Executive Summary

The feasibility of using a mechanical mixture of a $Co/MgO/SiO_2$ Fischer-Tropsch catalyst and a $Cu-ZnO/Al_2O_3$ water-gas-shift (WGS) catalyst for hydrocarbon synthesis in a slurry reactor has been established. Such a mixture can combine the superior product distribution from cobalt with the high activity for the WGS reaction characteristic of iron. Weight ratios of $Co/MgO/SiO_2$ to $Cu-ZnO/Al_2O_3$ of 0.27 and 0.51 for the two catalysts were studied at 240°C, 0.79 MPa, and *in situ* H_2/CO ratios between 0.8 and 3.0. Each catalyst mixture showed stable Fischer-Tropsch activity for about 400 hours-on-stream at a level comparable to the cobalt catalyst operating alone. The $Cu-ZnO/Al_2O_3$ catalyst exhibited a very slow loss of activity under these conditions, but when operated alone it was stable in a slurry reactor at 200-220°C, 0.79-1.48 MPa, and H_2/CO *in situ* ratios between 1.0 and 2.0. The presence of the water-gas-shift catalyst did not affect the long-term stability of the primary Fischer-Tropsch selectivity, but did increase the extent of secondary reactions, such as 1-alkene hydrogenation and isomerization.

The rate of synthesis gas consumption over the catalyst was measured at 220 to 240°C, 0.5 to 1.5 MPa, H_2/CO feed ratios of 1.5 to 3.5 and conversions of 6 to 68% of hydrogen and 11 to 73% of carbon monoxide. The inhibiting effect of carbon monoxide was determined quantitatively and a Langmuir-Hinshelwood-type equation of the following form was found to best represent the results:

$$-R_{H_2+CO} = \frac{a\, P_{CO} P_{H_2}}{(1 + b\, P_{CO})^2}$$

The apparent activation energy was 93 to 95 kJ/mol. Data from previous studies on cobalt-based Fischer-Tropsch catalysts are also well correlated with this rate expression.

Increasing space velocity (decreasing conversion) or decreasing reactor H_2/CO ratio decreased the yield of (undesired) C_1 products and increased the yield of (desired) $C_{10}+$ products. Reactor temperature and pressure had little effect on the carbon number distribution. These findings are interpreted in terms of the extent of the readsorption of 1-alkenes into growing chains on the catalyst surface. The relative selectivity to 1-alkenes by the primary synthesis and secondary reaction of 1-alkenes to n-alkanes and 2-alkenes depends on reactor H_2/CO ratio and CO concentration.

The cobalt-catalyzed reactions of C_2H_4, C_3H_6, or 1-C_4H_8 added to synthesis gas in concentrations ranging from 0.5 to 1.2 mol.% of total feed were studied at 220°C, and 0.45 to 1.48 MPa. H_2/CO feed ratios were varied between 1.45 to 2.25 and H_2 + CO conversions between 5 and 30% were observed.

1-Alkenes incorporate into growing chains on the catalyst surface, probably by initiating and/or terminating the chain growth process. Only ethene may propagate chain growth significantly. The propensity of the 1-alkenes to incorporate decreases with increasing carbon number of the 1-alkene and is affected by the extent of competitive reactions, notably hydrogenation to the alkane and isomerization to the 2-alkene. Incorporation is most evident in products above about $C_{10}+$.

The double-α behavior exhibited by most Fischer-Tropsch catalysts can be interpreted as the sum of two growth processes, one a stepwise single-carbon growth process and the other a 1-alkene incorporation process. Many of the effects of process variables on the hydrocarbon selectivity of Fischer-Tropsch catalysts are consistent with this theory.

The results of the study are divided into four parts, as outlined in the Table of Contents.

