5 times as active as the "standard-catalyst" developed by German workers for slurry phase synthesis. The proposed work will optimize the catalyst composition and pretreatment operation for this low-alpha catalyst. In parallel, work will be conducted to design a high-alpha iron catalyst this is suitable for slurry phase synthesis. Studies will be conducted to define the chemical phases present at various stages of the pretreatment and synthesis stages and to define the course of these changes. The oxidation/reduction cycles that are anticipated to occur in large, commercial reactors will be studied at the laboratory scale. Catalyst performance will be determined for catalysts synthesized in this program for activity, selectivity and aging characteristics.

The research is divided into four major topical areas: (a) catalyst preparation and characterization, (b) product characterization, (c) reactor operations, and (d) data assessment.

To accomplish the objectives of the project, these topics have been organized into the following technical tasks:

a. Task 1.0 Development of Optimum Promoter Levels for Low- and High-Alpha Catalysts

The goal of this task is to identify and optimize procedure for the preparation of iron-based catalysts that combine high activity selectivity and life with physical robustness. Each of the subtasks address an area of considerable uncertainty in the synthesis of catalysts.

1.1 Determine Optimized Synthesis Procedure for High-Alpha Iron-Based Fischer-Tropsch Catalysts

- Role of precursor particle size on activity.
- Role of Cu in precipitated catalysts.
- Define attrition resistance.

1.2 Prepare Catalysts that can be Used to Determine the Role of Promoters for Low- and High-Alpha Catalysts

- Define optimum SiO_2 .
- Define optimum Al_2O_3 .

1.3 Prepare Catalysts that can be Used to Quantify the Role of K on Product Selectivity in both Low- and High-Alpha Catalysts.

1.4 Complete the Optimization of the Two Best Low-Alpha, Iron-Based Fischer-Tropsch Catalysts Developed during the Previous Contract.

b. Task 2.0 Definition of Preferred Pretreatment for both Low- and High-Alpha Fischer-Tropsch Catalysts.

The goals of this task are to define the preferred treatment, to define the role of Cu and K during the pretreatment on activity and selectivity and to define the chemical and physical changes which occur during the preferred pretreatment. The subtasks address each of these goals.

- 2.1 Determine the Role of Cu in the Activation of Precipitated Low- and High-Alpha, Iron-Based Fischer-Tropsch Catalysts.
- 2.2 Determine the Effect of K Content on Activation Procedures and Determine if the Method of Addition has any Effect on Catalyst Activity and Life.
- 2.3 Determine the Physical and Chemical Changes that Occur during Catalyst Pretreatment and Use and Determine how these Changes Effect the Strength of the Catalysts.
- 2.4 Evaluate the Effect of Carbon Deposition during Catalyst Activation on Activity, Selectivity and Aging Characteristics.

c. Task 3.0 Catalyst Structure and Characterization.

The goal of this task is to provide basic analyses (surface area, XRD) of all catalyst prepared and to provide additional techniques as required (Mössbauer, SEM, XPS, etc.) to answer specific questions or to provide basic required characterization data for the catalysts.

d. Task 4.0 Catalyst Testing.

The goals of this task are to operate the eight CSTR reactors, measure catalyst performance, determine the stable phases that exist during synthesis at low and high conversions and to determine the rates of interconversion of iron oxide and carbide.

- 4.1 Verify the Quality of Data Obtained from the CSTR's.

- 4.2 Measure Catalyst Performance.
- 4.3 Determine the Stable Phases that Exist during Synthesis at Low and High CO Conversion Levels.
- 4.4 Obtain Data on the Rates Involved in the Interconversion of Iron Oxide and Iron Carbide.

3. Results and Discussion

Following the nomenclature of Sasol, we shall refer to low temperature and high temperature operational modes. As practiced at Sasol, the high temperature mode produces lower boiling products than the low temperature synthesis. Thus, the high temperature operation may be viewed as a low-alpha operation whereas the low temperature operation may be viewed as a high-alpha operation. The current production capacities at the Sasol plants are summarized below according to reactor and temperatures modes (1):

Capacities	Bbl/Day			
	CFB	SAS	TFB	SP
Total installed cap	110,000	11,000	3,200	2,500
Capacity/reactor	6,500	11,000	500-700	2,500
Potential/reactor	7,500	20,000	1,550	10,000
CFB = Circulating Fixed Bed SAS = Sasol Advanced Synthol Fixed Fluid Bed TFB = Tubular Fixed Bed SP = Slurry Phase				

The product selectivities on a carbon basis for these two operational modes are:

PRODUCT	LTFT	HTFT
Methane	4	7
C ₂ -C ₄ olefins and paraffins	8 (50%) ^a	30 (80%) ^a
Gasoline	18	36
Middle distillate	19	12
Heavy oils and waxes	48	9
Water soluble oxygenates	3	6
a. Number in parenthesis is the carbon % olefins.		

Both of these distributions are fit by a "two-alpha" plot corresponding to synthesis by chain growth to produce a low molecular weight and a high molecular weight products. Based on the Sasol data for the low-temperature operation, it is calculated that about 50 carbon % is produced by each synthesis mode; however, for the high temperature mode 75% of the products are produced by the low-alpha synthesis pathway. As stated above, the high-temperature mode (low alpha mode) accounts for more than **95%** of the total installed capacity at the Sasol commercial plants.

During about 40 years of operation Sasol has made significant advances in their reactor technology. Thus, the older-type fixed bed reactors (Arge) have been replaced by a slurry-phase reactor; the slurry reactor has been operated for more than 2 years without problems and at, or above, the design capacity. One Sasol Advanced Synthol (SAS) fixed-fluidized bed reactor has been installed to replace Synthol-circulating fluidized bed (CFB) reactors and sufficient SAS reactors have been ordered to replace all of the remaining older CFB reactors.

The capacity of the high-temperature, low-alpha CFB and SAS units compared to the low-temperature, high-alpha units is overwhelming and corresponds to over 95% of the production capacity. The transportation fuel is split 60:40 gasoline:diesel in

South Africa. Since most of the reactor-wax produced in the low-temperature process is refined to supply the world's demand for paraffin wax, the contribution by Sasol to the diesel fuel requirements for South Africa must come from their high-temperature, low-alpha operation.

Sasol plans to replace the 110,000 capacity currently supplied by the CFBs with SAS fixed-fluidized bed reactors, and not with the high-molecular weight, low-temperature slurry reactors. Presumably Sasol is taking the view that the low-alpha, high-temperature synthesis will be an economical process for the next 20+ years. It should be obvious that Sasol considered both low- and high-temperature modes of operation before deciding to take the high-temperature route. Thus, Sasol's actions do not agree with the opinion of many that the only route available to produce transportation fuel is the low-temperature, heavy-product route.

It does not appear to be possible to operate with a cobalt or ruthenium catalyst in a mode other than one leading to high molecular weight products (high alpha mode). However, even for the cobalt catalyst the published data show the two-alpha product distribution. This means that 50%, and usually greater than 50%, of the products from the Co or Ru catalyst are too heavy to be utilized directly as transportation fuels. Thus, a second process step (hydrocracking) must be utilized to convert these high molecular weight products to transportation fuels.

In order to develop a process based on the cobalt catalyst, Shell has opted to utilize a fixed-bed reactor F.-T. process. Shell acquired the Gulf-Badger catalyst process technology from Chevron. The Shell fixed-bed operation in Malaysia utilizes a reactor system that is virtually identical to the one utilized by Sasol for their ARGE reactors that utilized an iron catalyst and that are now being replaced by slurry reactor

technology. The Exxon AGC-21 process utilizes a proprietary catalyst for both the F.-T. (presumably based on cobalt) and hydrocracking steps that are included in their process.

3.1. Iron Catalyst Preparation

Considering the vast literature back through the German work prior to and during WWII, it appears that the preferred iron catalyst is obtained through a precipitation procedure. The most economical source of iron in the U.S. is a concentrated solution of ferrous sulfate that is produced as a by-product in the manufacture of iron and/or steel. However, it is virtually impossible to remove all of the sulfate that is incorporated during the precipitation step even by repeated washing. Thus, in spite of the greater cost of iron, ferric nitrate appears to be the preferred source of iron for the preparation of iron Fischer-Tropsch catalysts.

