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**TECHNOLOGY DEVELOPMENT FOR IRON
FISCHER-TROPSCH CATALYSIS**

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2. Contract Objectives

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

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

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

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

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

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

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

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

c. Task 3.0 Catalyst Structure and Characterization.

d. Task 4.0 Catalyst Testing.

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

4.2 Measure Catalyst Performance.

4.3 Determine the Stable Phases that Exist during Synthesis at Low and High CO Conversion Levels.

4.4 Obtain Data on the Rates Involved in the Interconversion of Iron Oxide and Iron Carbide.

e. Task 5.0 Reports.

3. Summary of Activities

The water soluble C₁-C₄-oxygenates are formed in significant quantities during the Fischer-Tropsch synthesis. Thus, this water soluble oxygenate fraction represents about 1.5-2 wt.% of the hydrocarbon/oxygenate products; the alumina containing catalyst produces about 0.5 wt.% more oxygenates than the silica containing catalyst with a similar potassium content. In general, as the catalyst ages, the amount of oxygenates produced per unit of syngas converted gradually increases. The oxygenates production in general mirrors that of the CO conversion; that is, the higher the conversion the lower the oxygenates production.

The distribution of the compounds within the oxygenates is primarily determined by the amount of potassium in the catalyst but is essentially independent of the alumina or silica content. Thus, for a given alkali loading, the carbon number

distribution of the catalyst is independent of the amount of either alumina or silica in the catalyst in the 4 to 8 wt.% loading.

As the alkali loading of the catalyst is increased the normal alcohol fractions decrease. The oxygenate that increases most dramatically with an increase in potassium loading is the aldehyde class of compounds. The increase in ethanal is much less, relative to ethanol, than the increase in propanal relative to 1-propanol. At least some fraction of the ethanal is converted to products consistent with aldol condensation reactions to produce higher carbon number compounds that are not soluble in the aqueous phase. The ethanol-ethanal is essentially in equilibrium during synthesis using a C-73 catalyst manufactured by United Catalyst, Inc. (L.-M. Tau, H. A. Dabbagh and B. H. Dabbagh, *Energy & Fuels*, 5 (1991) 174); thus, the same ethanol/ethanal ratio was obtained whether ethanol or ethanal was added to the syngas feed. This was not the case in the present study. For the catalyst containing 3 to 5 wt.% potassium, the propanal/1-propanol ratio was about 4 whereas for the catalyst with 0.5 wt.% potassium this ratio was 0.1 or less. This observation implies that for the high loadings of potassium, the inability of the catalyst to establish this equilibrium is due to the enhancement of the desorption of the aldehyde and/or CO inhibition retards readsorption of the aldehyde. Furthermore, at least for the high potassium loadings, the formation of the high concentration of aldehyde implies that the aldehyde, and not the primary normal alcohol, is a primary product of the Fischer-Tropsch synthesis. It seems likely that the direct formation of the aldehyde occurs by a reaction pathway that competes with the Fischer-Tropsch synthesis and which is similar to or is a hydrocarbonylation reaction.

In summary, it appears that a Fischer-Tropsch plant that has the objective of developing a chemicals component based upon oxygenates would want to use alumina as the structural promoter. Furthermore, the operator could have some control over the amount and distribution of the oxygenate products by controlling the level of potassium that is present in the catalyst.

4. Status, Accomplishments, Results and Discussion

A.0. - Task 1.0. Development of Optimum Promoter Levels for Low- and High-Alpha Catalysts

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

A.1. Determine Optimized Synthesis Procedure for High-Alpha Iron-Based Catalysts

We have developed a supported catalyst (Fe/Cu/K on Al_2O_3) which has the required robustness for use in a CSTR. The testing of this catalyst is still going after 700 hours on stream. The results obtained to date verify our earlier work with respect to activity and is producing approximately 50 g hydrocarbon per day from the reactor. The run is being performed at 230°C and a 30 wt.% catalyst loading (10 wt.% Fe) and is having no problems with the catalyst/wax separation. The CO conversion is running at approximately 65% and has a production rate of approximately 0.4 g hydrocarbon/(day)(g-Fe). The methane and ethane selectivity for this catalyst composition is low and the selectivity to olefins is high for carbon numbers up to C_{20} . Work is continuing to optimize the catalyst composition. Even though the catalyst has

not been optimized, the catalyst has an activity and production rate that would make it commercially attractive.

A.2. Prepare Catalysts that can be Used to Determine the Role of Promoters for Low- and High-Alpha Catalysts

The mechanism of the Fischer-Tropsch Synthesis (FTS) has elicited an ongoing debate since its discovery in the 1920s. Initially it was viewed that a bulk carbide formed and was then hydrogenated to produce hydrocarbons. During the 1950s the oxygenate intermediate received wide acceptance, primarily due to the ^{14}C tracer studies of Emmett and his coworkers (Blyholder, G. and Emmett, P. H., *J. Phys. Chem.*, **64** (1960) 470 and references therein). Subsequently, the results from surface science studies led to the revival of the carbide intermediate, but one that involved only the formation of a surface carbide.