I. The Fischer-Tropsch Synthesis with a Mechanical Mixture of a Cobalt Catalyst and a Copper-Based Water-Gas-Shift Catalyst

Abstract

The feasibility of using a mechanical mixture of a $Co/MgO/SiO_2$ Fischer-Tropsch catalyst and a $Cu-ZnO/Al_2O_3$ water-gas-shift (WGS) catalyst for hydrocarbon synthesis in a slurry reactor has been established. Such a mixture can combine the superior product distribution from cobalt with the high activity for the WGS reaction characteristic of iron. Weight ratios of $Co/MgO/SiO_2$ to $Cu-ZnO/Al_2O_3$ of 0.27 and 0.51 for the two catalysts were studied at 240°C, 0.79 MPa, and *in situ* H_2/CO ratios between 0.8 and 3.0. Each catalyst mixture showed stable Fischer-Tropsch activity for about 400 hours-on-stream at a level comparable to the cobalt catalyst operating alone. The $Cu-ZnO/Al_2O_3$ catalyst exhibited a very slow loss of activity under these conditions, but when operated alone it was stable in a slurry reactor at 200-220°C, 0.79-1.48 MPa, and H_2/CO *in situ* ratios between 1.0 and 2.0. The presence of the water-gas-shift catalyst did not affect the long-term stability of the primary Fischer-Tropsch selectivity, but did increase the extent of secondary reactions, such as 1-alkene hydrogenation and isomerization.

I.A. Introduction

Cobalt-based Fischer-Tropsch catalysts exhibit many performance characteristics superior to those based on iron. Carbon formation on cobalt is minimal, which may increase catalyst life and facilitate purification of the product, and oxygenates such as aldehydes, ketones and alcohols are formed in much lower quantities, and make product workup easier. However an advantage of iron catalysts is that they are generally active for the water-gas shift reaction. Thus, Fischer-Tropsch reactors can be fed with the hydrogen-lean synthesis gas produced by modern coal gasifiers, and hydrogen can be generated *in situ* simultaneously with the synthesis reaction, via the water-gas shift reaction.

Cobalt catalysts lack water-gas-shift (WGS) activity at the optimum temperatures of the synthesis reaction. Thus, a mechanical mixture of a cobalt catalyst and a water-gas shift catalyst may make possible a combination of the product advantages of cobalt and the operating advantages of a slurry reactor.

Shell patents[1,2] indicate that a mechanical mixture of a $Co/ZrO_2/SiO_2$ Fischer-Tropsch catalyst and a $Cu/ZnO/Al_2O_3$ shift catalyst can be successfully used to carry out Fischer-Tropsch synthesis in a fixed-bed reactor. The cited preferred conditions are 175-275°C and 1 to 7.5 MPa. The ratio of cobalt to shift catalyst is adjusted depending on the H_2/CO feed ratio, with a higher portion of shift catalyst recommended for lower H_2/CO ratios.

Tominaga et al.[3] report results of studies with a fixed-bed at 0.3 MPa and between

220 and 280°C using a 10 wt.% Co on SiO_2 catalyst mixed with a Cu/Cr_2O_3 shift catalyst. The primary focus of their research was the Köelbel-Engelhardt synthesis, in which CO and H_2O, rather than synthesis gas, are fed to the reactor. However, they report some data on feeds containing only H_2 and CO with a H_2/CO ratio of 0.5. Two trends were observed. First, when the shift catalyst was added, the CO_2 in the products increased from 0.1 to 6.0 mol.%, indicating a large enhancement in shift activity. Second, the weight fraction of C_5+ products remained unaffected by addition of the shift catalyst to the system.

Post and co-workers give no information on possible change in activity and selectivity with time. Tominaga et al. report that the yield of CO_2 decreased to 50% of its initial value within the first 6 hours of operation, attributed to competitive inhibition of the shift reaction by hydrocarbons. They state that this decreased activity is the steady-state value, but present no data after 12 hours-on-stream.

Therefore, no data on the long-term stability of water-gas shift and a Fischer-Tropsch catalyst system are available. Further, the performance of such a system in a fixed-bed may be difficult to understand because of changing conditions along the bed. Poisons or reaction conditions may deactivate the shift catalyst or the Fischer-Tropsch catalyst in one region of the bed, while catalyst activity may be maintained in another region. In a well-mixed slurry reactor, as used here, operating conditions are the same throughout the vessel.

The primary objective of this work was to search for a combination of a shift catalyst and a cobalt Fischer-Tropsch catalyst that could operate simultaneously and efficiently in a slurry reactor. Ideally, the combined system should exhibit stable activity

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and selectivity, with neither catalyst adversely affecting the other.