3.1.1. Sasol

Catalyst robustness is a problem. Sasol utilizes a precipitation step for the preparation of the catalyst that is utilized in the fixed-bed ARGE and the slurry reactor (2). The same procedure is used to add the chemical and structural addition step that follows the precipitation and washing steps. Further processing of the fixed-bed ARGE catalyst involves filtering the slurry, extruding the "paste" and then drying the extrudate. For the preparation of the slurry-phase catalyst, the catalyst slurry is spray dried; the dried particles of the desired size are separated from fines and/or oversized particles using a cyclone/screening/scribbing system. It is found that the breakage of the spherical catalyst particles formed for the slurry reactor is inversely proportional to the mechanical strength of the particle. **However, it is reported that the formation of ultra fine particles due to abrasion does not necessarily follow this trend [of**

abrasion/mechanical strength]. This implies that the measurement of the mechanical strength of the oxide catalyst precursor does not have predictive value for catalyst integrity during use in a slurry reactor.

Sasol provides pictures representing a batch of **good** catalyst particles and **bad** catalyst particles (Figure 1). The good particles are spherically shaped and do not exhibit imperfections. The poor catalysts exhibit indentations that extend into the body of the pellet and is indicative of an operation that involves non-uniform drying during the spray-drying process. The catalysts spray-dried at UCI for the La Porte runs exhibit the characteristics of the **good** catalysts described by Sasol (Figure 2) (3). Furthermore, the attrition of the carbide form of the **good** spheres prepared by UCI show a gradual decrease in size during tumbling experiments under non-reacting conditions (3).

3.1.2. Ruhrchemie

Kuntze, et al. (4) tested a precipitated iron catalyst that they report to be similar to one used in the ARGE-process, at least during the early work at Sasol. The composition of the catalyst was (mass units): $\text{Fe}:\text{SiO}_2:\text{Cu}:\text{K}_2\text{O} = 100:25:5:5$. When this catalyst was reduced in hydrogen at 220°C , it was reported to have a reduction degree of 32% (not defined as to whether this means to Fe_3O_4 or to Fe; similar catalysts at CAER would be reduced to Fe_3O_4 under these conditions) and had a surface area of $235 \text{ m}^2/\text{g}$.

3.1.3. The "Reichsamt" Comparative Experiments

This test utilized six different catalysts representing the major German developers of the F.-T. process at that time (WWII period) (5). These tests were under the supervision of Herbet Kölbel. The tests were conducted at temperatures not to exceed 225°C , 10 atm. pressure, without recycle, and were to last for three months

without change of catalyst. The products that were produced had to resemble sufficiently those obtained with cobalt catalysts so as to be marketable as substitutes for the cobalt-produced products. The catalyst compositions are summarized below:

ORGANIZATION	CATALYST COMPOSITION
KWI	Fe,100:Cu,1:K ₂ CO ₃ ,1
Lurgi	Fe,100:Cu,1.0:SiO ₂ ,30:K ₂ O,2.0
Brabag	Fe,100:Cu,2.0,Zn,20:K ₂ CO ₃ ,1
IG	Sintered iron containing Al ₂ O ₃ and K ₂ O and CaF as support
Rührchemie	Fe,100:Cu,5:CeO ₂ ,10:kieselguhr,50
Rheinpreussen	Fe,100:Cu,5:CaCO ₃ ,100:K ₂ CO ₃ ,0.5-1.0

The above catalysts were tested in a 5-liter reactor and were presumably sufficiently robust to be utilized in a fixed-bed reactor. In general, there were only minor differences in the activity and limited product selectivities that were reported.

Sasol also uses a precipitation procedure that was described above.

3.1.4. Mobil

These workers utilized a precipitated iron catalyst that contained copper and potassium. Several formulations were utilized but the compositions appear to be considered proprietary and were not provided in their DOE report. In one run, the Mobil workers changed from a low-alpha operation to a high-alpha operation merely by adding a soluble organic potassium salt at a point during the run; thus, they utilized the same base catalyst for both the low- and high-alpha in at least one of their runs. Based on a Mobil patent for an iron catalyst, we speculate that the Mobil low-alpha catalyst resembled the catalyst used in La Porte run II (except for the Cu level which was in the 2% range in the Mobil patent and was 12% in the La Porte run).

3.1.5. Rentech

The catalyst preferred by Rentech was an unsupported precipitated iron catalyst promoted with copper and potassium (6). Metallic iron and copper were dissolved in nitric acid to form a mixture of ferrous/ferric iron and precipitation was effected by adding ammonium hydroxide to produce a pH of 7.4. The precipitate is washed free of ammonium nitrate. A slurry containing the proper amount of potassium carbonate was then spray dried to produce particles with diameters in the range of 5 to 50 microns. The final step in catalyst preparation was heating in a fluidized bed at 600°F (315°C).

3.1.6. China

These workers used a continuous precipitation procedure to produce their catalysts (7). They report that both low and high pH conditions are to be avoided in order to obtain a high surface together with the preferred pore size distribution.

3.2. Iron Catalyst Activation

3.2.1. The "Reichsamt" Comparative Experiments

A variety of activation procedures were utilized in this test (5). Presumably these were specified by the organization that provided the catalyst and represented the preferred procedure for each catalyst formulation. For the KWI catalyst listed above the activation consisted of reduction in synthesis gas ($H_2/CO = 2$) at 325°C and 0.1 atm. (absolute) for 24 hours. The Lurgi catalyst was reduced in hydrogen at about 250°C. The Brabag catalyst was activated by treatment in water gas at 235-240°C for 48 hours and the Rheinpreussen catalyst received a similar activation at atmospheric pressure. The Ruhrchemie catalyst was reduced in hydrogen at 300°C. The catalyst preparation and activation procedures are summarized in the following table:

Table 1
Summary of the Catalyst Preparation and Pretreatment Procedures

<u>Company</u>	<u>Catalyst Preparation</u>	<u>Pretreatment</u>
Ruhrchemie	Conventional precipitation with Fe,100:Cu,5:CaO,10:kieselguhr,150	Hydrogen reduction, 1 hr., at 300°C; or recycle gas.
Kaiser Wilhelm Inst., Mülheim)	Precipitated from nitrate solution Fe,100:Cu,1-3:K ₂ CO ₃ ,0.1-1.0	CO at 325°C, 0.1 atm.; Fe ₃ C formed, claimed as active phase.
I.G. Farbenindustrie A.G.	Paste of iron powder (from decomp. of Fe(CO) ₅ , 1% borax, sinter 800-900°C.	Hydrogen reduction at 800-850°C
I.G. Farbenindustrie AG (foam process)	Paste of iron powder (from decomp. of Fe(CO) ₅ with K ₂ CO ₃ or borate.	Hydrogen reduction at 350-400°C.
I.G. Farbenindustrie AG (tubular react.)	Paste of iron oxide powder with 5-25% 5-25% MgO or MgCO ₃ and 1-2% K ₂ CO ₃ or borate, sinter at 850°C in nitrogen.	Hydrogen reduction at 350-450°C.
I.G. Farbenindustrie AG (Synol process)	Melting iron in oxygen incorporating 2% alumina and 1% K ₂ O	Hydrogen reduction at 450°C.
Lurgie Gesellschaft für Wärmetechnik	Precipitated from nitrate solution with with sodium carbonate at boiling point, wash and add K ₂ CO ₃ . Fe,100:Cu,2.5:alumina,9:K ₂ O, 2:kieselguhr,30.	Hydrogen reduction at 250-350°C, 1 hr.
Rheinpreussen	Precipitated catalyst with Fe,100: Cu,1.0:kieselguhr,50:K ₂ CO ₃ ,2.	CO at low partial pressure.

3.2.2. Rentech

These workers (6) report that "Determining the 'best' activating procedure for a catalyst is difficult at best even if it is known what changes in the catalyst are needed to give the desired activity, selectivity and stability." They utilized a complex recipe, initially starting by heating in an inert gas, then switching to synthesis gas at a temperature higher than the synthesis temperature using a hydrogen-rich synthesis

gas. The inventors indicate that "It is believed that the presence of this water [from the activation] prevents over-carburization of the catalyst and thereby improves the activity and selectivity of the catalyst." and quote Koenig et al. as support for this view (8).

