Technology Development for Iron and Cobalt Fischer-Tropsch Catalysts

Quarterly Report

April 1, 1999 to June 30, 1999

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July 31, 1999

DE-FC26-98FT40308

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Abstract

CAER

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

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Potassium K-edge X-ray absorption near edge structure (XANES) spectra of Fe-Zn-K-Cu oxides and their carbides showed that K was well dispersed on Fe or Zn oxides while K was present as K_2CO_3 in the carburized samples. Fe K-edge XANES showed an absorption energy at 7.123 keV beyond the pre-edge (7.113 keV), indicating the presence of low oxidation state species like FeO besides the predominant Fe_2O_3 species. *In-situ* Fe K-edge XANES of Fe-Zn-K-Cu oxides in CO showed that Fe carbides had an absorption energy at 7.112 keV. The extended X-ray absorption fine structure (EXAFS) spectra confirmed the Fe-Fe distance in carbides at 2.0 Å. *In-situ* Fe K-edge XAS spectra of Fe-Zn-K-Cu oxides in synthesis gas showed that Fe carbides were formed in the dominant bulk Fe oxides, and that the extent of carburization increased with increasing space velocity and with time on stream. The effects of K on secondary hydrogenation and isomerization reactions of primary α -olefins and the effects of Cu on the activities for FTS and WGS reactions were examined on Fe-based catalysts. The results showed that Fe-Zn-Cu catalysts were active for secondary hydrogenation and isomerization reactions of α -olefins. The introduction of K to these catalysts titrated these active sites. The addition of Cu increased FTS and WGS reaction rates. The promotion effects of Cu on these activities were less marked than those observed with K promotion. The addition of Cu to Fe-based catalysts had little effect on hydrocarbon production and olefin selectivity. The D_2 - H_2 exchange studies showed that the H_2 dissociation step was reversible and quasi-equilibrated in FTS. D_2O tracer studies showed that water dissociation proceeded slowly and was not quasi-equilibrated. Based on the kinetic data, a mechanism for the overall CO conversion reaction on Co/SiO₂ catalysts was proposed.

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Executive Summary

CAER

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

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

Filtration results for the CAER are summarized below:

Summary of Filtration with Iron and Cobalt Catalysts			
Alpha	Iron, Unsupported	Iron, Supported	Cobalt, Supported
Low ($< \approx 0.7$)	No Problem	No Problem	---
Intermediate (0.7 to 0.85)	Problems in some runs	-----	No Problem
High (> 0.85)	Problems	Problems	No Problem

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During this reporting period, X-ray absorption measurements were carried out at the Stanford Synchrotron Radiation Laboratory (SSRL). We measured potassium K-edge spectra of Fe-Zn-K-Cu oxides and their carbides. We also measured *in-situ* Fe K-edge spectra of a typical

Fe-Zn-K-Cu oxide (Zn/Fe=0.1, K/M=0.02, Cu/M=0.01, M=(Fe+Zn)) during the reduction in H₂, and during the reduction and carburization in CO and in synthesis gas.

Potassium K-edge X-ray absorption near edge structure (XANES) spectra of Fe-Zn-K-Cu oxides and their carbides showed that K was well dispersed on Fe and Zn oxides rather than present as K₂CO₃, while K was present as K₂CO₃ in the carburized samples. For Fe-Zn-K-Cu oxides, beyond the pre-edge (7.113 keV), the Fe K-edge XANES showed the absorption energy at 7.123 keV, indicating the presence of low oxidation state species like FeO besides the predominant Fe₂O₃ species. *In-situ* Fe K-edge XANES of Fe-Zn-K-Cu oxides in CO at temperature up to 500°C showed that Fe carbides had an absorption energy at 7.112 keV. The EXAFS spectra confirmed the Fe-Fe distance in carbides at 2.0 Å. *In-situ* Fe K-edge XAS spectra of Fe-Zn-K-Cu oxides in synthesis gas at 270°C showed that Fe carbides were formed in the dominant bulk Fe oxides, and that the extent of carburization increased with increasing space velocity and time on stream.

We have also continued to investigate the effects of K and Cu on Fe-catalyzed FTS reactions. The effects of K on secondary hydrogenation and isomerization reactions of primary α -olefins formed during FTS were examined on Fe-based catalysts (Zn/Fe=0.1, Cu/M=0.01) with different K contents (K/M=0-0.04). Fe-Zn-Cu catalysts were active for secondary hydrogenation and isomerization reactions of α -olefins. The introduction of K titrated these active sites. At 235°C, the K-free catalyst was active for secondary reactions while K-promoted catalysts showed no activity for these reactions. At 270°C, these K-promoted catalysts became active for secondary reactions but their activities were much lower than for the K-free catalyst.

The effects of Cu on the activities for FTS and WGS reactions were examined on Fe-based catalysts (Zn/Fe=0.1, K/M=0.02) with varying Cu loading (Cu/M=0-0.04). The addition of Cu increased FTS and WGS activities. Further addition of Cu to Fe-based catalysts (Cu/M=0.02) had no additional promotion effects. In addition, the promotion effects of Cu on these activities were less marked than those observed for K. The addition of Cu to Fe-based catalysts had little effect on hydrocarbon productions and olefin selectivities.

In this quarter, the study of cobalt-based FTS was continued with focus on the reaction mechanism. The D₂-H₂ exchange, which was carried out under FTS conditions, showed that HD formation rates were much higher than the corresponding rates of hydrogen conversion to hydrocarbons (almost 20 times higher at zero CO conversion). This indicated that the H₂ dissociation step was reversible and quasi-equilibrated in FTS. D₂O tracer studies showed that the deuterium content in the H₂ isotopomers and hydrocarbons increased with increasing bed residence time. This indicated that water dissociation proceeded slowly and was not quasi-equilibrated during FTS on Co-based catalysts. The observed positive effect of water on the synthesis rate and C₅₊ selectivity can be explained if surface C* reacted with both H* and OH₂*. The latter pathway was affected by the partial pressure of gas phase water. Combined with the results of D₂-H₂ exchange and D₂O tracer experiments, we proposed a mechanism for the overall CO conversion.

1. $H_2 + 2* \leftrightarrow 2H^*$
2. $CO + 2* \leftrightarrow C^* + O^*$
3. $C^* + H^* \rightarrow CH^* + *$
4. $C^* + OH^* \rightarrow COH^* + *$
5. $O^* + H^* \rightarrow OH^* + *$
6. $OH^* + H^* \rightarrow OH_2^* + *$
7. $OH_2^* \leftrightarrow H_2O + *$

Applying the pseudo-steady state approximation through step 1 to step 7, we obtained a Langmuir-Hinshelwood type rate expression: $r_{\text{CO}} = aP_{\text{CO}}^{1/2}P_{\text{H}_2}^{1/4}(bP_{\text{H}_2}^{1/2} + cP_{\text{H}_2\text{O}})^{1/2}/(1 + dP_{\text{H}_2}^{1/2} + eP_{\text{H}_2\text{O}} + fP_{\text{CO}}^{1/2})^2$, where a, b, c, d, e, and f are temperature-dependent kinetic or thermodynamic parameters. The reaction kinetics of FTS was studied on a Co/SiO₂ catalyst over a wide range of reaction pressures and H₂/CO/H₂O ratios. This data will be regressed nonlinearly and fitted to a Langmuir-Hinshelwood type rate expression, which will be more representative of the true FTS mechanism on cobalt-based catalysts.

Task 1. Iron Catalyst Preparation

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

The effects of heat and gas composition on volume change of an unpromoted iron catalyst was studied using visual examination of a catalyst bed in a 1 inch diameter Pyrex tube.

Iron oxide pellets were prepared by precipitation of aqueous $\text{Fe}(\text{NO}_3)_3$ with NH_4OH (same preparation method used for RLS001). The gel was washed with at least seven volumes of distilled deionized water to remove excess NH_4 then extruded to form cylindrical pellets approximately 3 mm in diameter and 1 to 1.5 cm in length. The pellets were dried overnight at 120°C and calcined in a muffle furnace at 350°C for 8 hours. The catalyst was held in the center of the tube between glass wool plugs forming a bed approximately 3 cm long. The reactor tube was heated in a shell furnace controlled by a thermocouple inserted in the catalyst bed and video recordings were made at various points during heating to allow measurement of the pellets.

Initially the reactor was heated to 270°C in H_2/CO flow ($\text{H}_2:\text{CO} = 0.42$). Inspection after 1 hr. Showed no changes; however, after 24 hr. A shiny silver colored deposit was observed on the glass wool and inside wall of the Pyrex tube upstream from the catalyst bed. The charge was removed and attempts to clean the tube by scrubbing and heating proved unsuccessful; only soaking in aqua regia and subsequent washing removed the deposit. Analysis of the film identified it as an X-ray amorphous material consisting of C and Fe.

A number of changes were made to the system in an effort to eliminate the deposition of including: replacement of glass wool and beads with stainless steel screens to maintain the shape of the catalyst bed, changing from Pyrex to a quartz reactor tube, heating an inert gas before admitting H_2/CO or pure CO, diluting the CO stream with N_2 , testing the furnace for “hot spots”, carefully washing to remove all traces of catalyst fines upstream of the bed, reducing the temperature and finally heating the empty tube in flowing CO. In all cases the formation of a carbonaceous deposit on the inside of the reactor was observed at temperatures as low as 150°C even when empty. As a result, this method of measuring change in catalyst volume was determined to be unsuccessful.

Task 2. Catalyst Testing

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

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

Abstract

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

the case where α is small and all products are in the vapor phase, allowing evaporation of the startup solvent and a “drying out” of the reactor can a product accumulation produce a two- α plot.

Introduction

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

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

Continuous Stirred Tank Reactor

The continuous stirred tank reactor provides the advantage that all catalyst particles have the same average catalyst life (based on usage), all catalyst particles are exposed to the same synthesis gas composition, and the reaction temperature is uniform in the catalyst slurry. Thus, the typical CSTR for Fischer-Tropsch synthesis is operated under constant temperature, pressure and reactant compositions. A certain amount of paraffin is charged to the reactor as starting solvent to provide a slurry phase. Reactant gases, i.e., CO and H_2 , continuously flow into the reactor at constant rates. Vapor phase products, i.e., unconverted CO and H_2 , CO_2 , water, and volatile hydrocarbons, continuously flow out. Liquid phase products are either removed continuously or allowed to accumulate in the reactor for some time interval. In the latter mode of operation, the excess reactor liquid is drained periodically, as necessary, so that the reactor is operated at a nearly constant liquid level. The drained liquid is added to the vapor phase product to obtain the total reaction product for the sampling period.

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

F_{CO}, F_{H_2}, F :	molar flow rate of feed CO, feed H_2 , and total flow after reaction, respectively
X_{CO} :	CO conversion to hydrocarbons
x_i, y_i, z_i :	individual hydrocarbon molar fraction in reactor slurry, vapor stream, and the combined streams after reaction, respectively
k_i :	vapor-liquid equilibrium constant
L :	moles of reactor liquid
V :	molar flow rate of vapor stream

Fischer-Tropsch Reaction

For the Fischer-Tropsch reaction, it is assumed that CO and H_2 react stoichiometrically to produce hydrocarbons (exclusively paraffins for simplicity) and water following a single α ASF distribution and constant catalyst activity. Also, the fraction of CO converted to hydrocarbons (X_{CO}) is assumed to be constant through any reaction time period. Therefore, with constant reactant flow rates, the total flowrate of the stream after reaction (F) is constant. In addition, the each component in the reactor effluent (z_i) is constant with time. The water gas shift reaction, which is significant with an iron catalyst, is not included explicitly in this model because it is an equal molar reaction that does not impact the total reactor effluent flow. This reaction does not affect hydrocarbon product distribution if the gases are insoluble, or of limited solubility, in the reactor liquid.

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

and the composition of each hydrocarbon produced by the reaction

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

Vapor-Liquid Separation

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

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

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

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

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

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

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

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

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

Model Simulation

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

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

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

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

The paraffin vapor pressure was also estimated using Antoine's equation whose constants are obtained from API Project 44 (19). The difference between vapor pressure from these two sources and their impact on FT product distribution will be discussed later. A temperature dependent correlation from the literature (20) is used to estimate the partial molar volumes of paraffins in the FT liquid. Other conditions for simulation are Newton's method for iteration of Equation (6), accuracy of the sum of liquid molar fraction of 0.0001 (Eq. (7)), and time interval of 0.01h for each numerical calculation.