I.B. Experimental

Our approach was to study the Fischer-Tropsch synthesis and the water-gas-shift reaction independently before combining these catalysts. The experiments were performed in a continuous, mechanically-stirred, one-liter autoclave. The slurry reactor and ancillary equipment are described in detail elsewhere.[4,5,6] In all runs, an impeller speed of 800 RPM or higher was used, to eliminate possible mass transfer effects.

I.B.1. Water-Gas-Shift (WGS) Catalysts. Three commercially-available WGS catalysts were studied by themselves. Two $Cu-Cr_2O_3$ catalysts (52% CuO and 48% Cr_2O_3 or 50% CuO, 4% MnO and 46% Cr_2O_3) were found to have insufficient stability or activity and are not discussed further here (for details, see Yates[7]). Satisfactory performance was achieved with Katalco 52-2 (33% CuO, 33% ZnO and 33% Al_2O_3, surface area = 36 m^2/g, bulk density 62 lb/ft^3, as reported by the manufacturer).

The three shift catalysts were each ground and sieved to 50 to 90 μm and loaded into the reactor, which had been previously charged with recrystallized octacosane, the carrier used in our slurry Fischer-Tropsch experiments. The octacosane was recrystallized in HPLC grade tetrahydrofuran as recommended by Huff and Satterfield.[4] The catalysts were then reduced according to the manufacturers' guidelines (see Table 1). For the studies reported here, which utilized the $Cu/ZnO/Al_2O_3$ catalyst, the reduction procedure was slightly modified as outlined in Table I-1.

Following completion of the reduction, flow of vapor comprising 42.9 mol.% CO, 21.4 mol.% H_2, and 35.7 mol.% H_2O at 0.019 Nl/min/g.cat. (unreduced basis) was

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begun. The rate at which water was fed is approximately five times that which would be typically synthesized in our reactor with a cobalt Fischer-Tropsch catalyst.[7] For the initial stability testing, temperature and pressure were held constant at 200°C and 0.79 MPa. All data presented here on gas composition and gas flow rates are on a wet-gas basis.

Water was delivered by a Waters Associates, Inc., Model 6000A pump, which is accurate to ± 0.005 ml of liquid/min (1.12×10^{-4} Nl of water vapor/min). Before being charged, the water was purified in a two-step process. First, the water was passed through a reverse-osmosis Millipore HEMO-RO*60 filtration system which removes ions and produces water with a resistivity of greater than 10 MΩ/cm. The deionized water was then passed through a Millipore Milli-Q Reagent H_2O system with ion-exchange and activated carbon beds. The purified water was verified by HPLC to contain less than 1 ppm of total impurities.

The water was fed to the reactor through a 0.159 cm (1/16 inch) O.D. tube which was heated to 20°C above reactor temperature to vaporize the water. The outlet of the tube was at the same height as the reactor's impeller and was therefore submerged in slurry wax during operation. The temperature of the outlet line from the reactor was held at 250°C to minimize the possibility of reflux of water during operation.

Activity was monitored by calculating the percent approach to equilibrium, either from disappearance of CO or appearance of H_2 and CO_2. Based on CO, X_{CO} is given by:

$$-X_{CO} = 100\left[\frac{(\mu_{inlet} - \mu_{out})}{(\mu_{equilibrium} - \mu_{inlet})}\right] \tag{1}$$

As a cross-check for a material balance, the equivalent value based on the products, H_2 and CO_2, $X_{product}$ is defined as:

$$X_{product_k} = 100\left[\frac{(\mu_{out_k} - \mu_{inlet_k})}{(\mu_{equilibrium_k} - \mu_{inlet_k})}\right] \tag{2}$$

where, for component k

$$\mu_{out,k} = \text{measured flow rate at outlet [mmol/min]}. \tag{3}$$

$$\mu_{inlet,k} = \text{measured flow rate at inlet [mmol/min]}. \tag{4}$$

$$\mu_{equilibrium,k} = \text{outlet flow rate at equilibrium [mmol/min]}. \tag{5}$$

The inlet CO_2 is zero. Ranging from 0% at no activity to 100% at equilibrium conversion, equations 1 and 2 provide a convenient benchmark for comparison of different feed compositions and/or flow rates. All material balances on WGS-only data were required to close within 3% on carbon.