3.2.3. China

These workers made a study of the effect of activation on the catalytic properties of their iron catalyst (7). They report that reduction of the catalyst with hydrogen leads to the production of Fe and a catalyst with a low surface area and low catalytic activity. They conclude that reduction in hydrogen is not a preferred activation procedure. They also studied the use of syngas mixtures in which the H_2/CO ratio was varied from 1 to 9. The more active catalyst appeared to be produced following activation with the lower H_2/CO synthesis gas at the lower activation pressure (0.3-1.0 MPa). However, they preferred a staged activation in which the treatment with syngas is carried out in steps of increasing temperature.

3.2.4. CAER

Extensive pretreatment studies have been conducted at the CAER with a variety of iron catalysts. Initially, the catalyst activation approach followed a staged heat-up in syngas ($H_2/CO = 0.7$) to finally attain a temperature of about 20°C higher than the reaction temperature (270°C). Presumable because of some residual sulfur in the catalysts prepared to by UCI to be screened for La Porte Run II, sufficient sulfur accumulated on the surface so that the catalytic activity was low following this pretreatment procedure. The same catalysts could be activated successfully in pure CO, either at atmospheric or reaction (170 psig) pressure.

Using pure CO, CAER workers found that they could obtain an active material following 24 hours in CO at 270°C. Four activation runs were made at the CAER in the

2 inch diameter x 6 foot long using the spray-dried Round-Robin batch of unsupported iron catalyst of the same formulation used for La Porte Run II. These runs were made to produce activated (carbided) catalyst samples to be used in filtration studies at Mott. The first resulted in a "poor" run due to the use of a low CO flow rate; the other three runs were at a lower pressure and provide reproducible data (Figure 3). These runs were conducted until the catalyst had accumulated an amount of carbon, based upon the cumulative production of CO₂ measured in the exit gas, to produce about 10% more carbon than required to produce Fe_{2.2}C. The data generated in the CSTR studies at the CAER had the same shape as those obtained in the 2"x6' slurry reactor except that it took 17, rather than 18 hours, to attain the desired amount of carbon deposition. The activation at LaPorte for Run II used a similar activation procedure (40 wt.% slurry) and produced data that followed closely the "poor" curve in Figure 4.

Synthesis gas and pure hydrogen streams are, or can be, easily attained at a commercial F.-T. site. However, it is not easy to obtain a pure stream of CO at a commercial F.-T. site. Thus, while CO pretreatment may be of interest for laboratory studies or for use at La Porte, it does not appear to be easily practiced at a commercial site.

Activation in CO occurs in steps. Initially, there is a rapid reaction to convert the Fe₂O₃ to Fe₃O₄; the formation of Fe₃O₄ has been confirmed by Mössbauer spectroscopy. After the formation of Fe₃O₄ is complete, a slower reaction occurs to deposit carbon in the form of an iron carbide (and possibly carbon to coat the iron carbide particle).

Activation in synthesis gas at reaction pressure appears to be dependent upon the catalyst formulation. For instance, the catalyst that Ruhrchemie provided to DOE

could be successfully activated in syngas at reaction pressure. A catalyst with a similar composition that was prepared at the UCI could not be successfully activated using syngas. It appears that it is essential to have copper (or some metal that functions in a similar manner) present if the catalyst is to be activated in synthesis gas at or near reaction pressure. Even when copper is present, it appears that the approach to maximum activity requires days of operation in the synthesis mode.

The effectiveness of an activation at reaction pressure using gas flow rates at or near to those to be used for the synthesis depends upon the hydrogen partial pressure. Thus, an active catalyst was obtained when pure CO was passed over the catalyst for 24 hours prior to changing to the synthesis conditions (Figure 5). However, there appears to be a linear decline in activity as the partial pressure of hydrogen in the feed gas is increased.

On the other hand, activation with synthesis gas was easily accomplished at atmospheric pressure during 24 hours at reaction temperature. This observation is in agreement with much of the early German work on activation of iron catalysts.

Reduction in hydrogen is a complex operation. Initially Fe_3O_4 is formed; this stage is followed by the reduction to metallic iron at a higher temperature and/or longer reaction time. During a 24 hour period at 270°C it is found that about 30% of the iron is present in the metallic form and the remaining iron is present as Fe_3O_4 . When synthesis gas contacts the reduced catalyst at reaction temperature, within 2 hours or less the metallic iron is converted to iron carbides. The presence of copper has been shown to result in a lowering by $20\text{-}40^\circ\text{C}$ the temperature where each of these two reductions occur. In general, reduction in hydrogen prior to contact of the catalyst by synthesis gas can produce an active catalyst, and this appears to be the procedure that

is utilized at Sasol in their commercial operation. On the other hand, it does not appear that the optimum degree of conversion to metallic iron has been reported in the open literature. It has been reported that complete reduction to metallic iron is to be avoided since the metallic iron sinters rapidly at this temperature to produce a low area material that results in a low-activity catalyst.

3.3. Cobalt Catalysts

The catalysts utilized in the German commercial plants prior to and during WWII was primarily based upon cobalt and these were operated at atmospheric or low pressure conditions. Roelen encountered severe loss in activity during the use of the cobalt catalyst in the early plants but overcame these problems, primarily by separating the interfering elements from the cobalt by precipitation prior to catalyst preparation (9).

During the past 30 years, a vast amount of patent and open literature has developed on cobalt catalyst; these are primarily devoted to the use of one or more elements to modify the catalytic properties of the cobalt.

During the 1970s, Gulf Oil workers found that a Group VIII element, such as ruthenium (Ru), incorporated in a much smaller amount compared to cobalt (Co), greatly increased the activity of the finished catalyst; as an example, a catalyst containing 20 wt.% Co would contain 1 wt.% Ru (10). In addition to cobalt and the Group VIII metal, other components, such as magnesia and thoria (Shell now uses zirconia) were incorporated in order to improve the performance of the catalyst. A catalyst based upon the Gulf patent formulation became the basis for the Gulf-Badger process for the production of hydrocarbons using the Fischer-Tropsch synthesis. Two designs were tested - fixed-bed and fluidized-bed reactors - were tried. The operation of the fluidized-bed reactor was not satisfactory. Gulf Oil, working with Badger,

designed, built and operated a 1 inch diameter, 40 ft. length (two-section) tubular reactor using the Gulf cobalt catalyst. The aged catalyst was reported to be restored to its original activity following an oxidation and reduction cycle.

Gulf Oil workers also patented the use of two stage operation with the first stage employing a Fischer-Tropsch catalyst and the second stage employing an acidic catalyst such as the silicalite catalyst developed by Union Carbide. Alternatively, both the F.-T. and the acidic catalyst could be added to a single reactor. The utility of this concept was adequately demonstrated by the Mobil work carried out under DOE contract.

Unsupported cobalt catalysts have not been found to be satisfactory. A wide range of supports have been utilized; these include alumina, silica, titania, zirconia, magnesia, silica alumina, carbon, and molecular sieves. Recently, Statoil has been issued patents in which it is claimed that the use of alumina, in contrast to other supports, leads to the catalyst with a superior activity compared to Co on other supports (11). The Statoil work also indicates that the incorporation of alkali decreases the catalytic activity and increases the alpha value from about 0.7 for the cobalt only catalyst to 0.9 or greater as the K/Co ratio increases. However, the conclusion for the alteration of the alpha-value by cobalt, from a scientific viewpoint if not from a patent viewpoint, is tenuous at best.

Exxon workers contend that the activity of all cobalt catalysts, with the exception of a titania supported cobalt, exhibits the same activity (site time yield) (Figure 6) (12). Thus, it appears that the Statoil and the Exxon data may be in conflict provided one makes the comparison upon the cobalt dispersion. In the Exxon view, the preferred catalyst involves placing cobalt on the external portion of the support ("egg-shell" type)

to improve the selectivity towards the C_{5+} fraction. Exxon workers have provided extensive published work to indicate that, because of olefin reincorporation, a balance between the kinetics and the diffusional factors must be taken into account. Thus, a structural parameter (χ in Figure 7), dependent upon the pellet diameter, the average pore size of the support, and the density of the metal sites within the pellet, acts to determine the F.-T. product distribution for supported Ru and Co catalysts. Thus, the proper control of the parameter χ allows one to maximize the production of C_{5+} products and, at the same time, minimize the amount of undesirable methane.

There are many patents that purport to provide recipes to prepare cobalt catalysts in such a manner that a superior catalyst is produced with respect to activity, selectivity, and/or ability to handle the exothermic reaction. Unlike the case of the Exxon open literature reports on scientific aspects of the catalyst impact upon the F.-T. synthesis, little exists in the open literature to evaluate the various claims of these patents. It appears that legal actions are underway to resolve some of the perceived or real differences among some of the patents.