Before reaction, a certain amount of C_{28} paraffin is added to the reactor as start-up solvent. This volume is used as the liquid volume to be maintained in the reactor. The catalyst volume is ignored in this simulation. The reaction effluent enters the separator, with vapor

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

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

Simulation Results

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

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

Figures 5 and 6 show the simulation results with $\alpha=0.65$ when the reactor is drying-out at 508 h due to excessive evaporation of the start-up solvent. The vapor stream is the only product collected since the reactor liquid level decreases with time-on-stream, and hence no liquid can be drained from the reactor. As shown in Figure 5, the hydrocarbon fraction in the reactor liquid decreases with carbon number except when the reactor is close to drying-out, in contrast to

normal operation (Figure 2) in which liquid fraction increases with carbon number and then decreases after reaching a maximum. Figure 6 shows the vapor phase composition, together with the theoretical ASF plot (dotted line). It is interesting to note that after some time on stream (e.g., 400 h), the vapor composition begins to show positive deviation from the ASF distribution. Obviously, this is due to the flashing-off of previously-accumulated heavier hydrocarbons, in agreement with earlier observations (17). Misinterpretation of this phenomena may lead to the conclusion of a two α product distribution. It should be noted that, with single α chemistry, positive deviation is possible only under drying-out conditions. Under the extreme situation when the reactor is dry (508 h, liquid level 0.1% of initial level in this simulation), an abnormal phenomena occurs. The plot at this time on stream indicates that the α value can be larger than unity over a range of carbon numbers, which is impossible from the chemical reaction stoichiometry.

As mentioned previously, a correlation from the literature is used to calculate the paraffin vapor pressure for vapor/liquid separation. Data from other sources may lead to different product distribution. Figure 7 compares the differences for the paraffin vapor pressure at 270°C from two sources, the one used in this simulation and the other one from API Project 44 (19). For carbon numbers higher than about 40, the vapor pressure deviates from each other, and the deviation becomes greater with increasing carbon number. As a result, predicted product distribution in both vapor phase and liquid phase depend on the data used. For the example shown in Figure 8, vapor pressure from API Project 44 predicts higher concentration of C_{30+} paraffins in the vapor phase, and a lower concentration in liquid phase. However, when the reactor reaches “steady-state”, the total reaction product distribution is represented by a single α straight line. The dependence of vapor and liquid on vapor pressure is canceled out when the drained liquid is added to the vapor to produce the total reaction product. It is therefore reasonable to predict that as long as the reactor is operated under normal conditions, the total reaction product distribution is independent of the vapor-liquid equilibrium constant (k value), although vapor and liquid compositions will vary.

Conceptual Illustration

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

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

For easier discussion, it is assumed that the liquid phase density is constant so that its volume is directly proportional to its mass. The vapor phase and liquid phase are not necessarily in equilibrium, nor do they need to be an ideal mixture. This binary separation process can be described as:

- 1) During any time interval Δt_i ($t_i - t_{i-1}$), F amount of A flows in, V_i amount of A flows out, and Δ_i is the amount of A leftover in the liquid phase.

- 2) Vapor flows out continuously, but the liquid level might increase due to accumulation of A. The liquid is drained to the level of L_0 instantaneously or at time t_n , if L_n is higher than L_0 .

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

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

Total component A collected in vapor phase: $V = \sum V_i = nF - \sum \Delta_i = F_{in} - \sum \Delta_i$

Total component A drained from liquid phase:

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

Total A sampled

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

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

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

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

the flowing vapor. In FT synthesis, product distribution will exhibit positive deviation from ASF distribution. When the reactor is nearly dry (Case 4), F_{out} is much larger than F_{in} , which explains the “hump” in Figure 6.

Liquid Sampling Instantaneously (constant liquid level)

In this case, liquid level is kept constant by draining extra liquid instantaneously at each time interval. The liquid level is kept at the amount of L_0 after liquid draining. Table 2 shows the material balance of component A at each time interval. Similar to the above example where liquid is allowed to accumulate, the amount of A in output cannot be higher than its input unless under drying out conditions.

Summary

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

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Table 1 Amount of Component A at Any Time Interval When the Liquid Is Allowed to Accumulate

Time	A in Vapor	Amount of Liquid Phase	Concentration of A in Liquid Phase
0		L_0	A_0/L_0
t_1	$V_1 = F - \Delta_1$	$L_1 = L_0 + \Delta_1$	$C_1 = \frac{A_0 + \Delta_1}{L_1} = \frac{A_0 + \Delta_1}{L_0 + \Delta_1}$
t_2	$V_2 = F - \Delta_2$	$L_2 = L_0 + \Delta_1 + \Delta_2$	$C_2 = \frac{A_0 + \Delta_1 + \Delta_2}{L_2} = \frac{A_0 + \Delta_1 + \Delta_2}{L_0 + \Delta_1 + \Delta_2}$
t_3	$V_3 = F - \Delta_3$	$L_3 = L_0 + \Delta_1 + \Delta_2 + \Delta_3$	$C_3 = \frac{A_0 + \Delta_1 + \Delta_2 + \Delta_3}{L_3} = \frac{A_0 + \Delta_1 + \Delta_2 + \Delta_3}{L_0 + \Delta_1 + \Delta_2 + \Delta_3}$
.....			
t_i	$V_i = F - \Delta_i$	$L_i = L_0 + \Delta_1 + \Delta_2 + \dots + \Delta_i$	$C_i = \frac{A_0 + \Delta_1 + \Delta_2 + \dots + \Delta_i}{L_i} = \frac{A_0 + \Delta_1 + \Delta_2 + \dots + \Delta_i}{L_0 + \Delta_1 + \Delta_2 + \dots + \Delta_i}$

Table 2 Amount of Component A at Any Time Interval When Liquid Is Drained Instantaneously

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

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

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

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

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

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

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

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

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

Figure 9. Schematics of a binary separation system.

Task 3. Catalyst Characterization

The objective of this task is to obtain characterization data of the prepared catalysts using routine and selected techniques.

No scheduled or further activity to report.

Task 4. Wax/Catalyst Separation

The objective of this task is to develop techniques for the separation of catalysts from FT reactor slurries.

For the use of an iron Fischer-Tropsch synthesis catalyst in a continuous bubble column slurry reactor, a serious problem is the continuous separation of the heavy wax product from the catalyst slurry. Various approaches have been utilized to separate wax from the catalyst slurry. These include gravity settling with removal of the clean wax, centrifugation, and either external or internal filtration.

While the separation of wax from the catalyst slurry is a problem at the commercial scale, it usually becomes even more difficult as one reduces the scale to one that is practical at the laboratory level. In the following we describe some results obtained at the laboratory scale.

The surface area of our precipitated iron catalysts is of the order of 300 m²/g. TEM examinations show that the individual particles have nearly spherical shape. Both TEM and surface area measurements indicate that the individual particles are about 3.0 nm (30 Å) in diameter. These small particles agglomerate into clusters that are in the 1-3 micron size range. Spray drying of the slurry allows the individual agglomerates to be formed into spherically shaped particles which have an average diameter that depends upon the variables utilized during spray drying. The SEM pictures at four magnifications of a typical product from the spray drying of the precipitated iron catalyst are shown in Figure 1. At the lower magnification, one can readily see that very uniform spheres are produced by spray drying and that they have the appearance of a good catalyst as defined by Sasol (1). At the highest magnification of one of these spheres, it is evident that the spheres consist of 1-3 micron particles.

Using the 2"x6' bubble column reactor, four activations were performed with a spray dried iron catalyst batch that was prepared by United Catalyst Inc. The activation consisted of treating in flowing carbon monoxide for twenty-four hours, ramping the temperature to 200°C in nitrogen and then to 280°C during three hours. At the end of the twenty-four hour activation period, the shape and size of the catalyst particles were identical to the initial catalyst spheres (2). A sample of the activated catalyst was placed in an oil and tumbled at room temperature for increasing periods of time. It was found that, under these conditions, the iron spherical particles attrited by a gradual removal of the outer layers of the sphere rather than by fracturing the product into two or more fragments (schematically illustrated in Figure 2).

There are two properties of the iron/carbon system that contribute to the problem. The first is the change in volume as the iron oxide is converted to the iron carbide form that is needed to have an active catalyst. As the iron oxide is converted to the carbide, there is merely 100% decrease in the density as determined from X-ray diffraction. Likewise, if the iron carbide is oxidized during usage, there will be a nearly 100% expansion in size. This expansion/contraction exerts severe strain on the particle and leads to loss of the integrity of the

catalyst particle that was formed by spray drying. There are two extreme views of the impact of the contraction/expansion: in one instance the spherical catalyst particle would remain the same size and any volume change would be restricted to the smaller particles that make up the primary catalyst sphere and in the other instance the entire catalyst sphere would undergo shrinkage to nearly one-half in size as the carbide was formed (schematically shown in Figure 3). The limited data obtained in the 2" diameter slurry bubble column reactor show that the catalyst sphere remains the same size after carbiding as it had in the oxide form. This means that the size of the individual particles making up the catalyst sphere undergoes a volume contraction during carbide formation and that this will significantly increase the void space between the individual particles and, at the same time, greatly reduce the contact area between individual particles that serve to hold the sphere together.

A second factor is the hardness of the iron oxide. An empirical relationship has been established between strength, hardness and melting-point of inorganic solids with respect to the ability to form pellets. As illustrated in Figure 4, the properties of iron oxide cause it to fall in a region where it would be unpelletable. Thus, the forces that develop during drying that are caused by the presence of water at the points of contact are not sufficiently strong to overcome the hardness of the iron oxide particle. The result of this is that the agglomerate that forms during spray drying is held together by very weak forces, and is therefore easily broken down to the 1-3 micron sized individual particles. To alleviate this problem, some component needs to be present that will assist in making a stronger bond between the individual particles as the spherical particle is formed during the spray drying operation.

SUMMARY OF FILTRATION WITH DIFFERENT CATALYSTS

We have utilized a variety of catalysts for Fischer-Tropsch synthesis in the CSTR using internal filters. Our experience with many runs with each type of catalyst is summarized in table 1.

Table 1			
Summary of Filtration with Iron and Cobalt Catalysts			
Alpha	Iron, Unsupported	Iron, Supported	Cobalt, Supported
Low ($< \approx 0.7$)	No Problem	No Problem	---
Intermediate (0.7 to 0.85)	Problems in some runs	-----	No Problem
High (> 0.85)	Problems	Problems	No Problem

Our filtration experience with alumina and silica supported cobalt catalysts, with a few instances when the alumina support did not possess attrition resistance, have been successful. We have run for periods of three months without encountering problems with filtration. This has been the case even when the catalyst loading was so large that the amount of wax produced required us to filter two times per day.

Our limited experience with iron supported catalysts (silica, alumina, magnesium silicate and magnesium aluminate) has, in general, not been reproducible. All four supports show

attrition resistance during the CSTR runs. Thus, it appears that the filtration problems, when encountered, are due to the iron particles being removed from the support and interfering with the filtration and/or separation by gravity settling. More work needs to be done to confirm this.

Problems are not encountered in removing the small amount of reactor wax from the reactor when using the low-alpha precipitated, unsupported iron catalyst. With intermediate iron catalysts, filtration problems are encountered in some runs but not in others. These runs may be of 1,000 hours duration or longer. For the high alpha, precipitated, unsupported iron catalyst we almost always encounter filtration problems at some point in the run; however, the point at which this occurs is very variable.

Estimation of Filtration Rate at Sasol

One approach to evaluate the needed filtration rate is to try to estimate one that is realized in a commercial operation. In the following we utilize the published data for the size of the Sasol slurry reactor (5m x 22m) and the productivity of the reactor (2,500 bbl/day). Assuming that the reactor is only 2/3rds filled with slurry and that the hydrocarbon has a density of one, one can calculate that the productivity is 57.8 kg/hr/m³ reactor volume. It is further assumed that the filter has a cylindrical shape and occupies 1% of the reactor volume; that is, the reactor volume would be reduced by 1% by the filter. It is assumed that 75% of the total product is removed from the reactor through the filter and the remainder goes overhead. One m³ of reactor volume will contain 1.36 m² of filter area. With these assumptions, the filtration rate is 0.53 kg/min/m² of filter area. It is realized that there may be significant errors introduced in the assumptions leading to this calculated value; however, attempts have been made to make assumptions on the conservative side so that the value should be viewed as a conservative estimate.