I.B.2. Fischer-Tropsch Catalyst. The cobalt Fischer-Tropsch catalyst was prepared by an outside supplier and is of the approximate composition of the cobalt catalysts used at Ruhrchemie.[8] The nominal composition of the catalyst, as reported to us by its manufacturer, is 21.4 wt.% Co (as Co), 3.9 wt.% Mg (as Mg), and the remainder diatomaceous earth.

Supplied as an extrudate, the catalyst was ground and sieved to 50 to 90 μm. Following sieving, the catalyst was placed in an external reduction vessel. It was held in this unit with a 7 μm frit while hydrogen (prepurified, MedTech Gases, Inc.) was brought

on stream at a flow of 1.36 Nl/min (approximately 10,000 V/V/hr). At this flow rate the pressure in the vessel was approximately 0.72 MPa. The temperature of the reduction tube was increased steadily from 25°C to 330°C over 4.75 hours while the inlet flow rate was held constant. The reduction unit was then held at 330°C for 0.75 hours and subsequently the unit was pressurized with helium and rapidly cooled.

I.B.3. **Combined System.** The reduced cobalt catalyst was transferred under helium to the autoclave reactor which contained the reduced water-gas-shift catalyst, also under helium. The reactor was brought on-stream at 0.79 MPa, 187°C, and $H_2/CO = 1.5$ at a flow rate of 1.0 Nl/min. The CO used in these experiments was CP grade (North East Airgas, Inc.) and the H_2 was prepurified grade (MedTech Gases, Inc.).

The reactor conditions were held constant for the first 66 hours and then the H_2/CO feed ratio was adjusted to about 1.0 with an inlet flow of 0.59 Nl/min and the temperature was increased to 240°C over a period of 8 hours. The following reactor conditions were then considered to be "standard" conditions: 0.79 MPa, 240°C, and inlet $H_2/CO = 1.0$ at a flow rate of about 0.60 Nl/min.

Two combined-system runs were performed. Run L was operated with 9.0 grams of $Co/MgO/SiO_2$ catalyst and 33 grams of $Cu-ZnO/Al_2O_3$ (both on an unreduced basis) for a weight ratio of 0.27; run H was operated with 17.0 grams of $Co/MgO/SiO_2$ catalyst and 33 grams of $Cu-ZnO/Al_2O_3$ catalyst for a weight ratio of 0.51. In run L, "standard" conditions were utilized for the entire run of about 400 hours-on-stream. Under these conditions, about 16.5% of the $H_2 + CO$ fed was converted to Fischer-Tropsch products.

In run H, "standard" conditions were held for the first 220 hours-on-stream. Subsequently, the feed to the reactor was varied systematically over a H_2/CO feed ratio

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of 1 to 2, and at either of two flow rates, about 0.30 and 0.60 Nl/min. These conditions provided conversions of $H_2 + CO$ between 29 and 75%. At 350 hours-on-stream, operating conditions were returned to "standard" to verify catalyst stability, and the run was ended after about 400 hours on stream. All material balances reported on the combined Fischer-Tropsch/water-gas-shift system closed within 3% on oxygen. Oxygen was chosen as the material balance closure element because carbon and hydrogen accumulate in the reactor in the form of heavy waxes under Fischer-Tropsch synthesis conditions, which makes it more difficult to base material balances on these elements.

I.C. Results and Discussion: Water-Gas-Shift Catalyst Alone

A preliminary run with the $Cu/ZnO/Al_2O_3$ catalyst showed stable activity, but it appeared desirable to modify the reduction procedure (see Table I-1) by increasing the length of the helium purge and decreasing the severity of the final reduction period. This reduction procedure was found to be superior.