For cobalt catalyst, those containing magnesia had been in use in Germany since 1938. The introduction of the magnesia catalysts were claimed to have made possible catalyst lives of up to eight months at normal pressure. According to the managing director of Ruhrchemie A.-G. the magnesia was added **solely** to increase the hardness of the resulting catalyst and thus to reduce its tendency to disintegrate to dust in the reactor (13).

3.4. Comparison of Cobalt and Iron Catalysts

A major difference between cobalt and iron catalysts is the ability of iron to catalyze the water-gas-shift (WGS) reaction:

At Fischer-Tropsch synthesis conditions, the equilibrium for the above WGS reaction lies far to the right; that is, WGS is a thermodynamically favored reaction. Furthermore, the reverse reaction is slow, compared to the forward reaction, under Fischer-Tropsch conditions. However, the forward reaction depends upon the partial pressure of water.

For the F.-T. reaction, cobalt produces hydrocarbons and water whereas the iron catalyst, in the extreme condition, will produce hydrocarbons and carbon dioxide. Thus, for each CH_2 produced as hydrocarbon, cobalt will produce a H_2O whereas iron will produce CO_2 . In this instance, iron will consume two CO molecules for each CH_2 formed whereas the cobalt catalyst will consume only one CO for each CH_2 formed. Thus, the "conventional wisdom" is that cobalt is the preferred catalyst since it makes more efficient use of the CO in the syngas.

For a coal derived syngas, this "conventional wisdom" is an illusion. To produce CH_2 and H_2O by the F.-T. reaction two molecules of H_2 are required as shown in the following equation:

Thus, using a ratio of $\text{H}_2/\text{CO} = 0.7$ (the "middle-ground value" for a syngas produced from coal), there is a deficiency of hydrogen when the cobalt catalyst is used. The above F.-T. reaction can only take place provided an additional amount of CO is converted to CO_2 and H_2 to provide a synthesis gas to pass over the cobalt catalyst that has a ratio $\text{H}_2/\text{CO} = 2$. Thus, with a syngas derived from coal the only difference between the use of the two catalysts is that with the iron catalyst the WGS reaction can be carried out in the same reactor as the F.-T. reaction whereas with the cobalt catalyst the WGS reaction must be carried out in a process operation that precedes the F.-T.

reactor. The preferred catalyst, on the basis of the usage of syngas to produce hydrocarbons, will depend only on the economics of whether it is preferable to conduct the WGS reaction in the F.-T. reactor or in a separate operation.

With a syngas derived from natural gas, the H_2/CO ratio is 2 so that "conventional wisdom" teaches that cobalt, without WGS activity, is definitely the preferred catalyst. This assertion is both "true" and "false." At high CO conversions, the WGS reaction is an important component of the synthesis using an iron catalyst and hydrogen is formed in excess of that needed to produce CH_4 . Thus, the "conventional wisdom" assertion for iron catalysts is "true" at high CO conversion levels. However, the extent of WGS reaction relative to the F.-T. reaction is very dependent upon the CO conversion level for an iron catalyst. Thus, the fraction of CO converted by the WGS reaction is low at low CO conversions (Figure 8). Thus, up to CO conversion of about 60%, the WGS reaction does not make a significant contribution to the overall reaction of CO. **Thus, below about 60% CO conversion iron and cobalt catalysts produce essentially the same products and therefore the same relative utilization of hydrogen and carbon monoxide.** Therefore, it is only true that a cobalt catalyst is preferred for an operation that derives the syngas from natural gas when the iron catalyst is to be utilized in a process configuration that requires high CO conversion in a single-pass operation. Thus, the "conventional wisdom" assertion to favor cobalt over iron catalyst is "false" for operations with an iron catalyst involving recycle or multiple reactors so that CO conversion is kept at about 60% or less.

Thus, iron and cobalt catalysts have a similar selectivity for CO conversions at the 60% or lower levels.

The other "conventional wisdom" viewpoint that favors the cobalt catalyst over the iron catalyst is that the cobalt catalyst is more active. Again, this "conventional wisdom" is both "true" and "false." The CO conversion for a cobalt catalyst is considered to depend only upon the dispersion of the cobalt as shown in Figure 9. This is not the case with an iron catalyst. As shown in Figure 10, the rate of F.-T. synthesis with an iron catalyst increases nearly linearly with time up to a conversion level of about 60% and then to increase only slowly with time above this level. Furthermore, the usage of hydrogen and carbon monoxide varies with CO conversion. Thus, if we compare cobalt and iron catalysts at high CO conversion levels the "conventional wisdom" that Co is more active catalyst than iron is "true". However, if we compare the two catalysts at temperatures where the production of CH₄ is low (e.g., 220°C for cobalt and 270°C for iron), the grams of hydrocarbon produced per gram of catalyst is comparable. Thus, based on an operation using iron catalysts at 60% conversion and using recycle or multiple reactors to attain the high overall conversion of syngas, the "conventional wisdom" is "false".

The above is based upon an analysis of the situation by CAER. Similar conclusions have been reached by Sasol investigators (14). Based upon syngas conversion, they show that using an iron catalyst at 240°C at high relative space velocities, the iron catalyst matches or even exceeds the activity of the cobalt; only at short relative space velocities (high conversion levels) does the conversion obtained with a cobalt catalyst exceed that of the iron catalyst. Furthermore, on the basis of a comparison of the two catalysts, the cobalt catalyst is more productive than an iron catalyst only at the lower relative space velocities and lower pressures (Figure 11). Also, as the operating temperature for the iron catalyst is increased, the dividing line in

Figure 12 will lower so as to favor iron over cobalt to even higher conversions.

Presumably the data in Figure 12 is for an iron catalyst designed to produce higher molecular weight products (high-alpha catalyst); thus, the use of an iron catalyst to produce low molecular weight products (low-alpha catalyst) would lower the dividing line to favor the iron catalyst by an additional amount. The Sasol workers report that the activity of their cobalt catalyst compares favorably with patented alternative cobalt catalysts. The above comparison was at an $H_2/CO = 2$ ratio; i.e., a syngas that would be produced from natural gas.

The Sasol workers provide stability data for their cobalt catalyst operated at 220°C, 20 bar (essentially 20 atm, 290 psi) and 0.5 relative space velocity. The authors state that a commercial syngas feed was used that contained $H_2/CO = 2$ and contained 25 vol.% inerts. Under these conditions there was a rapid decline in activity during about 5 days and then a very slow decline in activity during the next 20 days. These authors attribute the initial decline with build-up of waxes in the catalyst pores and the slow decline as probably due to a low level of sulfur poisoning.

Based upon the knowledge in the open and patent literature, it does not appear valid to make a choice between a cobalt and an iron catalyst unless the choice is based upon a particular process in which the operational conditions are specified.

3.5. Slurry Reactor Studies

3.5.1. German

3.5.1.1. Roelen

In spite of studies directed toward industrial development, the KWI pilot plant studies showed that the optimal stoichiometric ratio of $CO:H_2$ was 1:2 (9). In

November 1930 the pilot plant staff attempted to run the F.-T. in the liquid phase,

and they were successful in maintaining the heat flow problem. However, the typical catalysts of that day had an activity that was too low to have practical commercial interest.

3.5.1.2. Kölbel

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. The reactor was 1.55 m in diameter and 8.6 m in height. 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 (15). 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. A typical catalyst used by Kölbel would have a composition of Fe:Cu:K₂O = 100:0.1:0.05-0.5; thus, the catalyst used by Kölbel 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 a Mobil patent and the one used for La Porte run II (low, not the actual high Cu content).

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. 15)		
	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

At the conversion level shown in the above table, only 178 g of hydrocarbons were produced per m³ gas (from the original paper in German, it was 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 (2). Kölbel et al. report that through polymerization of lower olefins, about 18 g/Nm³ CO+H₂ of alkylate gasoline can be produced. 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 the only way, based upon CAER results, 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.

3.5.2. British

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. For example, low catalyst activity

and rapid catalyst aging were problems than limited the usefulness of the data produced during the period of operation of the plant.