In operating the CAER CSTRs we have made estimates of the rate of filtration through Mott sintered metal filters. In making this estimate, it has been assumed that the filter is completely immersed in the slurry and that the total filter area is utilized. In actual practice, it is likely that during part of the filtration time the filter is only partially immersed, and this will make the measured rate be lower than the actual filtration rate. Likewise, it is assumed that the removal of wax occurs during the entire draining period. In actual practice, the wax removal will occur during the earlier portion of the time the valve is open, and this will also make the measured value be lower than the actual value under optimum operation. During one of the runs the measured rate was 2.4 kg/min./m² filter area. Thus, the sintered metal filter will easily provide the filtration rate, and much higher, than is estimated for the Sasol commercial operation. If this is the case, then the filtration problems are associated with technique, and not with the initial capacity of the sintered metal filter.

CAER Filtration Procedure

A schematic of the CSTR system is shown in Figure 5. Two paths are available for the reactor products to exit, depending on the configuration/arrangement of the valves associated with the sample traps. The components of interest are the hot (or rewax) letdown valve and trap, the warm (or wax) letdown valve and trap, and the equalizing valve between the hot/rewax and warm/wax traps).

The primary path for products to exit the reactor is via a line that connects a port on the upper, inner surface of the reactor head to the warm/wax trap. Ideally, these products are in the vapor phase. After exiting the reactor head, they pass through a 7 μ m sintered stainless steel filter and then through the warm/wax trap letdown valve to pass through the warm/wax product

trap (typically set for a temperature of 100°C). The reactor effluent then flows to the oil trap to condense the oil fraction (usually set for 0°C). The remaining product gas passes through the back pressure regulator, where the pressure is reduced to a value slightly above atmospheric, and then to either an on-line gc or to the vent line.

An alternate path for the products to exit the reactor is via the rewax filter. This filter has been positioned at several levels below the inner top surface of the reactor head, ranging from the liquid-gas interface to being immersed in liquid near the bottom of the reactor. The porosity of the rewax filters have ranged from 0.5 to $2\mu\text{m}$. The material exiting the rewax filter then passes through the hot trap letdown valve and then on into the hot/rewax product trap (normally set to 200°C). The products then pass through an "equalizing" valve located between the rewax and wax traps and then passes in turn through the wax and oil traps and finally through the back pressure regulator to either the gc or the vent line. Note that in this configuration the wax trap letdown valve is closed, thus eliminating a short circuited path for the reactor effluent. This ensures that the reactor effluent flows through the series arrangement of first the rewax trap, then the wax trap, and finally the oil trap.

Ideally, the system should be operated to have a continuous gas plus liquid products exit the reactor. To accomplish this the reactor product should continuously exit the reactor through the rewax filter and pass through the series arrangement of the rewax, wax, and oil traps. In this mode of product removal the wax trap letdown valve would be closed so that no product could be shunted around the rewax trap. In theory, utilizing this mode of operation for product letdown would allow for an accumulation of reactor contents to a fixed level, which would be determined by the positioning of the rewax filter. Once the slurry level had increased to the level of the rewax filter, both gas and liquid product would be continuously at the slurry-gas interface from the reactor through the rewax filter (thereby achieving a volumetric steady state condition). If the slurry level did rise to completely submerge the rewax filter, the reactor inlet gas pressure would temporarily rise and this should be sufficient enough to force the excess liquid product out through the filter, allowing the pressure to return to the desired setting once gas breakthrough occurred. This mode of operation is appealing in theory, in that a fixed volumetric inventory could be maintained. Unfortunately, the accumulation and build up of product/catalyst with time on the rewax filter causes a pressure drop across the rewax filter to increase; this results in an increase in the reactor pressure. In fact, in the past, the increased pressure drop across the rewax filter has resulted in the reactor pressure attaining a value equal to the inlet pressure of the mass flow controllers, resulting in no flow into the reactor.

Due to the inability to operate in the continuous mode mentioned above, a different technique for the letdown of reactor products was developed. The continuous method was modified by allowing the rewax trap to be bypassed for the majority of the sample period. Sample periods are typically one day in duration, with the exception of those following weekends and holidays when longer periods are encountered. The valving arrangement for this modified technique has the rewax trap letdown valve in the closed position and with both the wax trap letdown and the wax/rewax trap equalizing valve in the open position, for the majority of the time. In this configuration, the slurry in the reactor can increase to levels above that of the rewax filter, resulting in an unsteady state volumetric condition. Usually, several hours prior to the daily collection of trap products, the rewax letdown valve would be opened and the wax trap letdown valve would be closed, while the wax/rewax trap equalizing valve would remain in the open position. This permitted the reactor product (gas and/or liquid) to exit exclusively through the rewax filter (either 0.5 or $2\mu\text{m}$ filter) as opposed to essentially an open port in the top of the

reactor head (which does have the 7 wax filter). In this configuration, it was expected and realized that the reactor pressure would increase, particularly if the level of the reactor's contents was sufficient to completely immerse the rewax filter. To insure that the reactor pressure did not increase to values much higher than that of the specified pressure for FTS or to pressures that would stall out the mass flow controllers, required continual monitoring of the reactor pressure. If and when the reactor pressure increased to an unacceptable level, the wax letdown valve would be opened slightly to allow venting down of the pressure build up in the reactor, and then the wax letdown valve would be closed to continue the reactor liquid product letdown procedure.

Not only did this procedure result in pressure swings during the liquid letdown period, but at best, the reactor inventory would oscillate about some level, neither of which to be considered steady state. In fact, there was no guarantee that the amount of liquid reactor product withdrawn was equivalent to that which was being produced in the reactor for a given sample period. Later, a technique was adopted that utilized a computerized mass balance method designed to predict the day-to-day reactor accumulation of product.

Another valving modification and letdown technique that was tried was to have all the valves associated with the sample traps (i.e., the letdown valve for the rewax trap, the wax trap, and the equalizing valve between the rewax and wax traps) in the open position at all times. It was thought that the two parallel paths for the reactor products to exit the reactor, which recombine at the inlet to the wax trap, would allow for the continuous removal of both the gaseous and liquid products to exit without variations in the reactor pressure. The reactor pressure did in fact remain constant as there was always a path for the overhead condensable gaseous products to exit the reactor via the wax discharge line (through the 7 μ -wax filter and then through the letdown valve leading to the wax trap). The second of the two parallel paths for products to exit, which is for the removal of the accumulated liquid reactor product, incorporates the 0.5 or 2 μ m rewax filter, which is internal to the reactor, and the letdown valve leading to the rewax trap. As mentioned, the discharge line from the rewax trap feeds through a "wax/rewax trap equalizing" valve into the inlet of the wax trap. The pressure difference across the path for removal of the accumulated liquid product is at least equal to, or slightly greater than, that of the pressure difference that exists across the discharge path for the condensable gas products. It was thought that the force that was generated as a result of this pressure difference, although small in value, would be sufficient to provide the necessary driving force to aid in the removal of the accumulated liquid reactor product. In practice, this was not the case and liquid would accumulate in the reactor more rapidly than it was removed through the rewax filter.

Experimental Data-Process Operations

The initial runs effected separation of reactor product from catalyst slurry using a 0.5 μ Mott Metallurgical Corporation sintered stainless steel filter (0.5 " O.D. and 1" in length for a surface area of 0.0109 ft²). This filter was positioned so that the bottom surface is about 3 inches from the upper internal surface of the head of the one-liter CSTR, which has an internal diameter of 3" and an internal height of 10 $\frac{1}{4}$," with a hemispherical bottom and a cylindrical shaped top. Since using the Polywax PWR3000 high molecular weight wax (average molecular weight of 3,000) as a reactor solvent, problems have persisted in that the filter was increasingly being blinded off, resulting in an increasing inability to remove the reactor product (i.e., the heavy liquid product at reactor temperature and pressure we refer to as 'rewax'), allowing the reactor to ultimately fill up, resulting in aborting the runs. Potential solutions to this problem have been suggested and/or implemented.

The first attempt, which has been incorporated, was to lower the filter to insure that it is completely immersed in the catalyst slurry. This allows the filter to be continually washed by the slurry and eliminate or at least minimize the blinding off of the filter. To accomplish, the filter is lowered at an elevation so that its bottom surface is about seven inches below the upper surface of the reactor; that is, the bottom of the filter is positioned about 1/4 inch above the upper surface of the gaspersator blades.

The first run using this lowered filter configuration was LGX263 using a low-alpha catalyst (100Fe:4.60Si/2.72Cu/0.00K). As shown in Figure 6 (i.e., Rewax Flux Density vs Sample Day for Run LGX263), problems were encountered in attempting to remove the rewax for the first 12 days of operation. This was due to the fact that the line from the reactor head to the rewax trap was heated at a too low of a temperature, specifically lower than the melting point of the Polywax PWR3000 (130°C). When additional heat tracing was applied to the line, rewax removal was then permitted as can be seen for sample days 13-17. The rewax collected during this run showed no visible traces of iron. The filtration rate was about 0.06 gallon/min/ft² filter area/min., a value that compares favorably with that estimated for the Sasol commercial plant.

Another run that also incorporated the lowered filter utilized a high alpha iron catalyst (LGX266; (100Fe:4.60Si/2.72Cu/7.52K). Figure 7 shows the performance of the filter, as measured by flux density (gpm/ft²), decreased with time. The implication is that blinding of the filter increases with subsequent rewax letdown periods. As in run LGX263, the rewax product showed no visible evidence of iron catalyst content. Two rewax samples, LGX266-005 and LGX266-007, were analyzed for iron content and showed 0.03wt% Fe and 0.01wt% Fe, respectively. Also, note that on this figure there is reference to the Regimesh Filter that has a flux density of 0.13-0.20 gpm/ft, surface area of 0.175 ft², and a porosity of 18μ (corresponding to about 16 times the area and an increase of 36 times the porosity of the Mott SS-filter that we were using). With the maximum pressure drop across the Mott SS-filter at 75 psi and the pressure drop across the Regimesh filter unknown, a comparison of the performance of the filters is not possible. From the liquid flow characteristic graphs supplied with the Mott product catalog, by changing the μ-grade from 0.5 to 20μ (while holding the viscosity and pressure drop constant) the flux density should increase about 100-fold. However, if the pressure difference is varied and the μ-grade and viscosity held constant, the relationship between the flux density and pressure drop is linear.

After the completion of run LGX266, an attempt was made to test a 2μ Mott SS-filter. This was accomplished by opening up the reactor after it had cooled to 130°C and replacing the 0.5 μ-filter with a 2μ-grade filter. Comparing the liquid flow media charts in the Mott catalog for the 0.5μ and 2μ filters, at equal pressure differences and viscosities, the average flux density should increase by a factor of seven. Once the reactor was back to normal operating conditions, the rewax valve was opened for a rewax letdown period of one hour. About 300g of reactor contents were removed. The collected product contained catalyst but it was not possible to decide if:

- 1) the wax/catalyst leaked through an improperly tightened filter fitting,
- 2) had it passed straight through the 2μ filter,
- 3) was due to the fact that the level had dropped so much that the filter was exposed to the gas/froth space that may contain finely ebullated catalyst particles, or
- 4) possibly a combination of the above.

Since the results of the 2 μ filter at the end of Run LGX266 were inconclusive, another 2 μ filtration test was attempted after Run LGX268 was completed (LGX268 used the 100Fe:4.60Al/2.72Cu/3.66K as well as a 0.5 μ filter). The results from this series of rewax letdowns was more promising since the rewax product collected appeared catalyst free. Thus, a run was made with the installation of a 2 μ filter prior to the start of a run (LGX271; (100Fe:4.60Al/2.72Cu/15.87K). During a 240 hour run, with CO conversion at about 30%, rewax could be removed that did not contain catalyst. The run was terminated because of the low catalytic activity.