We present here the results of a single run that extended over about 1030 hours and is outlined in Table I-2. No process changes were made during the first 300 hours-on-stream. Then, either the pressure, temperature or feed composition was changed and the % of equilibrium conversion was monitored for an interval of 48 to 100 hours. The reactor was then returned to "base case" conditions which would in turn be monitored for 48 to 100 hours. Thus, we were able to monitor both the effect of the process change on activity and on catalyst stability.

I.C.1. Stability. Figure I-1 shows the % of equilibrium conversions for the "base case" conditions. As Figure I-1 illustrates, the catalyst deactivated very slowly with time-

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on-stream.

I.C.2. **Effect of Pressure.** Total pressure does not affect the equilibrium of the shift reaction, so increasing pressure would be expected to change conversion only by its effect on the reaction rate, which in turn may change the concentrations of the components in the reactor. After 303 hours-on-stream, the pressure was increased from 0.79 to 1.48 MPa. Temperature, space velocity, and feed composition were held constant. After a further 55 hours, the reactor was returned to the "base case" conditions and held there for 67 hours.

Figure I-2 shows the conversion data for the time period before, during, and after the pressure change. Increased pressure has no significant effect on the rate of water-gas shift or the long-term stability of the catalyst.

I.C.3. **Effect of Inlet H_2/CO Ratio.** The H_2/CO ratio is an important consideration for evaluating the stability of a shift catalyst for the Fischer-Tropsch synthesis. A $(H_2/CO)_{in}$ ratio of 0.5 was chosen for the base case, because, after undergoing the shift reaction, it provided an *in situ* H_2/CO ratio of approximately two, the usage ratio for cobalt catalysts. To elucidate the effect of H_2/CO, two additional feed ratios, 0.7 and 1.0, were studied. These produced *in situ* H_2/CO ratios near 2.5 and 3, respectively. Higher H_2/CO ratios were examined because higher hydrogen partial pressures might increase the likelihood of sintering and higher CO partial pressures are reported not to have deleterious effects on low-temperature shift catalysts.[9,10]

Figure I-3 shows that the % of equilibrium fell about 3 to 5% upon increased reactor H_2/CO ratios. In order to simplify the figure, the component conversions are not shown. This decrease is consistent with a simple equilibrium-limited rate expression,

presented by Moe[9], of the form:

$$R_{\text{water-gas shift}} = k \left[P_{CO}P_{H_2O} - \frac{P_{H_2}P_{CO_2}}{K_p} \right] \qquad (6)$$

In equation 6, increasing P_{H_2} and decreasing P_{CO} would decrease the "driving force" for reaction, thereby slowing the rate of reaction.

I.C.4. Effect of Temperature. Because copper-based shift catalysts sinter readily[11], catalyst manufacturers recommend that these catalysts not be used above 250°C. For most of the run, the reactor was operated at 200°C, the lowest temperature at which $Cu/ZnO/Al_2O_3$ catalysts reportedly have appreciable activity.[10] Figure I-1, which presents the "base case" data, indicates that at 200°C the catalyst converted approximately 65-70% of the H_2O and CO fed. After 637 hours-on-stream, the reactor temperature was increased from 200 to 220°C, and at 693 hours-on-stream, the temperature was returned to 200°C. At 220°C, % of equilibrium conversion increased to around 80% (Figure I-4), but it reverted to its former performance when the temperature was returned to 200°C.

I.C.5. Effect of 1-Butene. It has been suggested that alkenes may adsorb on the surface of shift catalysts, inhibiting their activity. To test this possibility, 1-butene was added to the feed at 924 hours-on-stream, in the form of a mixture of 2 mol.% 1-butene in prepurified H_2 (Matheson Gases, Inc.). 1-Butene is representative of 1-alkenes from the Fischer-Tropsch reaction and is easy to study in our reactor system, as it is the highest molecular weight 1-alkene that is not condensed in the product traps.[12,13]

Figure I-5 shows that shift activity remains essentially unchanged by the addition

of the 1-butene at this concentration. The amount of hydrogen consumed by 1-butene hydrogenation was negligible. About 96% of the added 1-butene was either hydrogenated to butane or isomerized to *cis*-2-butene and *trans*-2-butene; no significant amount was cracked to smaller hydrocarbons. The product composition was about 4% 1-butene, 53% n-butane, 29% trans-2 butene and 14% cis-2 butene. The hydrogenation probably occurs on reduced copper, a known hydrogenation catalyst, and the isomerization on acidic sites on the Al_2O_3 support. *Cis*-2-butene and *trans*-2-butene are formed in almost equilibrium ratios.