3.5.3. U.S. Bureau of Mines

The Bureau of Mines operated a 3 inch diameter x 8 foot long reactor as well as a larger 8 inch diameter reactor in the oil-recycle mode. 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. Some experimental operating difficulties 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.

3.5.4. Mobil

The initial runs in the pilot plant (Figures 13 and 14) at Mobil Oil, based upon the catalyst compositions in Mobil's patents, would utilize a catalyst with a composition that resembles the one reported above for Kölbel's work and the catalyst intended (low, not high, Cu content) for the La Porte Run II. Mobil's data from work funded by DOE have become the "standard" for both economic (e.g., 16) and technological evaluations (e.g., 17). 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 (18). 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 (about 15 atm; 215 psi) 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 15. 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 16.

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.

3.5.5. 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 (2). 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 a 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 cause severe catalyst poisoning, causes a significant loss in productivity, the reactor is

emptied and a fresh catalyst batch added during a short period. 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 four years of commercial operation.

The authors (2) 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, 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 becomes 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. It is reported that "by proper scheduling of catalyst renewal, it is possible to maintain a steady selectivity profile for a single reactor while minimising 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 properly handled.

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 and to the separation processes. The technique currently in use in the commercial operation is considered to be proprietary information.

3.5.6. 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 products (7). 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 13,14). 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 published data on the Chinese F.-T. only operation, it is difficult to reach definitive conclusions on catalyst performance.

3.6. Products

3.6.1. Low Temperature vs High Temperature

The product distribution reported by Kölbel was typical of high temperature (low alpha) operation: C_{1-2} : C_{3-4} :gasoline (25-190°C):diesel oil (190-310°C):heavies (>310°C) = 7:17:62:10:3 (19). The olefin content of the C_{2-4} , 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 the following table:

Table 3			
Variations in Product Composition from the Kölbel Reactor (from ref. 19)			
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

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. 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 the above table, 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 approaching 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 $>450^{\circ}\text{C}$ 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.

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 the above table. 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.

3.6.2. Deviations from Anderson-Schulz-Flory

3.6.2.1. Positive Deviations

Since its introduction about 1950, the Anderson-Schulz-Flory distribution for the products from Fischer-Tropsch synthesis has been accepted. However, only a few investigators have been able to attain a product distribution that adheres to this single alpha distribution. Anderson, in his review in the 1950 showed data for products from large scale German and U.S. plants and these exhibited the "double-alpha" plot that has now been reported by many. Donnelly et al. (20) published an approach to calculate the two alphas from the experimental product distribution. Sasol workers report that it is difficult to obtain an accurate evaluation of the higher alpha value because of the small amount of wax production in laboratory studies. These workers report, however, that the Donnelly et al. approach is "suitable for the extrapolation of selectivities," (14). On the other hand, Shell workers (21) report that "In a few hundred independent F.-T. synthesis experiments with various catalyst formulations [iron, ruthenium and cobalt] under different operating conditions it was confirmed that the carbon number distribution were in close agreement with the AFS chain growth kinetics discussed above, with α values varying between 0.7 and 0.95 (Figure 17)." However, these authors did not provide data in their paper (Figure 17) that would cover adequately the carbon number ranges of both alpha values.

¹⁴C tracer studies carried out at the CAER using an iron catalyst produced data that led to the postulation of a double alpha ASF distribution with the additional provision that the lower alpha produced all F.-T. products but that the higher alpha

pathway produced only alkanes. More recent ^{14}C tracer studies included a measurement in the activity in the higher carbon number alkenes. This more recent data indicate that the ^{14}C distribution in the alkenes is consistent with a single ASF pathway. Accumulation of paraffins in the reactor provide a "product accumulation disguise" so that the second alpha products are due to reactor operation and not to two reaction pathways. Thus, based upon CAER data, the observation of a double alpha value is introduced by the operation of the reactor and not by the F.-T. mechanism.

As noted in another section, Sasol workers consider that an iron catalyst can be modified by the use of chemical promoters (e.g., potassium) but that cobalt cannot. On the other hand, the selectivity of cobalt is sensitive to the pressure but not the iron catalyst. Thus, the Sasol workers attribute the observations of the impact of chemical promoters as being due to pressure effects. Thus, they report the chain growth probability as a function of pressure (Figure 18). This translates into the product selectivities shown in Figure 19. It is obvious that if wax is the desired product pressure makes very little difference with the iron catalyst (25 atm appears optimum) but for the cobalt the wax production is still increasing relative to other products even at 40 atm pressure. The Sasol workers report that the wax boiling above 350°C can be easily hydrocracked to extinction, yielding about 80% diesel with a cetane number of at least 70.

3.6.2.2. Positive Deviation at Higher Carbon Numbers

There are many examples of this type of deviation and these examples have been produced in many laboratories as well as at large pilot or commercial plants (22). A number of reasons have been advanced to account for this distribution. Included

among these are two or more chain growth pathways, the impact of alkali, and alkene reincorporation.

A more logical explanation for the deviation is reactor operation and the hold-up of heavier materials.

3.6.3. Cut Off of Product Distribution

At the start-up of a slurry or even fixed-bed reactor a period of time is required until the vapor-liquid equilibrium is established. The length of time that it takes to reach vapor-liquid equilibrium depends upon carbon number; the higher the carbon number the longer the time it takes. Satterfield, Bell and others have shown the impact of this factor. This effect is a result of normal reactor operation and is independent of F.-T. selectivity deviations.

3.6.3.1. Chinese

Yang et al. (23) considered literature reports and proposed a new product distribution formulation. They proposed that ASF growth was followed but that on any metal crystal size, only molecules with a lower carbon number than the cut-off value could be produced. They fit an equation they derived to three sets of data and showed a good correlation between theory and experimental data. One set of data was for a series of carbon supported iron catalysts that had different distribution of metal crystallite sizes (24). There are two problems with the use of these data: (1) the metal crystallite size will have little meaning since under reaction conditions the supported Fe crystallites will be converted to iron carbide and/or iron oxide and (2) products were analyzed by an on-line g.c. with a transfer line that was heated only to a temperature that is consistent with the cut-off of products being due to vapor pressure effects rather

than metal crystallite size. A consideration of other data (25-35) show that the selectivities were most likely due to operational rather than F.-T. mechanistic factors.

Thus, while many accounts have been provided to show that cut-off has been accomplished, none of these studies have been conducted under realistic conditions for a sufficient length of time to ensure that liquid-vapor equilibrium had been established.

3.6.3.2. Syntroleum

The Syntroleum Process involves the conversion of gas to liquids and offers a variety of options. Agee (36) reports that work began on a program to produce a catalyst that limits the growth of hydrocarbon chains to eliminate wax production and at the same time minimizing the production of light hydrocarbons (C_1 - C_4). Agee reports that multi-week test runs in a fluid bed reactor at the pilot plant yielded a product profile that indicates success. Based upon data presented at the AIChE meeting, and repeated at the Spring ACS meeting (37), the C_1 - C_4 gases are low, and the products cut off by carbon number 25. The most surprising feature of this example is that there is a linear decline in the products with increasing carbon number in the C_1 - C_4 range. This cannot happen in a normal polymerization reaction unless the higher carbon number components also continue a similar decline. Agee indicates that the new chain-limiting catalyst eliminates the need for a hydrocracking step; presumably he did not eliminate hydrocracking as an operation that is combined with F.-T. However, this would have to be a new kind of hydrocracking since significantly more C_4 is produced than C_1 - C_3 during normal hydrocracking. Based upon currently practiced petroleum technology, it appears that the only way that the distribution shown Figure 20 is possible, would be for the C_2 - C_4 products to be converted to higher carbon number materials. This would imply that either the C_2 - C_4 fraction is primarily alkenes and that these alkenes are in

some manner caused to reincorporate in the F.-T. process to produce higher carbon-number products or to be oligomerized by some proprietary catalyst; this would explain the absence of the usual amounts of the C₂-C₄ fraction but still would not explain how these authors are able to terminate chain growth. If on the other hand, the products from the F.-T. step are not olefinic, then olefin reincorporation cannot explain their results and they would have to have discovered some new catalysis that will activate saturated alkane hydrocarbons, something that is being widely investigated today but so far with little success. In any event, the Syntroleum process produces a better product distribution than the very severe hydrocracking of F.-T. wax in the Shell process (Figure 21). At this time, Syntroleum has non-exclusive licensing agreements with three companies: Marathon Oil Co., Texaco, Inc. and Arco.