The second of the potential solutions to address the problem of rewax removal and reactor overfilling was to develop a mass balance for the system to allow for the prediction of the amount of rewax to be removed so that a constant reactor inventory could be maintained. Simply stated,

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

Two versions of this mass balance were developed. The first just accounts for the mass of the gas out based on the Carle Series 400 AGC chromatographic data and is referred to as the simplified mass balance. The second, and certainly more sophisticated, utilizes chromatographic data from the HP-5790 as well as the AGC data. By adding either reactor accumulation terms to the starting weight of the wax/catalyst slurry, a predicted reactor inventory is determined. Runs LGX's 267, 269, and 270 have had either one or both of these mass balances applied to them, with mixed results. Figure 8 shows run LGX267 (100Fe:4.60Al/2.72Cu/0.00K) using the second mass balance which predicted that there was about 127g remaining in the reactor, while in fact the reactor contents were measured at 92g after the completion of the run. Note that the dashed line across the graph indicates the starting weight of the of the reactor slurry, which was 318.68g. Figure 9 is for run LGX269 (100Fe:4.60Al/2.72Cu/7.52K), which also had a starting weight of 318.68g. Both mass balances are presented and up until run hour 144, agree rather well with one another. After run hour 144 there is a divergence of predicted reactor contents in which there is an approximate 50g difference in values. At the end of the run the disagreement was at about 40g, but the actual measured amount of wax/catalyst in the reactor for this run was at 598g, 55% more than the second mass balance predicts and 73% more than the first, i.e., the simplified mass balance prediction. These discrepancies have yet to be resolved. A final application of the mass balances, to date, was used for run LGX270 (100Fe:4.60Al/2.72Cu/11.58K) shown in Figure 10. For this run the predicted reactor contents agree to within about 20 g of one another, 384.8g for the simplified and 363.2g for the second method (within 6% of each other), as well as both prediction models compared to the final measured wax/catalyst weight of 310g (24% high for the simplified method and 17% high for the second method). Although there is some disagreement with either method and the final actual weight of the reactor contents, this is potentially a very useful technique for maintaining and predicting reactor inventory, as well as predicting the amount of rewax to be removed from the reactor on a daily basis.

The third of the solutions for addressing the problem of reactor rewax removal and that of avoiding reactor overfilling involves the installation of a liquid back flush bomb for the rewax filter. Presently, the rewax bomb itself can be used as a gas charging vessel by closing the rewax letdown valve and the equalizing valve between the rewax and wax traps. An inert gas can then be introduced into the rewax bomb at a pressure higher than that of the reactor, the rewax valve opened and the gas pressure can force the hydraulic column of rewax (contained in the rewax line and the rewax filter) to back flush the filter. Although this capability does exist and has been

used, there is probably not enough rewax present in the line and filter to perform an adequate backflush. In addition, the rewax letdown valve is a flow control/throttling type of valve and does not allow for an instantaneous surge of higher pressure gas to force the rewax material as, for example, a ball valve would allow. With a bomb installed on the branch of a tee (with a ball valve separating the bomb and the branch of the tee) and the run of the tee plumbed between the reactor head rewax discharge port and the existing rewax valve, liquids such as C-30 oil could be used to facilitate this back flush. Such an apparatus will be constructed and tested.

The most recent method/technique used in assisting the removal of reactor liquid product involves isolating and charging the hot/wax trap (see Figure 5) to a pressure about 75 psi lower than that of the reactor. Once the trap is at the desired pressure, the hot trap letdown valve can be opened to allow the pressure difference to force out the reactor liquid product. A variation of this technique uses the gas law to predict the pre-letdown pressure for a desired volume of reactor liquid removal.

The importance of cleaning the filter cannot be understated, and can be demonstrated by returning to Figure 7. It is seen that as time progresses, the flux density decreases, requiring longer periods of letdown time to remove the desired amounts of rewax, which are determined by using either of the reactor mass balance techniques. This was experienced for FTS runs LGXs 267, 269, and 270. The situation was such, that to remove the necessary amount of rewax, the letdown periods were approaching six to seven hours in duration.

References

1. B. Jager and R. Espinoza, *Catal. Today*, **23**, 17 (1995).
2. R. Srinivisan, L. Xu, R. L. Spicer, F. L. Tungate and B. H. Davis, Fischer-Tropsch catalysts. Attrition of carbided iron catalyst in the slurry phase, *Fuel Sci. & Tech. Intl.*, **14**, 1337 (1996).

Figure 1. Scanning electron microscope pictures of spray-dried, precipitated, iron catalyst at four increasing magnifications ($\times 100$, $\times 200$, $\times 500$, $\times 1,000$; size scale indicated in picture).

Figure 2. Schematic of attrition of spray-dried precipitated iron catalyst by a gradual decrease in size of the primary particle.

Figure 3. Schematics of size changes in activation of an iron catalyst and then reoxidation for: (top) whole particle changes size and (bottom) whole particle remains same size and individual units of particle changes size.

Figure 4. Relationship of physical properties and pelletability of compound classes.

Figure 5. Schematic of CAER reactor system (top) and CSTR (bottom).

Figure 6. Rewax flux density vs. sample day for run LGX263_{R7}
(100Fe:4.60Al/2.72Cu/0.00K).

Figure 7. Rewax withdrawal weight and rate vs. sample day for run LGX266_{R7} (3.0wt.% Cu, 5.0 wt.% K, $T_{\text{syn}} = 230^{\circ}\text{C}$).

Figure 8. Predicted reactor inventory vs. time-on-stream for run LGX267_{R1}.

Figure 9. Predicted reactor inventory vs. time-on-stream for run LGX270_{R4}.

Task 5. Oxygenates

The objective of this task is to obtain a better understanding of the factors that affects catalyst selectivity toward oxygenates for iron-based Fischer-Tropsch catalysts.

An HP G-2350A gas chromatograph with an Atomic Emission Detector (AED) has been purchased in April 1999 at no cost to this project. This instrument has an oxygen channel which will detect only compounds which contain oxygen. This channel in combination with the carbon channel will allow oil samples to be screened for small concentrations of oxygenates.

Task 6. Literature Review of Prior Fischer-Tropsch Synthesis with Co Catalysts

The objective of this task is to prepare a critical review of prior work on cobalt Fischer-Tropsch catalysts.

No scheduled or further activity to report.

Task 7. Co Catalyst Preparation

The objective of this task is to prepare a limited number of cobalt-based Fischer-Tropsch catalysts that can be used to obtain baseline data on cobalt-based Fischer-Tropsch synthesis.

No scheduled or further activity to report.

Task 8. Cobalt Catalyst Testing for Activity and Kinetic Rate Correlations

The objective of this task is to conduct initial screening of the cobalt catalysts prepared in Task 7 to select three baseline catalysts that will then be used to generate a data base on the performance of cobalt-based Fischer-Tropsch catalysts in slurry reactors.

A. Ru, K, Pt, Re promoted cobalt silica catalysts

Davisil silica gel 644 produced by W R Grace was used as support material. Particle size of silica gel is 100-200 mesh, surface area is 300m²/g and pore volume is 1.15cm³/g. Incipient wetness impregnation technique was used to prepare the catalyst. 2kg of silica gel was impregnated by cobalt nitrate solution and then dried by air in a fluidized vessel. Three steps of impregnation was carried out to get 15% cobalt loading.

Ruthenium, potassium, platinum and rhenium promoted cobalt silica catalyst was prepared by incipient wetness impregnation also and precursor used were: ruthenium nitrosyl nitrate, potassium carbonate, tetramineplatinum nitrate and rhenium oxide respectively. For each promoter, four catalysts with different metal loadings were prepared. Ruthenium loadings are 0.2%, 0.5%, 1.0%, 2.0% (weight percent). To platinum and rhenium promoted catalysts, Pt:Co and Re:Co atomic ratios are the same as Ru:Co atomic ratios in ruthenium promoted catalysts. Potassium loadings of Co-K/SiO₂ catalysts are: 0.5%, 1.5%, 3.0% and 5.0% (weight percent) respectively. All promoted catalysts were dried in a rotary evaporator and then calcined at 400°C for 4hrs.

B. Cobalt silica catalysts with different cobalt loading

Davisil 952 silica gel by W R Grace was used as support material, particle size 60-80 mesh, surface area $309\text{m}^2/\text{g}$ and pore volume $1.61\text{cm}^3/\text{g}$. Five catalysts with different cobalt loadings (weight percent 5%, 10%, 15%, 20% and 25%) were prepared by incipient wetness technique using cobalt nitrate as precursor, multiple impregnation steps were used to prepare high cobalt loading catalysts. All the catalysts were dried in a rotary evaporator and followed by calcination at 400°C for 4hrs.

C. Preparation of boron-modified Co/TiO₂ catalysts

A series of boron-modified TiO₂ carriers (0.05, 0.10, 0.50 and 1.00 wt% boron) were prepared by pore volume impregnation of Degussa P-25 TiO₂ (72% anatase, $45\text{m}^2/\text{g}$, calcined at 673 K for 6 h) with solutions containing various amounts of boric acid (Aldrich). Samples containing 1.00 wt% boron was prepared by double impregnation of the TiO₂ using one-half the required amount of boron for each impregnation step. Samples were dried at 393 K for 4 h between impregnation steps. All samples in the series were finally dried at 393 K for 16 h and then calcined in air for 6 h at 693 K.

Cobalt (10 wt%) was deposited on the boron-modified (or boron-free) TiO₂ carrier by pore volume impregnation with cobalt nitrate (Alfa) solution. Samples were dried at 393 K for 16 h and calcined at various temperatures before they were used.

D. Preparation of Ru-modified Co/TiO₂ catalysts

Co-Ru/TiO₂ catalysts were prepared by impregnating pretreated (10 wt%) Co/TiO₂ with solutions containing different amounts of ruthenium nitrosyl nitrate (Alfa). The samples were dried at 393 K for 16 h and calcined at various temperatures before they were used. The ruthenium contents were 0.05, 0.10, 0.20 and 0.40 wt%, respectively, corresponding to an atomic Ru/Co ratio of 0.00292, 0.00583, 0.0117 and 0.0233.

Task 9. Cobalt Catalyst Life Testing

The objective of this task is to obtain life data on baseline cobalt Fischer-Tropsch catalysts.

No scheduled for further activity to report.

Task 10. Cobalt Catalyst Mechanism Study

The objective of this task is to determine the impact of secondary reactions on the relationship of cobalt Fischer-Tropsch catalysts under conditions appropriate to slurry bubble column reactors.

No scheduled or further activity to report.

Task 11. University of California, Berkeley (Subcontract)

The objective of this task is the characterization of the structure and function of active sites involved in the synthesis of high molecular weight hydrocarbons from CO and H₂ on multi-component catalysts based on Fe as the active component.

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III. REFERENCE

I. FISCHER-TROPSCH SYNTHESIS ON IRON CATALYSTS

1. Background

1.1. *Structure and Function of Active Phases in Fischer-Tropsch Synthesis*

Fe-based oxides have been used as commercial catalysts for Fischer-Tropsch synthesis (FTS) to produce a large variety of paraffin and olefin products, ranging from methane to high molecular weight waxes [1]. During activation by synthesis gas and subsequent FTS reaction, several phases including metallic iron, iron carbides and iron oxides are known to co-exist at steady-state conditions [2-5]. The distribution and amounts of these phases depend on exposure to various activation and reaction conditions, leading to different catalytic performances in FTS. Some researchers [6] have proposed that surface iron atoms are responsible for FTS activity, while some others considered surface carbides or a mixture of carbides [7,8] and metallic iron [9] to be the active phase. There are also some reports that suggest that magnetite Fe_3O_4 is the active phase in FTS [10-12]. Although these studies have each provided some evidence to support their specific proposals about the active phase, the available information remains phenomenological, and a method to identify the active phase during reaction and to count the number of active sites has not yet been established.

Based on the previous research on Co [13,14] and Fe catalysts [15,16] for FTS as well as our last quarterly work on TPSR of Fe oxides in H_2 , our characterization during this research period involved temperature-programmed reactions of Fe-based catalysts with flowing streams of CO or H_2 -CO mixtures. We monitored the gas phase concentrations throughout the reduction and carburization processes by means of an on-line mass spectrometer, and followed the evolution of bulk phases and crystal size by X-ray diffraction and of surface area by nitrogen physisorption measurements. In this way, we can determine the temperature required for the formation of Fe carbides as well as the stoichiometry and structure of such carbides. Our goal is to develop a new synthesis method to improve the compositional and structural purity of Fe carbides formed, and consequently to refine the structure-function relationships that we have previously proposed to interpret the catalytic behavior of Fe-based catalysts.