In summary, a reduction procedure was achieved that allowed stable water-gas-shift behavior for a $Cu-ZnO/Al_2O_3$ catalyst in a slurry reactor. Within the ranges studied, the catalyst was not adversely affected by increased temperature, pressure, *in situ* ratio of H_2/CO, or the presence of 1-butene.

I.D. Results and Discussion: Fischer-Tropsch plus Water-Gas-Shift Catalyst

Two weight ratios of [Co/MgO/SiO$_2$] to [Cu-ZnO/Al$_2$O$_3$] were studied, termed run L and run H, with results summarized in Table I-3 and displayed in Figures I-6 through I-16.

I.D.1. Fischer-Tropsch Activity. Figure I-6 shows that, for each run, the combined catalyst system retained steady-state Fischer-Tropsch activity for the entire time of about 400 hours-on-stream. The average rate of H$_2$+CO consumption was 0.53 mmol/min-g.Co-cat., on an unreduced basis, for run L and 0.55 mmol/min-g.Co-cat. for run H (both at "standard" conditions). The reactor gas compositions were different for the two runs, but the inherent Fischer-Tropsch activity can be compared to each other and to that of the Co/MgO$_2$/SiO$_2$ catalyst operating alone by the following rate expression developed for this cobalt catalyst.[14]

$$-R_{H_2+CO} = \frac{aP_{CO}P_{H_2}}{(1+bP_{CO})^2} \tag{7}$$

At 240°C, a=75.76 mmol/min-g.cat.-MPa^2 and b=11.61 MPa^{-1}.

Figure I-7 shows the average rate of H$_2$+CO consumption and the rate as predicted from equation 7 for the reactor conditions of run L. The activity of the combined system appears to be slightly higher than that predicted. This may represent additional hydrogen consumption by hydrogenation on the water-gas shift catalyst, or may have been caused by a slight variation in the reduction procedure of the cobalt catalyst. Within our ability to reproduce catalyst reduction procedures, the cobalt catalyst acting alone and the cobalt catalyst operating in conjunction with the water-gas

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shift catalyst display similar activity.

Since operating conditions were varied during run H, comparisons can be made of not only the absolute Fischer-Tropsch activity, but also the form of the rate equation. Equation 7 can be linearized as follows:

$$\left[\frac{P_{H_2}P_{CO}}{-R_{H_2 \cdot CO}}\right]^{\frac{1}{2}} = \frac{1}{a^{\frac{1}{2}}} + \frac{b}{a^{\frac{1}{2}}}P_{CO} \tag{8}$$

Figure I-8, a plot of the left side of equation 8 versus P_{CO} for run H, shows that the form of this equation is obeyed in the presence of the WGS catalyst as well as in its

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absence. The parameter values for the combined system were non-linearly regressed and found to be $a = 81.7 \pm 9.7$ mmol/min-g.Co-cat.-MPa^2 and $b = 8.1 \pm 0.8$ MPa^{-1} at 240°C. These values are remarkably close to the values obtained with the Co-based Fischer-Tropsch catalyst acting alone.

Figures I-6 through I-8 show that neither the absolute activity nor the long-term stability of the cobalt Fischer-Tropsch catalyst was adversely affected by the presence of the copper WGS catalyst.

I.D.2. Water-Gas-Shift Activity. At the temperatures of interest for the Fischer-Tropsch synthesis, the equilibrium of the water-gas-shift reaction favors the production of H_2 and CO_2. Thus, a good measure of shift activity is the extent to which H_2O reacts to form CO_2 as measured by X_{WGS} where:

$$X_{WGS} = \frac{P_{CO_2}}{(P_{CO_2} + P_{H_2O})} \tag{9}$$

X_{WGS} is independent of Fischer-Tropsch synthesis gas consumption, as it depends only on the relative rates of formation of CO_2 and H_2O. At 240°C, if the system achieved equilibrium conversion, X_{WGS} would exceed 0.99. For the fused iron ammonia synthesis catalyst used in a similar manner in many previous studies in our laboratories, X_{WGS} ranged from 0.8 at 232°C to 1.0 at 263°C.[15]