3.7. Slurry-Wax/Catalyst Separation

3.7.1. British

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 significantly coke formation, reliable data for wax/catalyst separation is not available.

3.7.2. Kölbel

A finely divided powder catalyst was utilized; the starting material has a particle size $<30\mu\text{m}$ but sizes during or after use is 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 (Kölbel) 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.

3.7.3. U.S. Bureau of Mines

The U.S. Bureau of Mines operated a 7.6 cm ID x 3.05 m high slurry reactor (e.g., 38). This unit utilized a parallel downflow slurry recycle line that was equipped with a porous metal filter. During a 52 day operating period, upsets in maintaining slurry circulation through the recycle line were encountered. It is not known whether this effect was responsible for the catalyst activity decline that occurred during the period of operation. For either the precipitated or fused iron catalyst, the original oxidic material was ground to provide $<60\ \mu\text{m}$ particles; following use the particle size was reduced to about $1\ \mu\text{m}$.

3.7.4. Mobil Oil

Mobil operated a slurry reactor and performed 13 runs during the course of its DOE contract (18). A simplified flow diagram of the two-stage plant is shown in Figure 13. During this run it is reported that:

"The improved on-line F.-T. reactor-wax separation system enabled us to increase the flexibility and reduce the manpower requirement for the reactor-wax/slurry separation. A schematic of this system is shown in Figure 14. During normal operation, slurry is withdrawn continuously from

the F.-T. reactor at the 610 cm level [762 cm to start of the conical shaped reactor area in Figure 14], and entrained gas is disengaged in a small disengager pot which is connected to the reactor-top. The gas-free slurry is passed through a dip-tube into a two-liter settling pot. The dip-tube length is designed to maintain 80% of the settling pot volume above its tip. The concentrated slurry exits the settling pot through a conical section, and is pumped back to the slurry reactor at the 305 cm level through a positive-displacement slurry pump. The pump is inverted, i.e., feed enters at the top and effluent exits at the bottom. This prevents catalyst settling in the feed line to the pump, but requires spring loading of the pump check valves. The clean reactor-wax is withdrawn from the top of the settling pot either semi-continuously by periodically opening a valve, or it can be withdrawn continuously by using a metering valve."

It was reported that the clean reactor-wax contained 0.03 % solids. During this operation the reactor slurry was reported to contain 25-27 wt% solids. This means that 0.12% of the solids in the reactor are removed in the clean wax. While this type of reactor-wax/catalyst separation may work at the pilot plant, it appears that the separation/reactor volumes would be very large for a commercial plant reactor.

3.7.5. Sasol

In a patent specification, Sasol workers define a wax/catalyst separation device and operational procedures for its use (Figure 22). A number of these separation devices are located in the reactor slurry. Reactor-wax can be withdrawn through the separation device; depending upon the catalyst size distribution some portion of catalyst fines will be removed together with the reactor-wax. The design of the

separation device is illustrated in Figure 23. A unique feature of this design is the use of a trapezoidal shaped wire utilized so that the filter exposes the smaller opening-size to the catalyst/wax slurry side and its larger opening-size to the clean reactor-wax side. This design is utilized so that any blockage of the separation device opening occurs on the catalyst/reactor wax side and can be easily removed by over-pressuring on the clean wax side at appropriate intervals. A unique feature of this design is that any particle that passes through the opening on the catalyst/reactor-wax side will be able to traverse the pore without being impeded by a pore constriction.

3.7.6. Exxon

Included in the more than 200 patents issued to Exxon is one that describes "a reactor housing having a plurality of reaction tubes vertically disposed therein for conducting slurry phase hydrocarbon synthesis reactions under substantially plug flow conditions, and wherein provision is made for uniformly distributing gas bubbles in slurry liquid into the reaction tubes (Figure 24).

Included in this patent is a description of a reactor-wax/catalyst separation device. This device is described thusly (39):

"...Above the liquid space is another tube sheet **30** holding filter cartridges **31** which may contain sintered metal mesh, woven metal fibers, glass fibers, cloth, fibrous carbon that can remove the catalyst particles while allowing passage of the liquid. The filter cartridges are each vertically aligned with each reaction zone and prevent catalyst particles from reaching the upper portion of the housing **8**. Above the filter cartridge tube sheet is a gas-liquid disengagement zone **36** topped by a foamy interface **38**. Liquid product from the hydrocarbon synthesis may

be removed via line **40**, or alternately via line **33** at or above the filter cartridge tube sheet. A demister **41** finally separates gas from liquid droplets and residue gases are withdrawn via line **42**. Thus, the liquid space above the upper tube ends and below the filter tube sheet allows fluid communication between the upper tube ends and the alternate slurry addition/removal conduit **32** as well as the space above the filter tube sheet. The space above the filters and filter tube sheet allows fluid communication of the gas outlet means, the liquid outlet means and the space below the filter tube sheet, thereby further allowing fluid communication to the upper ends of the reaction tubes."

3.7.7. Statoil

Patent applications by Statoil describe 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." (40). The drawings included in these applications are similar to the word description and/or the schematic drawings in the above patents.

The only examples of actual operation given in the Statoil patent applications are for a cold model using oil, alumina and nitrogen gas. The cold model was operated for about 40 hours without major plugging problems that inhibit liquid flow. However, it does not appear that the applications provide any data to substantiate the claims that they have overcome the problems enumerated in the DOE report.

3.7.8. China

The operators encountered problems in separating reactor-wax from the catalyst slurry in both the bench scale and the large plant. The data reported for the small bench scale plant indicated that the reactor wax discharged contained consistently 7.5 wt. % catalyst. Considering that the reactor contained a slurry with 12 wt.% catalyst, the separation was not very efficient. These workers indicate that the catalyst loss is the reason for the decline in activity and state that "...if we solve the problem of catalyst loss, long-term operation is very possible." (7).

3.8. Process Considerations

The relative usage of hydrogen and carbon monoxide depends upon the CO conversion level (Figure 10). A similar curve has been obtained by UOP workers (41). Thus, the hydrocarbon productivity per gram of iron and per reactor volume is higher at lower CO conversion levels. Furthermore, the fraction of CO that is converted to hydrocarbons is greater at lower CO conversion levels. Thus, up to CO conversion levels of about 50%, the iron and cobalt catalyst will exhibit similar activity and

hydrocarbon distribution selectivity properties. However, the iron catalyst operated at 50% or lower CO conversion will produce a very olefinic product. From the point of view of chemicals, such as could be utilized with a pioneer plant, the iron catalyst would provide a significant advantage. In fact, iron would be the preferred catalyst for any operation where chemicals would be a serious consideration.

Thus, in order to take full advantage of the activity and selectivity properties of the iron catalyst, it should be utilized in a process employing recycle or multiple reactors. It would appear that a process utilizing multiple reactors with water knock-out between reactors and the addition of make-up syngas, would be the preferred option.

An additional advantage of the iron catalyst is that it can be operated at a higher temperature than the cobalt catalyst. This would permit the generation of higher quality steam and with the iron catalyst the generation of electricity could be considered as an approach to utilize some of the energy rejected during the hydrocarbon synthesis step.

3.9. Supercritical Phase Fischer-Tropsch Synthesis

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. (42) 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 (about 50 atm.; 728 psi), 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, CO_2 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. The authors considered these differences to be significant and attribute the lower CO_2 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 should be viewed as suggestive at best.

Fujimoto et al. (43) report that the addition of a small amount of heavy 1-olefin in a supercritical-phase or liquid-phase F.-T. reaction medium greatly enhanced the selectivity of wax products, 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 25). The impact shown in Figure 25 is 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 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 remain the same; i.e., the rate of production of all carbon-number products should increase but should still be produced in the same ratio as they were when no alkene was 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. (44) 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. They did report slightly higher selectivities for the 1-alkenes during supercritical operation (Figure 26). They indicate that this suggests 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.

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Figure 1. SEM pictures of spray-dried iron catalyst: (a) Typical Sasol spray-dried catalyst; (b) catalyst with dimpled particles (from ref. 2).

Figure 2. Scanning electron micrograph from the UCI sample after carbiding and fraction of population versus particle size (from ref. 10).

Figure 3. Generation of carbon dioxide, a measure of activation of an iron catalyst with carbon monoxide in the CAEP autoclave (LEX 110) and slurry bubble column (LXU runs) reactor.