1.2. *Effects of Zn, K and Cu*

Many components have been added to Fe catalysts in order to improve their mechanical and catalytic properties. Our previous studies have shown that zinc, alkali and copper [16,17] promote the catalytic properties of Fe oxides. Zinc oxide, as a non-reducible oxide in FTS conditions, appears to stabilize the surface area of Fe oxide. Alkali, as a modifier of the adsorption enthalpies of H_2 and CO, increases the selectivity to desired C_{5+} products. Copper promotes the carburization processes and decreases the temperature required for the activation of iron oxide. Here, our efforts have focused on Fe-Zn-K-Cu catalysts. We have prepared a series of Zn and Fe co-precipitated oxides with varied Zn/Fe ratios and then introduced varying amounts of K and Cu. We are examining the surface area, bulk structure, required reduction and carburization temperatures as well as the catalytic behavior of these catalysts, in order to identify optimum Zn/Fe ratios and Cu and K contents that give maximum site density and catalytic activity.

2. Synthesis Procedures for Fe-Zn-K-Cu Oxides

All catalysts were prepared by co-precipitation of zinc and iron nitrates at a constant pH of 7.0 in order to form porous mixed oxides. Then, these oxide precursors were impregnated with an aqueous solution of potassium and copper salts using incipient wetness methods. The Zn/Fe oxide precursors were prepared first. Fe nitrate (1.4 M) and Zn nitrate (3.0 M) solutions were mixed at a given atomic Zn/Fe ratio. A solution of ammonium carbonate (1 M) was prepared separately. Deionized water (ca. 50 ml) was added into a large flask, which was heated on a hot plate with a magnetic stirrer and held at 80 °C throughout the preparation process. The mixed Zn/Fe solution was added at 2 cm³/min flow into the flask through a feeding pump. At the same time, the ammonium carbonate solution was fed separately, and its flow was controlled to maintain the slurry pH at 7±0.1, as monitored by a pH meter. The resulting precipitates were washed several times with about 1 l water per gram of catalyst, dried at 120 °C overnight, and then calcined at 350 °C for 1 h. The calcined material was promoted with 2 at.% K using K₂CO₃ solution (0.16 M) by incipient wetness and then dried. The same process was repeated in order to promote samples with 1 at.% Cu using Cu(NO₃)₂ solutions (0.16 M). Finally, the dried material was treated in dry air at 400 °C for 4 h. This final calcination temperature was chosen from temperature-programmed oxidation data, which showed that this temperature is sufficient to decompose all metal nitrates and carbonates except K₂CO₃. The catalysts contain CuO, ZnO, Fe₂O₃ and K₂CO₃. These catalysts were pressed at 443 MPa into pellets, lightly crushed, and then sieved to retain the 80 - 140 mesh fraction for FTS reaction.

3. Catalyst Characterization

3.1. *Protocols for the Characterization of Fe-based FTS Catalysts*

This research program addresses the synthesis and the structural and catalytic characterization of the active sites of Fe-based catalysts for FTS. We have designed a matrix of samples that contains a systematic range of multi-components catalysts in order to determine the number and type of surface sites present on fresh catalysts and the samples after FTS reaction (Table 1.1). Our objective is to develop rigorous relationships between the synthesis methods, the resulting catalyst structures, and their function in FTS reactions.

3.2. *In-Situ X-ray Absorption (XAS) Studies on Fe Catalysts*

In-situ X-ray absorption near edge (XANES) and extended X-ray absorption fine structure (EXAFS) analyses provide us with the information about the oxidation states and the local structure of catalysts during FTS. In this reporting period, X-ray absorption measurements were carried out at the Stanford Synchrotron Radiation Laboratory (SSRL). We measured potassium K-edge spectra of Fe-Zn-K-Cu oxides and their carbides on beamline VI-2. Also, we measured *in-situ* Fe K-edge spectra of a typical Fe-Zn-K-Cu oxide (Zn/Fe=0.1, K/M=0.02, Cu/M=0.01, M=(Fe+Zn)) during TPR in H₂ on

Table 1.1. Matrix of Fe-Zn-K-Cu samples and characterization methods for FTS reaction

Composition of the Catalysts			Characterization Before and After FTS	FTS reaction
Zn/Fe mole ratio	K/(Fe+Zn) (at.%)	Cu/(Fe+Zn) (at.%)		
0	0	0	XRD Surface area In-situ XAS H ₂ -TPR CO-TPR (H ₂ +CO)-TPR	Effect of reaction condition 220 °C 21.4 atm 235 °C 21.4 atm 270 °C 5 atm Effect of CO ₂ addition
		1		
	2	0		
		1		
		2		
	4	1		
0.05	0	0		
	2	1		
	4	2		
0.1	0	0		
		1		
	2	0		
		1		
		2		
	4	1		
0.2	0	0		
	2	1		
	4	2		
0.4	0	0		
		1		
	2	0		
		1		
		2		
	6	1		

beamline VI-2, and the reduction and carbonization in CO and in synthesis gas on beamline II-3, respectively. Experiments were performed using a Si(111) monochromator crystal. X-ray absorption spectra were obtained in transmission mode. For potassium K-edge spectra, the solid samples were finely ground and sealed in a Prolene^{TM} envelope and fixed in the plate window. Thickness effects were not a problem for K spectra measurements since the specimens contained about 2-4 at.% K. For *in-situ* Fe K-edge spectra, we diluted the samples with graphite powder to obtain 7 wt.% Fe. The samples were ground with graphite, pressed into pellets, and sieved to retain the 45-60 mesh fraction, and loaded into a quartz capillary cell for measurement as described in the previous quarterly report.

3.3 *In-situ Fe K-edge XAS Measurement for Fe-Zn-K-Cu Oxide in H₂*

3.3.1. Fe K-Edge XANES

The Fe K-edge XANES spectra of Fe₂O₃, Fe₃O₄ and Fe foil are shown in Figure 1.1. The spectrum for Fe₂O₃ shows a strong absorption edge derived from the transition immediately above the threshold to the continuum, which is referred to as the white line. Fe₃O₄ shows a pre-edge peak below the absorption edge that is assigned to the *1s* to *3d* transition, and a sharp peak above the pre-edge derived from the transition of *1s* electron to continuum similar to that of Fe₂O₃. XANES spectrum for Fe metal shows a shoulder near the edge, but no white line. The XANES spectra of the Fe-Zn-K-Cu oxide (Zn/Fe=0.1, K/M=0.02, Cu/M=0.01, M=(Fe+Zn)) shows a pre-edge peak at 7.113 keV, reflecting a *1s* to *3d* electronic transition that is dipole-forbidden in centrosymmetric structures, but becomes allowed in tetrahedral or distorted octahedral structures because of p-d orbital mixing. Since the bulk phase of this Fe-Zn-K-Cu oxide is Fe₂O₃, and Zn is present in an amorphous form of ZnFe₂O₄, this pre-edge feature is most likely contributed by the presence of ZnFe₂O₄, where Fe occupies the distorted octahedral holes [20]. With an increase of temperature, the pre-edge features change and the absorption edges shift to lower energies. Above 280 °C, the spectra increasingly show more characteristic features of metallic Fe, suggesting that the oxide reduces.

3.3.2. Fe K-Edge XANES Differential Spectra

Figure 1.2 shows the Fe K-edge XANES differential spectra of standard compounds Fe₂O₃, Fe₃O₄, and Fe, and *in-situ* spectra of the Fe-Zn-K-Cu oxide in H₂ with increasing temperatures. Fe₂O₃, Fe₃O₄ and Fe metal show Fe K-edge energies at 7.127, 7.125 and 7.112 keV, respectively. For the Fe-Zn-K-Cu oxide, beyond the pre-edge (7.113 keV), the spectrum presents the first inflection point at 7.123 keV, which is lower than that of Fe₂O₃ or Fe₃O₄. This suggests the presence of a low oxidation state species like FeO in this Fe-Zn-K-Cu oxide besides the predominant Fe₂O₃ bulk phase. With increasing reduction temperature, the Fe K-edge shifts to lower energies and significant reduction to metallic Fe occurs at temperatures above 280 °C. This reduction temperature appears to be about 70 °C lower than that obtained from our TPSR experiment for the H₂ temperature-programmed reduction, where the reduction to metallic Fe occurs at about 350 °C. Although we can not quite explain the temperature difference between the XAS

results and that of TSPR, the reduction trend is consistent with the results from TPSR experiments.

Figure 1.1. Fe K-edge XANES spectra of Fe standard compounds: Fe₂O₃, Fe₃O₄ and Fe foil; *In-situ* Fe K-edge XANES spectra of a Fe-Zn-K-Cu oxide (Zn/Fe=0.1, K/M=0.02, Cu/M=0.01, M=(Fe+Zn)) in H₂ (8 mg sample; 7 wt.% Fe; 5 cm³/min H₂) at different temperatures.

Figure 1.2. Fe K-edge XANES differential spectra of Fe standard compounds: Fe_2O_3 , Fe_3O_4 and Fe foil; *In-situ* Fe K-edge XANES differential spectra of a Fe-Zn-K-Cu oxide ($\text{Zn/Fe}=0.1$, $\text{K/M}=0.02$, $\text{Cu/M}=0.01$, $\text{M}=(\text{Fe}+\text{Zn})$) in H_2 (8 mg sample; 7 wt.% Fe; $5 \text{ cm}^3/\text{min H}_2$) at different temperatures.

Figure 1.3. EXAFS of Fe K-edge for Fe standard compounds: (a) Fe_2O_3 , (b) Fe_3O_4 and (c) Fe foil; *In-situ* EXAFS of Fe-K-edge for a Fe-Zn-K-Cu oxide ($\text{Zn/Fe}=0.1$, $\text{K/M}=0.02$, $\text{Cu/M}=0.01$, $\text{M}=(\text{Fe}+\text{Zn})$) in H_2 (8 mg sample; 7 wt.% Fe; $5 \text{ cm}^3/\text{min}$ H_2) at (d) room temperature, (e) 180 °C and (f) 600 °C.

3.3.3. Fe K-Edge EXAFS

Figure 1.3 shows the Fe K-edge EXAFS Fourier transforms of standard compounds Fe_2O_3 , Fe_3O_4 and Fe metal, and the Fe-Zn-K-Cu oxide treated in H_2 at 180 °C and 600 °C. For Fe_2O_3 , Fe is coordinated to first and second closest neighbor oxygen atoms at 1.7 Å and 2.0 Å, respectively; Fe in Fe_3O_4 is coordinated to the first and second closest neighbor oxygen atoms at 1.8 Å and 2.0 Å, respectively. For Fe metal that is body-centered cubic structure, its Fourier transform shows two shells with the first and second closest Fe-Fe distance in the first shell at 2.2 Å and 3.5 Å, respectively. For Fe-Zn-K-Cu oxide, the Fe K-edge Fourier transform resembles that of Fe_2O_3 , indicating that it mainly consists of Fe_2O_3 . At 180 °C, some oxygen coordination is lost but Fe is still coordinated with most of oxygen atoms. At 600 °C, the end of H_2 TPR, the EXAFS spectrum looks like that of Fe metal, indicating the complete reduction of the Fe-Zn-K-Cu oxide to Fe metal.

3.4. In-situ Fe K-edge XAS Measurement for Fe-Zn-K-Cu Oxide in CO

3.4.1. Fe K-Edge XANES

Figure 1.4 shows the Fe K-edge XANES spectra of Fe-Zn-K-Cu oxide in CO at temperatures up to 500 °C. At 200 °C, there is no appreciable change of the absorption edge. When increasing the temperature by 100 °C, both the pre-edge feature and the edge energy change markedly, suggesting significant changes in structures and oxidation states. The pre-edge feature of Fe-Zn-K-Cu oxide disappears and an absorption shoulder similar to that in Fe metal begins to form. When the temperature increases up to 500 °C, the absorption edge features increasingly resemble those of Fe metal.

3.4.2. Fe K-Edge XANES Differential Spectra

Figure 1.5 shows the Fe K-edge XANES differential spectra of Fe-Zn-K-Cu oxide in CO. Again, the Fe-Zn-K-Cu oxide shows a pre-edge at 7.113 keV. Beyond the pre-edge feature, the spectrum presents the first inflection point at 7.123 keV. There are no evident changes in pre-edge and absorption edges when increasing the temperature up to 200 °C, indicating that the oxide is not reduced at 200 °C. After increasing the temperature by 100 °C, a new inflection point at 7.112 keV emerges as the pre-edge features disappear. This inflection point coincides with that of Fe metal. Since Fe carbides have been confirmed to be the bulk phase at 500 °C by our previous TPSR experiment, it is believed that this indicates that Fe carbide has the same absorption energy as Fe metal. As the temperature increases to 500 °C, the edge energy remains at 7.112 keV but the energies of the rest of the inflection points continuously increase or decrease. This suggests that the phase changes continue to occur through the temperature range of the reduction and carburization treatments.