Figure I-9 shows the extent of water-gas shift, expressed as shown in equation 9, for runs L and H. In run L, an average of 94% of the water formed was converted to CO_2, indicating that the system approached equilibrium. The shift catalyst retained its activity, even in the presence of the cobalt catalyst and the Fischer-Tropsch synthesis

products. Cobalt has little shift activity[7,8,16] and, therefore, the shift activity shown in Figure I-9 must come from the shift catalyst. The extent of the water-gas shift decreased steadily with time-on-stream for run H, but did not correlate with percent synthesis gas conversion, eliminating alkene inhibition as a possible cause of the deactivation.

The combined catalyst system in run L produced higher yields of methanol than were produced in run H or when the cobalt catalyst was operated alone (see Figures I-15a,b, and c), although these decreased with time (Fig. I-10). The $Cu-ZnO/Al_2O_3$ catalyst is active for methanol synthesis as well as the water-gas-shift. Despite intensive study, there is still controversy over the chemical state of copper on the catalyst during methanol synthesis and the kinetics of the reaction are complex.[17] The relative activity for the two reactions must vary in response to different nuances of surface structure and gas composition, judging from some of the results here. In run L the rate of methanol production decreased with time-on-stream, whereas the WGS activity remained constant, as did reactor conditions (Figure I-10). In run H, however, WGS activity decreased steadily with time (Fig. I-9).

I.D.3. **Product Selectivity.** Figures I-11a and I-11b show Schulz-Flory overhead product distributions (oxygenates plus hydrocarbons) at several times during the entire run, for runs L and run H. The distribution is essentially invariant for run L, but there is a moderate increase in the heaviest products with time for run H. This is probably caused by the subtle interaction of several effects. 1-Alkenes, formed as a primary product, may undergo secondary reactions such as hydrogenation to n-paraffins or isomerization, predominantly to 2-alkenes. Figures I-12a and I-12b show the ratio of 1-butene/n-butane and 1-butene/2-butene versus time-on-stream. The lower these ratios,

the greater the extent of secondary reaction. In run L secondary reaction activity did not seem to vary significantly with time-on-stream. For run H, the degree of secondary reactions appeared to decrease moderately with time-on-stream. The resulting increase in 1-alkene/alkane ratio would allow an increasing degree of alkene incorporation into growing chains (see below).

There are two possible explanations for the decrease in secondary reactions with time in run H. Catalyst sintering reduces the accessible surface area of the catalyst and would be expected to cause a decline in all three types of activity, hydrogenation on reduced Cu, isomerization on acidic Al_2O_3 sites, and water-gas shift. Young and Clark[11] recommend that low-temperature shift catalysts not be operated at temperatures above 250°C because of the low melting point of copper. Some sintering may have occurred at the temperature of 240°C used for the mixed catalyst runs, versus the WGS scouting experiments performed at slightly lower temperatures (200-220°C), which could explain the long-term stability of the catalyst then.

Alternatively, loss in hydrogenation and isomerization activity may have been caused by the loss in WGS activity. In run H, the extent of WGS activity decreased with time, causing the reactor H_2/CO to decrease as feed conditions were held constant (Fig. I-9). Hydrogenation is approximately first order in hydrogen partial pressure and inhibited by adsorbed CO.[7] Thus, as the data labels on figure I-12b show, the decrease in secondary reactions may not be an intrinsic characteristic of the catalyst system, but rather caused by a decreasing H_2/CO ratio.