Fischer-Tropsch HA - Activation in AFDU Bubble Column
(75% CO, 25% N₂ Feed @ 2000 sL/hr-kg-Fe)

Figure 4. Activation of the iron catalyst prepared by United Catalysts, Inc. in the La Porte Run II.

Figure 5. Catalyst activity (CO conversion) following activation at reaction conditions in a syngas containing an increasing amount of hydrogen.

Figure 6. Site-time yield of products during F-T. synthesis with various cobalt catalysts (from ref. 12).

Figure 7. The effect of catalyst structural properties (χ) and site density on the C₅₊ selectivity (from ref. 12).

Figure 8. The extent of the water-gas-shift reaction as a function of the carbon monoxide conversion using an iron catalyst.

Figure 9. Effect of cobalt dispersion and support on Fischer-Tropsch synthesis rates using a cobalt catalyst (from reference 12).

Figure 10. Conversion of hydrogen (Δ), carbon monoxide ($\square$) and $\text{H}_2 + \text{CO}$ ($\circ$) during Fischer-Tropsch synthesis with an iron catalyst.

Figure 11. Activity comparison between an iron and cobalt catalyst at 20 atmosphere (from reference 14).

Figure 12. Productivity comparison between an iron catalyst (240°C) and a cobalt catalyst (220°C) (from reference 14).

Figure 13. Simplified flow diagram of the Mobil Oil two-stage plant for synthesis gas conversion (from reference 18).

Figure 14. Schematic diagram of the continuous settling system for catalyst/wax separation (from reference 18).

Figure 15. Schulz-Flory distribution for the first stage Fischer-Tropsch products obtained by Mobil Oil at a reactor wax yield of 46 wt.% (from reference 16).

Figure 16. Schulz-Flory distribution based on Mobil Oil data at low, intermediate and high alpha synthesis conditions (from reference 16).

Figure 17. Typical carbon number distribution reported by Shell for their Fischer-Tropsch data (from ref. 21).

Figure 18. Chain growth probability α_2 as a function of reactor pressure at a constant superficial velocity (from ref. 14).

Figure 19. Mass% product distribution as a function of reactor pressure at constant superficial velocity for (left) iron slurry phase catalyst and (right) a cobalt catalyst (from reference 14).

Figure 20. Plot showing selectivity data for Syntroleum "chain-limiting" catalyst (drawn from talk given by M. Agee at AIChE Meeting, Houston, 1997).

Figure 21. Data from figure 20 superimposed upon hydrocracking data presented by Shell (from reference 21).

Figure 22. Schematic of reactor and filtration apparatus patented by Sasol.

Figure 28. Expanded scale drawing of Sasol wax/catalyst separation device.

Figure 25. Product distribution in the olefin-added supercritical-phase F-T reaction with a cobalt catalyst: (○) no olefin added; (△), 1-tetradecene added; (□) 1-hexadecene added (from reference 42).

Figure 26. Effect of supercritical Ft Synthesis on α -olefin (a) and 2-olefin (b) selectivity using an iron catalyst (from reference 44).

Figure 24. Schematic of reactor and filtration apparatus patented by Exxon (from reference 29).

Figure 25. Product distribution in the olefin-added supercritical-phase F.-T. reaction with a cobalt catalyst: (○) no olefin added; (△), 1-tetradecene added; (□) 1-hexadecene added (from reference 42).

Figure 26. Effect of supercritical Ft Synthesis on α -olefin (a) and 2-olefin (b) selectivity using an iron catalyst (from reference 44).

3.3.4.8 Fischer-Tropsch Data Calculations

The FTS data and calculations can be broken into several major groups, these being the run and sample conditions, feed and product stream data, conversions, rates, selectivity's, product distributions, and finally alpha values. All the data is stored in raw form in a Microsoft Access database. Any conversions, scaling, and further manipulation of the data is done entirely by SQL query of the database system, with the single exception of the curve fitting for the calculation of alpha values. This curve fitting is primarily done with the SAS system of Statistical Software. The system has a Microsoft Visual Basic 5.0 front end for data entry with reporting by Crystal Reports Professional Version 6.

Run and Sample Conditions:

The run conditions which are of interest here initial values which will be used for the first and subsequent samples feed gas flow rate (slph) and composition, and the weight of the catalyst (g) and the Active metal (Fe or Co) and its weight percent. Also the date and time of the start of synthesis is recorded.

The sample conditions of interest are the date and time of the sample along with the feed gas (slph) along with its composition, the product gas flow (slph) and the weight of any liquid stream sample which were taken these being the water, light oil, heavy oil, and the wax (rewax) phase all in grams.

Feed and Product Stream Data:

Gas analysis is done on a Carle Gas Analyzer (AGC) which provides the mol percent of Hydrogen, Carbon Monoxide, Carbon Dioxide, Nitrogen, Methane, Ethane, Ethene, Propane, Propene, n-Butane, i-Butane, 1-Butene, iso-Butene, 2-trans-Butene, 2-cis-Butene. This GC is calibrated with a standard gas. The area counts of the olefin

and paraffin's of the carbon numbers from 5 to 10 are provided by the HP 5790 GC. The mol percents of the C5's through C10 will be calculated by multiplying the area count by a response factor. This factor is the sum of the AGC C4 mol percents divided by the sum of the area counts of the C4's from the HP 5790 GC. In summary, the database stores mol percents from the AGC and area counts from the HP 5790 GC. The conversion from area counts to mol percents is done on the fly using SQL queries. Additionally, The SQL will normalize these values after correcting for the vapor pressure of water at 1 atmosphere and 28° C (assumed typical conditions for the laboratory). This results in all gas components being in normalized mol percents.

For the liquid product streams all data is based on the weight percent. Water phase data is from the HP 5790 GC. Both oil phases are combined and analyzed on the HP 5890 GC. Finally the wax (rewax) is analyzed on a High Temperature HP 5890. If the startup wax is one with a very high molecular weight this data must be corrected as the startup wax may not come off the column. For these cases, an internal standard is used to determine the correction factor need to account for this missing mass. This prevents the inflation of the product weight fractions due to the detector not seeing the startup wax which depending on the time on stream may be as high as eighty percent of the wax phase.

Conversions (%)

H ₂ and CO Conversions	$100 ((\text{component mols in}) - (\text{component mols out})) / (\text{component mols in})$
(H ₂ + CO) Conversion	$((\text{CO in}) (\text{CO Conv.}) + (\text{H}_2 \text{ in}) (\text{H}_2 \text{ Conv.})) / ((\text{H}_2 \text{ in}) + (\text{CO in}))$

Conversion Rates (Conv. % / g Catalyst)

H ₂ , CO, Conversion Rates	$((\text{Component Conversion}) / (\text{weight catalyst \{g\}})) / 100 (\text{Percent Composition of Active Metal})$
(H ₂ + CO) Conversion Rate	$(\text{H}_2 \text{ Conversion Rate}) + (\text{CO Conversion Rate})$

Rates (mol/h)

CO Rate	$(\text{CO Feed \{mol/h\}}) (\text{CO Conversion})$
CO ₂ Rate	$(\text{Gas Product \{slph\}}) (\text{CO}_2 \text{ \{mol \%\}}) / (22.414 \text{ \{mol/sl\}}) / 100$
FT Rate	$(\text{CO Rate}) - (\text{CO}_2 \text{ Rate})$
C1-C4 Component Rate	$(\text{Gas Product \{slph\}}) (\text{Component \{mol \%\}}) / (22.414 \text{ \{mol/sl\}}) / 100$
C5 Plus Rate	$(\text{CO Rate}) - (\text{C1 Rate}) - (\text{C2 Rate}) - (\text{C3 Rate}) - (\text{C2 Rate}) - (\text{C1 Rate}) - (\text{CO}_2 \text{ Rate})$
C5 Plus HC Rate	$(\text{C5 Plus Rate}) (14.027 \text{ \{FW of CH}_2\}) / (\text{Weight Catalyst \{g\}})$

Selectivity (Carbon Basis)

C1-C4 Component Selectivity	$(\text{Component Rate}) / (\text{CO Rate}) 100 (\text{Carbon Number})$
C5 Plus Selectivity	$(\text{CO Selectivity}) - (\text{C1 Sel.}) - (\text{C2 Sel.}) - (\text{C3 Sel.}) - (\text{C4 Sel.}) - (\text{CO}_2 \text{ Sel.})$