3.4.3. Fe K-Edge EXAFS

Figure 1.6 shows the Fe K-edge EXAFS Fourier transform spectra of Fe-Zn-K-Cu oxide in CO. At 200 °C, the EXAFS spectra resemble that of its Fe-Zn-K-Cu oxide. At 300 °C,

the Fe-Fe distance decreases from 2.5 Å in the starting Fe oxide to 2.0 Å, suggesting that a phase transformation occurs. With further carburization, more oxygen atoms are removed. Although a small amount of oxygen remains in the Fe carbide at the end of the carburization (500 °C), most of the Fe is in the carbide phase. We can conclude that the Fe-Fe distance at 2.0 Å can be ascribed to the Fe-Fe distance in Fe carbides. In addition, it appears that oxygen in Fe-Zn-K-Cu oxide can be removed completely at 500 °C if enough time or higher temperatures is allowed for carburization.

Figure 1.4. *In-situ* Fe K-edge XANES spectra of a Fe-Zn-K-Cu oxide (Zn/Fe=0.1, K/M=0.02, Cu/M=0.01, M=(Fe+Zn)) in CO (8 mg sample; 7 wt.% Fe; 5 cm³/min CO) at different temperatures.

Figure 1.5. *In-situ* Fe K-edge XANES differential spectra of a Fe-Zn-K-Cu oxide (Zn/Fe=0.1, K/M=0.02, Cu/M=0.01, M=(Fe+Zn)) in CO (8 mg sample; 7 wt.% Fe; 5 cm³/min CO) at different temperatures.

Figure 1.6. *In-situ* Fe-K-edge EXAFS for Fe-Zn-K-Cu oxide ($\text{Zn/Fe}=0.1$, $\text{K/M}=0.02$, $\text{Cu/M}=0.01$, $\text{M}=(\text{Fe}+\text{Zn})$) in CO (8 mg sample; 7 wt.% Fe; 5 cm³/min CO) at (a) RT, (b) 200 °C, (c) 300 °C, (d) 350 °C, (e) 400 °C, (f) 500 °C.

3.5. *In-situ Fe K-edge XAS Measurement for Fe-Zn-K-Cu Oxide in Synthesis Gas*

3.5.1. Fe K-Edge XANES

Figure 1.7 shows the Fe K-edge XANES spectra of Fe-Zn-K-Cu oxide in synthesis gas at 270 °C with varying space velocities. With increasing space velocity, we observed minor changes of the pre-edge features and the slight shifts of the absorption edges to lower energies. However, the global features resemble Fe-Zn-K-Cu oxide more than Fe metal.

3.5.2 Fe K-Edge XANES Differential Spectra

Figure 1.8 shows the Fe K-edge XANES differential spectra of the Fe-Zn-K-Cu oxide in synthesis gas with varying space velocities. At 200 °C, the absorption edge moves to lower energies in synthesis gas than in CO at the same temperature (Figure 1.5). This confirms our TPSR conclusion that reduction occurs at lower temperatures in H₂ than in CO, because H₂ dissociates on the reduced Cu at lower temperatures and consequently decreases the required reduction temperature. With increasing temperature up to 270 °C and with increasing space velocity, the absorption edge shifts slightly to lower energies and the peak at the pre-edge region increases and shifts slightly to lower energy regions. This shift and the increase of the peak at the pre-edge region indicate the formation of a new phase Fe carbide with an absorption edge energy at 7.112 keV.

3.5.3. Fe K-Edge EXAFS

Figure 1.9 shows the Fe K-edge EXAFS Fourier transform spectra of Fe-Zn-K-Cu oxide in synthesis gas. The Fe K-edge EXAFS in synthesis gas is more complicated than in CO or H₂. Although Fe is mainly coordinated to oxygen atoms, a peak at a radius of 2.0 Å begins to form, which represents the Fe-Fe distance in Fe carbide. This peak increases with increasing space velocity and with time on stream. This indicates that Fe carbide is formed, although the dominant bulk phase remains Fe oxide. When the temperature is decreased to 250 °C, Fe oxides continue to carburize. This suggests that the extent of carburization increase with increasing space velocity and with time on stream.

3.6. *Potassium K-Edge XANES of Fe-Zn-K-Cu Oxides and Carbides*

Figure 1.10 shows the potassium K-edge XANES spectra of K₂CO₃ and of several Fe oxide samples with varying K contents. The XANES spectra of K₂CO₃ are dominated by two major peaks: the first peak at ~ 3 eV represents the transition of 1s electrons to continuum, whereas the second peak with X-ray energy at 10 eV is the result of multiple scattering resonances. For K-promoted Fe oxides with different Zn contents (Fig 1.10 (a), (b), (d)), the post-edge features of the samples are significantly different from that in K₂CO₃. Although we need to examine other standard K compounds in order to identify the phases of K in these Fe catalysts, it is clear that K is not present as bulk K₂CO₃ crystallites. Rather, K is well dispersed on Fe and Zn oxides. After carburization in CO up to 800 °C (Fig1.10 (c)), the carbide samples have more characteristic post-edge features of K₂CO₃, and the higher the K and Cu contents, the more likely K is the form of

K_2CO_3 . It appears that the bonding between K and Fe or Zn is broken during carburization, and K recombines forming K_2CO_3 in Fe carbides.

Figure 1.7. *In-situ* Fe K-edge XANES spectra of a Fe-Zn-K-Cu oxide (Zn/Fe=0.1, K/M=0.02, Cu/M=0.01, M=(Fe+Zn)) in CO/H₂ (8 mg sample; 7 wt% Fe; CO/H₂=1/2, 0.5-3 cm³/min) at different temperatures and space velocities.

Figure 1.8. *In-situ* Fe K-edge XANES differential spectra of a Fe-Zn-K-Cu oxide (Zn/Fe=0.1, K/M=0.02, Cu/M=0.01, M=(Fe+Zn)) in CO/H₂ (8 mg sample; 7 wt% Fe; CO/H₂=1/2, 0.5-3 cm³/min) at different temperatures and space velocities.

Figure 1.9. *In-situ* Fe K-edge EXAFS spectra for a Fe-Zn-K-Cu oxide (Zn/Fe=0.1, K/M=0.02, Cu/M=0.01, M=(Fe+Zn)) in CO/H₂ (8 mg sample; 7 wt% Fe; CO/H₂=1/2, 0.5-3 cm³/min) at (a) RT (0.5 cm³/min), (b) 200 °C (0.5 cm³/min), (c) 270 °C (0.5 cm³/min), (d) 270 °C (1.5 cm³/min), (e) 270 °C (3 cm³/min), (f) 250 °C (3 cm³/min).

Figure 1.10. Potassium K-edge XANES spectra of K_2CO_3 and K-promoted Fe oxides. (a) $Zn/Fe=0$, $K/M=0.02-0.04$; (b) $Zn/Fe=0.1$, $K/M=0.02-0.04$; (c) $Zn/Fe=0$, $K/M=0.02-0.04$ after carburization in CO up to 800 °C (0.2 g sample; 10 °C ramping rate; 100 cm³/min, 20% CO in Ar); (d) $K/M=0.02$, $Zn/Fe=0-0.4$, and $M=(Zn+Fe)$.

4. Fischer-Tropsch synthesis on Fe-based catalysts

4.1. Investigation of K Effects on FTS Reactions

In the last quarter, we reported partial results about K effects on the catalytic activities for both the Fischer-Tropsch synthesis (FTS) and the concurrent water-gas shift (WGS) reactions and hydrocarbon selectivities on Fe-based catalysts. Experiments and data analyses on K promotion effects were completed during this reporting period. We report here K effects on secondary reactions (hydrogenation and isomerization) of primary α -olefin products on Fe-based catalysts (Zn/Fe=0.1, Cu/M=0.01) with varying K contents (K/M=0-0.04) in a fixed-bed reactor at different temperatures and pressures (235 °C and 21.4 atm; 270 °C and 5 atm) using synthesis gas with a H₂/CO ratio of 2:1. Some preliminary versions of the data presented here were initially reported last quarter.

4.1.1 Effects of K on the Secondary Hydrogenation of α -Olefins

During the FTS reaction, chains terminate either by β -hydrogen abstraction to form α -olefins or by H-addition to form paraffins. The primary α -olefin products undergo secondary hydrogenation reactions to form n-paraffins [16]. The linear α -olefins can potentially be used for the manufacture of high-value chemicals. For example, the C₆-C₁₆ linear α -olefins are used for the manufacture of biodegradable detergents and PVC plasticizers. Thus, from the viewpoint of producing chemicals and chemical feedstocks, FTS catalysts should have a high selectivity to linear α -olefins. The addition of K has been reported to inhibit secondary reactions of primary α -olefins, increasing their selectivities [19].

Fig. 1.11 shows the propene/propane ratio as a function of CO conversion on the catalyst with varying K loading at 235 °C and 21.4 atm. We use the propene/propane ratio as a measure of secondary olefin hydrogenation activity because of the high selectivity to C₃ and the high hydrogenation reactivity of propene (only lower than ethylene). The results show that these ratios are almost independent of CO conversion on K-promoted catalysts, suggesting that secondary hydrogenation reactions of propene are not present and the ratio is only determined by the relative probability of chain termination to propane and to propene. In contrast, propene/propane ratio decreases with increasing CO conversion on the K-free catalyst. This result indicates the presence of secondary hydrogenation of propene. The ratio was also plotted against propene residence time (e.g. space time), as shown in Fig. 1.12, which seems that the propene/propane ratio decreases with propene residence time, confirming that some propene was hydrogenated to form propane on the K-free catalyst. It is well known that acid sites catalyze olefin hydrogenation. Potassium, an alkaline metal, may titrate acid sites. Therefore, the K-promoted catalysts may lose the activity for hydrogenation at 235 °C.

Fig. 1.11. Propene/propane ratio as a function of CO conversion on the (Zn/Fe=0.1, Cu/M=0.01) with various K loadings (K/M=0-0.04) at 235 °C and 21.4 atm, $H_2/CO=2$.

Fig. 1.12. Propene/propane ratio as a function of propene space time on the catalyst (Zn/Fe=0.1, Cu/M=0.01) with varying K loading (K/M=0-0.04) at 235 °C and 21.4 atm, $H_2/CO=2$.

Propene/propane ratios decreased with propene residence times at 270 °C and 5 atm on K-free and K-promoted catalysts (Fig. 1.13). The K-promoted catalysts now show secondary hydrogenation reactions of propene due to the increase of temperature.

Fig. 1.13. Propene/propane ratio as a function of propene space time on the catalyst (Zn/Fe=0.1, Cu/M=0.01) with varying K loading (K/M=0-0.04) at 270 °C and 5 atm, H₂/CO=2.

4.1.2. Effects of K on the Secondary Isomerization of α -Olefins

The primary α -olefins produced by β -hydrogen abstraction during the FTS reaction undergo secondary hydrogenation reaction to form n-paraffins, as discussed previously. Similarly, the primary α -olefins may also undergo secondary isomerization reactions to produce internal or branched olefins [16]. The molar fraction of all internal and branched olefin isomers in total olefins represents the extent of isomerization of the primary α -olefins. In this report, we refer all internal and branched butene isomers as butene isomers.

The molar fraction of butene isomers as a function of CO conversion over all catalysts at 235 °C and 21.4 atm is shown in Fig. 1.14. The results show butene isomer molar fraction on K-free catalyst is much higher than the fraction on K-promoted catalysts. It is well known that acid catalysts are active for olefin isomerization. Therefore, it is expected that butene isomer molar fraction declines when K is introduced to the catalyst.

The molar fraction of butene isomers increased with CO conversion on the K-free catalyst. Assuming that all butene isomers were formed from primary α -butene, the residence time of primary α -butene can be calculated. The residence times of the primary α -butene on the three catalysts as a function of CO conversion are plotted in Fig. 1.15. Since these residence times of the primary α -butene increase with increasing CO

conversion, it is natural that the conversion of primary α -butene (e.g. isomerization) increases with CO conversion on the K-free catalyst.