Figure I-13 shows that the 1-alkene/n-alkane ratio of the Fischer-Tropsch products is indeed a strong function of the H_2/CO ratio in the reactor (run H). This

ratio was varied by feeding gas with three different H_2/CO ratios at each of two different space velocities. For any given reactor H_2/CO, a lower feed rate results in a lower 1-butene/n-butane ratio in the products. This shows that hydrogenation is occurring as a secondary reaction, which would increase as the residence time increases. Figure I-14 illustrates the effect of reactor H_2/CO on the hydrogenation activity of the cobalt catalyst studied alone.[7] Note that higher *in situ* H_2/CO values occurred here because the cobalt catalyst itself lacks WGS activity. For a specified reactor H_2/CO ratio, the ratio (1-butene/n-butane) was much higher, indicating less secondary hydrogenation. Apparently, much of the hydrogenation and isomerization activity of the mixed catalyst systems was derived from the WGS catalyst, making these runs more sensitive to changes in reactor conditions. Consistent with this hypothesis, the average 1-butene/n-butane ratio in run L was lower than that in run H (Figures I-12a and I-12b).

Figure I-15a is a representative component Schulz-Flory diagram from the Fischer-Tropsch cobalt catalyst studied alone[7], that may be compared to similar diagrams for the two mixed catalyst runs (Fig. I-15b and c). For similar operating conditions (Table I-3), the overall product distributions of the mixed catalyst systems are similar to that of the Co catalyst acting alone, with a few exceptions. In all cases, the predominant Fischer-Tropsch products are n-alkanes. Selectivity to 2-alkenes, 1-alkenes, and n-alcohols drops off sharply with increased C number. The presence of the WGS catalyst may increase the secondary reaction activity which impacts upon the component selectivity, and in turn, the overall molecular weight distributions.

Table I-3 gives the average selectivity to various product cuts for the three runs. The selectivity to fuel range products, C_5+, is approximately 50 wt.% for run L, 77% for

run H, and 76% for Co-only.

Recent work by Yates and Satterfield[18] suggests that yields of high molecular weight products on cobalt are significantly affected by the incorporation of low molecular weight alkenes into growing product chains. 1-Alkenes, the primary synthesis product, may undergo isomerization or hydrogenation, instead of incorporation into growing chains. Thus the low yield to heavy molecular weight products in run L may have been caused by a high degree of hydrogenation of 1-alkenes. At low space velocities (high conversions) these secondary reactions become more noticeable, decreasing alkene concentrations and thus the probability of alkene incorporation.

Figures I-16a and b show analyses of the pot liquid at the end of runs L and H. The normalized Schulz-Flory plots, with the carrier, $C_{28}H_{58}$, subtracted from the distributions, both show α values of 0.83. These represent the high molecular weight products that have accumulated throughout the run. The end-of-run slurry from the cobalt catalyst alone, operated over a wide range of conditions, exhibited an α of 0.87.[7] These values of α are comparable.

I.E. Conclusions

A Cu-ZnO/Al$_2$O$_3$ water-gas-shift catalyst was found to exhibit stable activity in a slurry reactor under typical Fischer-Tropsch conditions. The stability of the catalyst was not adversely affected by increased pressure, temperature, variation in *in situ* H$_2$/CO ratio, or the addition of 1-butene, a representative Fischer-Tropsch product. 1-Butene underwent considerable hydrogenation and isomerization, but did not crack.

A Co/MgO/SiO$_2$ Fischer-Tropsch catalyst was operated in conjunction with this shift catalyst at two different [Co/MgO/SiO$_2$]/[Cu-ZnO/Al$_2$O$_3$] weight ratios, 0.27 and

0.51. Operating conditions were 240°C, 0.79 MPa, and feed H_2/CO ratios from 1.0 to 2.0 at 0.3 to 0.6 Nl/min. In both runs, the Fischer-Tropsch catalyst maintained steady-state activity for the entire run of about 400 hours-on-stream at a level comparable to the cobalt catalyst operating alone. The rate of the Fischer-Tropsch reaction in the mixture followed a rate expression for the cobalt catalyst alone. The $Cu-ZnO/Al_2O_3$ WGS catalyst exhibited a very slow loss of its activity.

Each mixed catalyst system exhibited stable long-term Fischer-Tropsch selectivity, but the presence of the WGS catalyst increased the extent of the secondary reactions, thereby lowering the overall selectivity to fuel range products. The feasibility of a mechanical mixture of a cobalt-based Fischer-Tropsch catalyst and a Cu-ZnO WGS catalyst in a slurry reactor has been established.

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