Product Distribution (mol fraction by carbon number)

Mol Fraction	For each carbon number C1 to C100 the sum of mol fractions in the gas, oil, wax, and water phases
--------------	---

Olefin / Paraffin Selectivity (per Carbon Number)

Total Alkenes	(1-alkene) + (cis-2-alkene) + (trans-2-alkenes) {all in mols per hour}
Paraffin Ratio	(paraffin {mol/h}) / (total alkenes {mol/h})
Olefin Ratio	(1-olefin {mol/h}) / (total olefins {mol/h})

Mass Balance

Product Gas Effective Molecular Weight	Sum of each of gas components: (Mol Fraction) (Formula Weight)
Water Vapor {g/h}	Product gas is assumed to be saturated at 28° C and 1 atm.
Gas Prod {g/h}	(Gas Prod {slph}) (22.414 {mol/sl}) / (Effective MW {g/mol}) (Water Vapor {g/h})
Gas Feed {g/h}	(Gas Feed {slph}) (22.414 {mol/sl}) (28.01055 {FW of CO}) (CO Fraction) + (2.01594 {FW H ₂ }) (H ₂ Fraction))
Sum Liquid Product {g/h}	(water {g/h}) + (oil {g/h}) + (wax {g/h})
Mass Balance {g/h}	(Gas Feed {g/h}) - (Gas Product {g/h}) - (Sum Liquid products {g/h})
Mass Closure	(Mass Balance {g/h}) / (Gas Feed {g/h})

Alpha Values

Alpha values are primally fitted using the SAS Statistical Software. For a two alpha fit the data is fitted to $m(n) = x(1-a_1)a_1^{(n-1)} + (1-x)(1-a_2)a_2^{(n-1)}$. Where $m(n)$ is the mol fraction at carbon number n , x is the contribution by alpha 1, a_1 is alpha 1, and a_2 is alpha 2. For a single alpha fit: $m(n) = (1-a_1)a_1^{(n-1)}$. Where $m(n)$ is the mol fraction at carbon number n , and a_1 is the single alpha. For the fitting of data from literature where mol fractions have been reported for ranges of carbon numbers for example C1, C2-C4, C5-C10, C11-C20, and C20+ the internally written Alpha Fitter program was used.

SAS Program for Two Alpha Fit. (with sample data)

```
data a;
```

```
    input n y @@;
```

```
    cards;
```

```
1    0.047791693
2    0.040550869
3    0.035011413
4    0.020920487
5    0.013481663
6    0.010034115
7    0.007725418
8    0.006470921
9    0.005212527
10   0.004101158
11   0.00354337
12   0.002954146
13   0.002458323
14   0.002064626
15   0.001683087
16   0.001356415
17   0.001032646
18   0.000740856
19   0.000473017
20   0.000308679
```

21	0.000161864
22	0.000104361
23	6.27247E-05
24	3.94504E-05
25	2.37152E-05
26	1.61292E-05
27	9.86008E-06
28	6.6132E-06
29	4.34716E-06
30	3.20788E-06
31	2.25648E-06
32	1.7739E-06
33	1.06203E-06
34	8.12232E-07
35	5.66768E-07
36	4.37296E-07
37	3.16018E-07
38	2.50974E-07
39	1.51806E-07
40	1.51413E-07
41	1.21662E-07
42	7.46026E-08
43	6.56068E-08
44	6.40149E-08

45	5.68956E-08
46	5.62721E-08
47	4.98441E-08
48	4.98263E-08
49	4.41901E-08
50	4.37938E-08
51	3.82308E-08
52	3.87464E-08
53	3.29638E-08
54	3.37511E-08
55	2.86092E-08
56	2.9315E-08
57	2.43014E-08
58	2.45553E-08
59	1.97984E-08
60	1.96771E-08
61	1.44268E-08
62	1.56809E-08
63	1.16661E-08
64	1.25362E-08
65	9.49108E-09
66	1.1636E-08
67	8.09836E-09
68	7.88887E-09

```
69 4.77353E-09
70 5.51335E-09
71 2.848E-09
72 3.63534E-09
73 1.38808E-09
74 2.21318E-09
75 8.31286E-10
76 5.83877E-10
77 4.22772E-10
```

```
;
```

```
data r;
```

```
    set a;
```

```
    n = n;
```

```
    y = log(y);
```

```
proc nlin data=r method=dud best=10 smethod=golden;
```

```
    parms a1 = 0.5 to .99 by .1
```

```
        a2 = 0.5 to .99 by .1
```

```
        x = 0.01 to .99 by .1;
```

```
    bounds 0.01<a1<=0.99;
```

```
    bounds 0.01<a2<=0.99;
```

```
bounds 0.01<x<0.99;
```

```
z = x*(1-a1)*a1**(n-1) + (1-x)*(1-a2)*a2**(n-1);
```

```
model y = log(z);
```

```
output out=b p=yhat r=yresid;
```

```
data c;
```

```
set b;
```

```
y = exp(y);
```

```
yhat = exp(yhat);
```

```
proc plot data=b;
```

```
plot y*n='a' yhat*n='p' / overlay vpos=25;
```

```
plot yresid*n / vref=0 vpos=25;
```

```
proc univariate plot normal data=b;
```

```
var yresid;
```

```
proc capability data=b gout=gseg graphics;
```

```
var yresid;
```

```
histogram yresid / normal;
```

```
run;
```

```
quit;
```

Program for Single Alpha Fit (with sample data):

```
data a;
```

```
    input n y @@;
```

```
    cards;
```

```
1    0.047791693
2    0.040550869
3    0.035011413
4    0.020920487
5    0.013481663
6    0.010034115
7    0.007725418
8    0.006470921
9    0.005212527
10   0.004101158
11   0.00354337
12   0.002954146
13   0.002458323
14   0.002064626
```

15	0.001683087
16	0.001356415
17	0.001032646
18	0.000740856
19	0.000473017
20	0.000308679
21	0.000161864
22	0.000104361
23	6.27247E-05
24	3.94504E-05
25	2.37152E-05
26	1.61292E-05
27	9.86008E-06
28	6.6132E-06
29	4.34716E-06
30	3.20788E-06
31	2.25648E-06
32	1.7739E-06
33	1.06203E-06
34	8.12232E-07
35	5.66768E-07
36	4.37296E-07
37	3.16018E-07
38	2.50974E-07

39	1.51806E-07
40	1.51413E-07
41	1.21662E-07
42	7.46026E-08
43	6.56068E-08
44	6.40149E-08
45	5.68956E-08
46	5.62721E-08
47	4.98441E-08
48	4.98263E-08
49	4.41901E-08
50	4.37938E-08
51	3.82308E-08
52	3.87464E-08
53	3.29638E-08
54	3.37511E-08
55	2.86092E-08
56	2.9315E-08
57	2.43014E-08
58	2.45553E-08
59	1.97984E-08
60	1.96771E-08
61	1.44268E-08
62	1.56809E-08

```
63    1.16661E-08
64    1.25362E-08
65    9.49108E-09
66    1.1636E-08
67    8.09836E-09
68    7.88887E-09
69    4.77353E-09
70    5.51335E-09
71    2.848E-09
72    3.63534E-09
73    1.38808E-09
74    2.21318E-09
75    8.31286E-10
76    5.83877E-10
77    4.22772E-10
;
```

```
data r;
```

```
    set a;
```

```
    n = n;
```

```
    y = log(y);
```

```
proc nlin data=r method=dud best=10 smethod=golden;
```

```
parms a1 = 0.1 to .99 by 0.01;
```

```
bounds 0.1<a1<=0.99;
```

```
z = (1-a1)*a1**(n-1);
```

```
model y = log(z);
```

```
output out=b p=yhat r=yresid;
```

```
data c;
```

```
set b;
```

```
y = exp(y);
```

```
yhat = exp(yhat);
```

```
proc plot data=b;
```

```
plot y*n='a' yhat*n='p' / overlay vpos=25;
```

```
plot yresid*n / vref=0 vpos=25;
```

```
proc univariate plot normal data=b;
```

```
var yresid;
```

```
proc capability data=b gout=gseg graphics;
```



```
var yresid;  
histogram yresid / normal;
```

```
run;
```

```
quit;
```

3.4.0 Task 5. Reporting - Project Management

All reporting elements have been completed with the submittal of this final report.