Fig. 1.14. The molar fraction of butene isomers as a function of CO conversion on the catalysts (Zn/Fe=0.1, Cu/M=0.01) with various K loading levels (K/M=0-0.04) at 235 °C and 21.4 atm, $H_2/CO=2$.

Fig. 1.15. The space time of α -butene as a function of CO conversion on the catalysts (Zn/Fe=0.1, Cu/M=0.01) with various K loading levels (K/M=0-0.04) at 235 °C and 21.4 atm, $H_2/CO=2$.

However, the molar fractions on K-promoted catalysts are almost independent of CO conversion, suggesting that the butene isomers may not be formed from primary α -butene. If the butene isomers were formed from primary α -butene, the conversion of primary α -butene (isomerization) should increase with its residence time. This is inconsistent with our observations (Figs. 1.14 and 1.15). Hence, it can be concluded that the K-promoted catalyst has no activity for secondary isomerization of primary olefins and the olefin isomers are primary products during the FTS at 235 °C and 21.4 atm.

Fig. 1.16 shows the molar fractions of butene isomers as a function of CO conversion on all three catalysts at 270 °C and 5 atm. More than half of the butenes consists of internal butenes on the K-free catalyst at 270 °C, indicating that the K-free catalyst is very active for isomerization of olefins at high temperature. The molar fraction of butene isomers at 270 °C is higher than that at 235 °C, and increases with increasing CO conversion on K-promoted catalysts. These results suggest that at the higher temperature, the K-promoted catalysts become active for isomerization of primary α -butene. Since some butene isomers are formed from the primary α -butene, the molar fraction of butene isomers is expected to increase with increasing CO conversion because the residence time of the primary α -butene increases with CO conversion.

Fig. 1.16. The molar fraction of butene isomers as a function of CO conversion on the catalysts (Zn/Fe=0.1, Cu/M=0.01) with various K loading levels (K/M=0-0.04) at 270 °C and 5 atm, $H_2/CO=2$.

The molar fraction of butene isomers is higher on the catalyst with higher K loading than that with an intermediate K loading at the same CO conversion at 270 °C. This can misleadingly suggest that the catalyst with higher K loading is more active for isomerization at 270 °C. When the conversion of the primary α -butene was plotted against its residence time (Fig. 1.17), the data indicated that the opposite conclusion could be reached. The conversion of primary α -butene was calculated by assuming that

no other products besides butene isomers were formed from primary α -butene. Coincidentally, this conversion is equal in value to the molar fraction of butene isomers. It is clearly shown that the conversion of primary α -butene is higher on the catalyst with an intermediate K loading at the same residence time. Hence, this catalyst is more active for α -butene isomerization.

Fig. 1.17. The conversion of the primary α -butene as a function of the residence time of the primary α -butene on the catalysts (Zn/Fe=0.1, Cu/M=0.01) with various K loading levels (K/M=0-0.04) at 270 °C and 5 atm, $H_2/CO=2$.

In summary, Fe-Zn-Cu catalysts are active for secondary hydrogenation and isomerization reactions of α -olefins. The introduction of K to these catalysts can titrate their active sites. At 235 °C, the K-promoted catalysts show no activity for secondary reactions. At 270 °C, these K-promoted catalysts become active for secondary reaction but their activities are much lower than that of the K-free catalyst.

4.2. Investigation of Cu Effects on FTS Reactions

Copper has been widely used as one of the promoters on iron catalysts. Its function is to decrease the temperature required for the reduction and carburization of iron oxides [16, 21]. A synergistic effect between K and Cu was previously reported for FTS catalysts based on Fe-Zn oxides [21]. In this reporting period, we began a study of the promotion effects of Cu on FTS. We focused on the catalysts (Zn/Fe=0.1, K/M=0.02) with various Cu loading (Cu/M=0-0.02). The results at 235 °C and 21.4 atm are reported here.

4.2.1 Effects of Cu on the FTS and the WGS Activities

CO conversion for various Cu loading ($\text{Cu/M}=0\text{--}0.02$) studied at 235 °C and 21.4 atm is shown in Fig. 1.18. The Cu-free catalyst showed lower FTS rates. At the same space velocity, higher CO conversion was obtained on Cu-promoted catalysts. However, the catalyst with a higher Cu loading ($\text{Cu/M}=0.02$) did not exhibit a greater activity than the catalyst with an intermediate Cu loading ($\text{Cu/M}=0.01$). These results are in agreement with previous reports [16,21-22]. Kolbel *et al.* [22] observed an increase in the overall activity already at a very low Cu content (ca. 0.1 wt.% Cu), and further increases in Cu content had no additional effect. The reasons for the increased activity with the addition of Cu are not clearly understood. It is known that Cu facilitates reduction of iron and that the total surface area of the catalyst decreases with the extent of metal reduction [1]. This suggests that the higher activity of Cu-promoted catalysts to Cu-free catalysts may be attributed to the differences in the size and number of iron carbide crystallites during synthesis [21].

Fig. 1.18. CO conversion as a function of reciprocal space velocity on the catalysts ($\text{Zn/Fe}=0.1$, $\text{K/M}=0.02$) with various Cu loading levels ($\text{Cu/M}=0\text{--}0.02$) at 235 °C and 21.4 atm, $\text{H}_2/\text{CO}=2$.

During FTS, water is the primary oxygenate product, and CO_2 forms via a subsequent water-gas shift. Higher CO_2 selectivity means that more CO_2 is produced from water and CO, i.e., the catalyst is more active for water-gas shift reactions. Fig. 1.19 shows CO_2 selectivity as a function of CO conversion with varying Cu loading at 235 °C and 21.4 atm. CO_2 selectivity increased with CO conversion at all Cu loading. This is expected if more water is produced at the higher CO conversion. CO_2 selectivity was considerably increased after Cu was introduced into the catalyst. The increase in CO_2 selectivity with Cu is expected since Cu is a well-known low-temperature WGS catalyst. Additional

effects on CO₂ selectivity with higher Cu loading (Cu/M=0.02) were not observed. The promotion effect of Cu is smaller than that of K on WGS reaction, as shown in Fig. 1.20.

Fig. 1.19. CO₂ selectivity as a function of CO conversion on the catalysts (Zn/Fe=0.1, K/M=0.02) with various Cu loading levels (Cu/M=0-0.02) at 235 °C and 21.4 atm, H₂/CO=2.

Fig. 1.20. CO₂ selectivity as a function of CO conversion on the K-promoted catalyst (Zn/Fe=0.1, K/M=0.02, Cu/M=0) and the Cu-promoted catalyst (Zn/Fe=0.1, K/M=0, Cu/M=0.01) at 235 °C and 21.4 atm, H₂/CO=2.

4.2.2. Effects of Cu on Hydrocarbon Selectivity and α -Olefin to n-Paraffin Ratio

Figs. 1.21-23 show methane and C_{5+} selectivities and α -olefin/n-paraffin ratios as a function of CO conversion on the catalysts (Zn/Fe=0.1, K/M=0.1) with varying Cu loading (Cu/M=0-0.02) at 235 °C and 21.4 atm. The promotion effects of Cu on the hydrocarbon and olefin selectivities are much less marked than those observed for K.

Fig. 1.21. Methane selectivity as a function of CO conversion on the catalysts (Zn/Fe=0.1, K/M=0.02) with various Cu loading levels (Cu/M=0-0.02) at 235 °C and 21.4 atm, $H_2/CO=2$.

Fig. 1.22. C_{5+} selectivity as a function of CO conversion on the catalysts (Zn/Fe=0.1, K/M=0.02) with various Cu loading levels (Cu/M=0-0.02) at 235 °C and 21.4 atm, $H_2/CO=2$.

Fig. 1.23. α -Olefin to n-paraffin ratio as a function of CO conversion on the catalysts (Zn/Fe=0.1, K/M=0.02) with various Cu loading levels (Cu/M=0-0.02) at 235 °C and 21.4 atm, $H_2/CO=2$, CO conversion $\sim 15\%$.

4.3. Synergistic Effects of Cu and K on FTS Reactions

As we discussed above, the addition of K has a larger effect than the addition of Cu on hydrocarbon and olefin selectivities. Both K and Cu, however, improve the activity of Fe-Zn catalysts.

Fig. 1.18. CO conversion as a function of reciprocal space velocity on the singly and doubly promoted catalysts (Zn/Fe=0.1) at 235 °C and 21.4 atm, $H_2/CO=2$.

Fig. 1.24 shows CO conversion as a function of space time for two individually (K or Cu) promoted catalysts and doubly promoted catalyst. It is seen that simultaneous promotion of Fe-Zn with K and Cu leads to higher activity than the individually promoted catalysts, suggesting the synergistic effects of K and Cu. Soled *et al.* observed the same effect for the FTS in slurry reactor [16]. They observed that the catalyst promoted with only K or Cu had little effect on CO conversion, compared to the unpromoted Fe-Zn catalyst, while doubly promoted catalyst increased CO conversion from $\sim 40\%$ to 73% .

II. FISCHER-TROPSCH SYNTHESIS ON COBALT CATALYSTS

1. Background

We showed in the previous quarterly report that water, a reaction product of FTS, not only influences the reaction selectivity but also enhances the rate of primary CO hydrogenation on cobalt catalysts. The positive water effect on the synthesis rate has been observed by other investigators [23,24]. However, this subject is still controversial since water was also found to have no significant effect on CO consumption rate in some other studies [25,26]. So far, kinetic rate equations reported in literature for FTS with cobalt catalysts do not account for these water effects. During this reporting period, the reaction kinetics of FTS were studied on a Co/SiO₂ catalyst over a wide range of reaction pressures and H₂/CO/H₂O ratios. The D₂-H₂ exchange experiment was performed under FTS conditions in an attempt to examine the reversibility of hydrogen adsorption. Subsequently, a reaction mechanism for the cobalt-catalyzed FTS was proposed. Using this mechanism and applying the pseudo-steady state approximation (PSSA) the mechanism, a kinetic rate expression based on Langmuir-Hinshelwood model was obtained.

2. Experimental

Fischer-Tropsch synthesis kinetics was studied using a fixed-bed, single-pass flow reactor. The reactants, H₂ (Matheson, UHP) and CO/N₂ (Matheson, UHP, 81.5/18.5, molar ratio) were introduced into the reactor separately using mass flow controllers (Brooks, model 5850). The cobalt catalyst used was a 21.9 wt.% Co/SiO₂ catalyst. The preparation and pretreatment of the cobalt catalyst were described in the previous quarterly report. The reactor was kept at 20 atm, 200°C and H₂/CO = 2.0 for the first 100 h in order to allow the catalyst to achieve steady-state operation. For the kinetic studies, reactor pressures were changed from 13 to 33 atm and H₂/CO feed ratios from 1.3 to 8.5. The conversion of CO was varied from 5 to 30% by changing the space velocity. When the reaction conditions were changed, a period of at least 12 h was allowed between balance periods. N₂ (used as an internal standard), CO, CO₂, and light hydrocarbons (C₁-C₁₂) were analyzed by on-line gas chromatography (Hewlett-Packard 5890) using thermal conductivity and flame ionization detections. Synthesis rate was reported as a site-time yield (molar CO converted per g atom surface Co).

Isotopic exchange between H₂ and D₂ was carried out during FTS (200°C, 20 atm). The reactants, H₂ (Matheson, UHP), D₂ (Cambridge Isotope Laboratories, Inc., 99.8%), and CO/N₂ (Matheson, UHP, 81.5/18.5) were introduced into the reactor separately using mass flow controllers (Brooks, model 5850) at a molar ratio of H₂/D₂/CO/N₂ = 31/31/31/7. The deuterium fraction in hydrogen isotopomers was determined by off-line mass spectrometry (Leybod Inficon Instruments Co., Inc.). A blank run of D₂-H₂ exchange was also carried out with the SiO₂ diluent.

3. FTS on Cobalt-Based Catalysts

3.1 D_2 - H_2 Exchange and D_2O Tracer

D_2 - H_2 exchange was carried out during FTS (200°C, 20 atm). The formation rate of the HD was compared to the rate of hydrogen converted to hydrocarbons (Figure 2.1). The isotopic exchange rates presented here have been calibrated by subtracting those measured in a blank run using SiO_2 . The hydrogen exchange rate decreased from 450 h^{-1} to 200 h^{-1} as the CO conversion increased from 6% to 15% (by decreasing bed residence time), while the rates of hydrogen conversion to hydrocarbons were less than 50 h^{-1} . At zero CO conversion, the D_2 - H_2 exchange rate (590 h^{-1}) is almost 20 times larger than the conversion rate (30 h^{-1}). It is also observed that the isotopic exchange nearly reaches equilibrium at CO conversions of 6-15%. Therefore, the results of the D_2 - H_2 exchange experiment strongly suggest that the H_2 dissociation step is quasi-equilibrated during FTS.

Figure 2.1. Rates of hydrogen converted to hydrocarbons (♦), HD formation (□) and equilibrium HD formation (Δ) in the D_2 - H_2 exchange under FTS conditions on 21.9 wt.% Co/ SiO_2 catalyst (200°C, 20 atm $H_2/D_2/CO = 1/1/1$).

D_2O tracer experiments were performed in the last quarter. Here we re-analyze some of the data from that experiment in Figures 2.2 and 2.3 and proposed some mechanistic implications for the observed water effects. During cobalt-catalyzed FTS, the removal of

oxygen adatoms (released from CO dissociation) occurs mainly via the formation of water in the following the steps [27].

As a matter of fact, we found only trace amount of CO_2 and alcohols in the FTS products. In the mean time, water, either produced in FTS or added, may also adsorb on cobalt through the steps (3), (2) and (1) to produce OH_2^* , OH^* , H^* , and O^* . Figures 2.2 and 2.3 show that the deuterium content in the H_2 isotopomers, paraffins and olefins increases with increasing CO conversion by increasing bed residence time, indicating that the deuterium fraction in the surface H-D pool also increases with residence time. We assume that the water adsorption, step (3), is reversible and quasi-equilibrated. If this is the case, the following water dissociation, steps (2) and (1), should not be quasi-equilibrated. Otherwise, the deuterium content observed in the H_2 isotopomers and hydrocarbons would be independent of the residence time. When extrapolating the lines in Figures 2.2 and 2.3 to zero residence time, we obtain intercepts of about 0.03. This provides additional evidence that the steps (2) and (1) are not quasi-equilibrated, since the deuterium fraction in the reactants is 14%.

Figure 2.2. Deuterium fraction in hydrogen-isotopomers in FTS on 21.9 wt.% Co/SiO₂ catalyst (200°C, 20 atm $\text{H}_2/\text{CO} = 2.0$, 2 atm D_2O added).

Figure 2.3. Deuterium fraction in paraffins olefins in FTS on 21.9 wt.% Co/SiO₂ catalyst (200°C, 20 atm H₂/CO = 2.0, 2 atm D₂O added).

3.2 Proposed Mechanism

The Fischer-Tropsch synthesis is a polymerization reaction, although the mechanism and the nature of the intermediates remain a subject of active discussion [13,27,28]. The surface carbide mechanism, which was originally proposed by Fischer and Tropsch [2], is the currently accepted route for the formation of monomers. This mechanism states that CO dissociates on the metal of catalyst to form carbon adatoms. Subsequently, carbon adatoms undergo hydrogenation to form surface methylene groups, which are the precursor to hydrocarbons with a broad range of chain length and functionality.

Table 2.1 Kinetic rate expressions of the FTS on cobalt-based catalysts

Reference	Catalyst	Overall kinetic expression*
van der Baan, <i>et al.</i> , [29]	Co/Al ₂ O ₃	$-r_{CO} = aP_{H_2}P_{CO}^{1/2}/(1 + bP_{CO}^{1/2})^3$
Wojciechowski, <i>et al.</i> , [25]	Co/Kieselguhr	$-r_{CO} = aP_{H_2}^{1/2}P_{CO}^{1/2}/(1 + bP_{H_2}^{1/2} + cP_{CO}^{1/2})^2$
Satterfield, <i>et al.</i> , [30]	Co/MgO/SiO ₂	$-r_{CO+H_2} = aP_{H_2}P_{CO}/(1 + bP_{CO})^2$
Pannell, <i>et al.</i> , [31]	Co/La ₂ O ₃ /Al ₂ O ₃	$-r_{CO+H_2} = aP_{H_2}^{0.55}P_{CO}^{-0.33}$
Yang, <i>et al.</i> , [32]	Co/CuO/Al ₂ O ₃	$-r_{CO+H_2} = aP_{H_2}P_{CO}^{-0.5}$

* a, b, and c in these equations are temperature-dependent constants.

Some kinetic rate expressions FTS reported in the literature for cobalt-based are summarized in Table 2.1. According to these studies, the synthesis rate exhibits a positive order in H₂ while the influence of CO varies from negative to mildly positive depending on the CO concentration. However, none of these rate expressions contain a water partial pressure term, implying that these authors did not notice an effect of water. In these studies, the Langmuir-Hinshelwood type expressions were obtained by assuming that the rate-determining step involves the formation of surface methylene groups (CH₂*) from adsorbed C* and H*. We observed the enhancement of the synthesis rate by water on cobalt catalysts. To explain the positive water effect, an additional pathway for C* consumption had to be considered and this pathway must be influenced by gas phase water. From the D₂O tracer study, we know that the concentration of surface OH₂* depends on the relative amount of water in the gas mixture. It is expected that surface C* may react with OH₂* to form CHOH* species. The latter species may be hydrogenated or reacts with partially hydrogenated C_n* species through intermolecular dehydration. In fact, the presence of species containing C-O-H bands on cobalt FTS catalysts has been confirmed by IR spectroscopy [33]. Of course, other pathways may also lead to species containing C-O-H bands. The concentration of OH₂* will increase with water partial pressure, increasing the C* consumption through the proposed water-aided pathway. However, the hydrogenation of C* using hydrogen remains operative and it is the

dominant route when the water concentration is low. The proposed elementary steps for FTS on cobalt are presented as follows:

1. $\text{H}_2 + 2^* \leftrightarrow 2\text{H}^*$
2. $\text{CO} + 2^* \leftrightarrow \text{C}^* + \text{O}^*$
3. $\text{C}^* + \text{H}^* \rightarrow \text{CH}^* + ^*$
4. $\text{C}^* + \text{OH}^* \rightarrow \text{COH}^* + ^*$
5. $\text{O}^* + \text{H}^* \rightarrow \text{OH}^* + ^*$
6. $\text{OH}^* + \text{H}^* \rightarrow \text{OH}_2^* + ^*$
7. $\text{OH}_2^* \leftrightarrow \text{H}_2\text{O} + ^*$

The dissociative H_2 adsorption (Step 1) is a quasi-equilibrated step (based on the results of D_2 - H_2 exchange). In addition, it is not likely to be a rate-determining step because the FTS rate has a positive order in CO partial pressure for low CO concentrations [25]. CO chemisorbs molecularly and then dissociates to produce adsorbed C and O, respectively. The extent to which these processes are reversible remains unresolved [28]. In this work, we assume that CO adsorption (Step 2) is also quasi-equilibrated. We suppose two parallel pathways that consume surface C^* , namely, C^* reacting with H^* (Step 3) and with OH_2^* (Step 4). According to the D_2O tracer study, the water dissociation steps (steps 5 and 6) are largely irreversible, whereas the water adsorption/desorption (step 7) is quasi-equilibrated. Thus, we have the synthesis rate, $r_{\text{CO}} = k_3[\text{C}^*][\text{H}^*] + k_4[\text{C}^*][\text{OH}_2^*]$. We assume that the important surface species are empty sites, and adsorbed C^* , O^* , OH_2^* and H^* . Other species, though present, are not important in the stoichiometric balance of surface sites. Applying the pseudo-steady state approximation to step 1 through 7 leads to a Langmuir-Hinshelwood type expression.

$$r_{\text{CO}} = aP_{\text{CO}}^{1/2}P_{\text{H}_2}^{1/4}(bP_{\text{H}_2}^{1/2} + cP_{\text{H}_2\text{O}})^{1/2}/(1 + dP_{\text{H}_2}^{1/2} + eP_{\text{H}_2\text{O}} + fP_{\text{CO}}^{1/2})^2, \text{ in which,}$$

$$\begin{aligned} a &= (K_1^{1/2}K_2k_5)^{1/2} \\ b &= K_1^{1/2}k_3 \\ c &= k_4K_{-7} \\ d &= (K_1)^{1/2} \\ e &= K_{-7} \\ f &= (K_2(k_5/k_3 + k_3/k_5))^{1/2} \end{aligned}$$

Since CO adsorption is much stronger than H_2 and water adsorption on cobalt [13,25], the term in the denominator containing CO partial pressure becomes much larger than the others if the relative amount of CO in the gas phase is not too low. Then, the rate expression simplifies to

$$r_{\text{CO}} = aP_{\text{CO}}^{-1/2}P_{\text{H}_2}^{1/4}(bP_{\text{H}_2}^{1/2} + cP_{\text{H}_2\text{O}})^{1/2}, \text{ where,}$$

$$\begin{aligned} a &= k_1^{1/4}k_5^{1/2}/(K_2^{1/2}(k_5/k_3 + k_3/k_5)) \\ b &= K_1^{1/2}k_3 \\ c &= k_4K_{-7} \end{aligned}$$

3.3 Kinetic Study

Reaction kinetics of FTS was studied over a broad range of H₂/CO ratios (1.3 to 8.5) and pressures (13 to 33 atm). The experimental results are presented in Table 2.2. For this set of data, it was difficult to do a regression using only the two adjustable parameters, P_{CO}, P_{H₂}. Thus, it was decided that the rate expression should contain another adjustable parameter, P_{H₂O}. These data were first fitted using a multilinear regression, leading to a power law rate expression: $r_{CO} = 56.3H_2^{0.43}CO^{-0.53}H_2O^{0.38}$.

This data will be regressed nonlinearly and fitted to a Langmuir-Hinshelwood type rate expression, which will be more representative of the true FTS mechanism on cobalt catalysts.

Table 2.2. Experimental results of FTS kinetic study over 21.9 wt.% Co/SiO₂ catalyst*

No	Partial pressure (atm)			CO conversion	CO conversion	CH ₄ formation	C ₅ ⁺ synthesis
	H ₂	CO	H ₂ O	(%)	rate (h ⁻¹)	rate (h ⁻¹)	rate (h ⁻¹)
1	11.6	5.4	0.5	17.2	48.3	4.6	41.8
2	11.6	5.7	0.3	8.7	36.9	4.2	28.7
3	9.3	6.0	0.2	7.7	29.9	2.8	24.1
4	18.3	6.0	0.1	4.5	32.3	5.8	17.8
5	17.2	5.1	0.6	20.4	64.7	8.8	53.7
6	17.9	5.9	0.2	8.0	42.5	6.6	29.8
7	24.0	5.3	0.5	16.6	70.4	12.1	51.1
8	25.0	6.0	0.2	7.6	50.1	10.0	29.3
9	11.9	5.8	0.2	7.4	41.8	5.2	32.2
10	11.3	5.3	0.6	21.3	59.7	5.2	50.8
11	11.9	5.9	0.2	6.6	37.2	5.2	27.5
12	10.8	2.6	0.3	20.4	57.2	7.3	42.7
13	11.5	2.8	0.1	7.7	43.9	8.0	30.8
14	10.2	2.3	0.5	32.9	68.6	9.4	58.1
15	11.8	5.8	0.2	5.3	30.1	4.4	22.2
16	11.4	5.5	0.5	17.1	54.0	4.9	43.4
17	11.2	5.2	0.6	21.5	60.4	5.4	50.4
18	11.4	1.4	0.1	10.0	57.0	13.1	--
19	10.6	1.3	0.2	23.1	64.7	12.6	--
20	9.7	1.2	0.3	38.5	80.3	16.4	60.4
21	11.3	5.2	0.6	20.4	57.2	5.3	47.5
22	11.6	8.7	0.2	4.8	27.4	3.2	20.6
23	11.3	8.6	0.3	6.6	30.4	3.0	22.9
24	11.7	5.4	0.5	18.0	50.5	5.1	42.5

* Reaction conditions: 200°C, H₂/CO ratios from 1.3 to 8.5, pressures from 13 to 33 atm, water partial pressure is the average of water pressures at the reactor inlet and outlet.

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Task 12. Reporting/Project Management

Three monthly and one quarterly reports have been completed.