The production of methanol from syngas should follow a simpler mechanism than the FTS and, at the same time, provide some insight into the FTS mechanism. However, even the mechanism for the methanol synthesis is complex and involves controversy. Klier and co-workers (Klier, K., *Advan. Catal.*, **31** (1982) 243) advanced the view that methanol is synthesized from the CO component of the reactant mixture and that CO_2 served to maintain the catalyst in a partially oxidized state. On the other hand, other workers have claimed that methanol is formed directly from CO_2 and not from CO (Bowker, M., Hyland, J. N. K., Vandervell, H.D., and Waugh, K. C., *Proc. 8th Int. Congr. Catal.*, **1984**, Vol. II, p. 35; Bowker, M., Hadden, R. A., Houghton, H., Hyland, J. N. K., and Waugh, K.C., *J. Catal.*, **109** (1988) 263). It appears that the contribution of CO and CO_2 to the synthesis of methanol depends upon the process

conditions, and especially the partial pressures. While there are many differences between the FTS and methanol synthesis, they do have the commonality of having both CO and CO₂ present in either the reactant feed or during the synthesis due to the activity of the iron-based catalysts for the water-gas-shift (WGS) reaction.

The present work was initiated as an effort to assess the contribution of the WGS to the Fischer-Tropsch reaction since it was conceivable that CO₂ could be formed by a mechanism involving the two reaction steps shown below:



Thus, the products from a combination of reactions [1] and [2] would be the same as if the WGS had operated. On the other hand, if the WGS reaction was rapid compared to the FTS we would expect ¹⁴C, added in the CO₂, to rapidly redistribute and to be present in the CO. Surprisingly, when this experiment was performed, we found that the radioisotope distribution was such that it indicated that chain initiation could occur from an intermediate derived from CO₂ but that chain growth occurred using carbon derived only from CO (Xu, L., Bao, S., Tau, L.-M., Chawla, B., and Dabbagh, H., "11th Ann. Int. Pittsburgh Coal Conf. Proc.", 1994, p 88). Furthermore, of the CO₂ that was converted, half, or more than half, was converted to hydrocarbons (Xu, L., Bao, S., Tau, L.-M., Chawla, B., and Dabbagh, H., "11th Ann. Int. Pittsburgh Coal Conf. Proc.", 1994, p 88).

In view of the incorporation of CO₂ as well as CO and this similarity to the methanol synthesis, it was of interest to re-examine the formation of oxygenates and their dependence upon the promoter level. Thus, we have compared the amounts of

oxygenates in the aqueous phase product fraction from catalysts with various levels of potassium promoter and with either alumina or silica as the added structural promoter. While some oxygenates, and especially the higher carbon number compounds, will be in the hydrocarbon layer, the amount of oxygenates present in the aqueous phase should be related to the total amount of oxygenates formed. In addition, the oxygenates present in the aqueous phase are more easily recovered for potential use as chemicals than those that are present in the hydrocarbon fractions.

The run to determine the incorporation of CO₂ was conducted in a 1-liter CSTR system (Xu, L., Bao, S., Tau, L.-M., Chawla, B., and Dabbagh, H., "11th Ann. Int. Pittsburgh Coal Conf. Proc.", 1994, p 88) using a catalyst containing 4.4 Si and 0.71 K (based on Fe = 100). The catalyst was pretreated with syngas (H₂/CO = 0.7) for 24 hr. at 270°C and 1 atm absolute. The synthesis was effected at 175 psig and 270°C with the molar gas compositions (H₂/CO/CO₂) and flows as follow: 0 to 480 hr. (50/25/25), 3.4 NL/hr-g.Fe; 504 to 720 hr. (66/0/34), 2.54 NL/hr-g.Fe; 744 to 1200 hr. (60/10/30), 2.83 NL/hr-g.Fe. Starting at hour 1,032 and continuing for 72 hr., ¹⁴CO₂ was added as a component of the feed gas. The ¹⁴CO₂ was added with the unlabeled CO (0.22 mole% ¹⁴CO₂). The hydrogen, CO and CO₂ streams feed to a mixing tank where the gases could be completely mixed prior to entering the CSTR. The analyses for the products have been described (Xu, L., Bao, S., Tau, L.-M., Chawla, B., and Dabbagh, H., "11th Ann. Int. Pittsburgh Coal Conf. Proc.", 1994, p 88).

The runs to define the production of oxygenates were conducted as described above but without CO₂ added to the synthesis gas. The catalysts were prepared by precipitation at a pH of 8.5-9.5 by feeding the required amounts of streams of

concentrated ammonium hydroxide and iron nitrate plus either aluminum nitrate or dispersed silica obtained by hydrolysis of tetra-butoxy silicon to a CSTR where the residence time was about 6 min. The precipitate was washed two times with distilled water by repeated filtration/redispersion cycles. After the solid was dried at 110°C for about three days, the required amount of a potassium nitrate solution was added by the incipient wetness technique to produce the desired amount of potassium in the final catalyst. The catalyst was pretreated with CO as described above or with syngas at 1 atm. for 24 hours at 270°C prior to the synthesis runs. The reaction conditions were those utilized in the above example for a flow of synthesis gas of 3.4 NL/hr-g.Fe; the temperature used to effect the synthesis was 270 or 230°C. The aqueous phase was collected separately and the content of alcohols was measured using g.c. with a Porpack column. The synthesis with these catalysts at the conditions employed will produce 208 g hydrocarbons and oxygenates/m³ synthesis gas converted. The total oxygenates are based upon this yield of liquid and gaseous hydrocarbon plus oxygenate products.

CO₂ Incorporation Run

The conversion data during the run to determine the incorporation of CO₂ are illustrated in figure 1. During the period when equal molar amounts of CO and CO₂ were added (0 to 480 hr.), a portion of the CO was converted to CO₂ and the CO₂ conversion therefore appears to be negative. During the period when only H₂ and CO₂ were fed (504 to 720 hr.), the CO₂ conversion was about 25%. The conversion of CO₂ decreased when the amount of CO was increased during the third period of the run and, as expected, the lower partial pressure of CO led to a lower percentage conversion of CO.

During the period of $^{14}\text{CO}_2$ addition the conversion of H_2 was about 32%, of CO about 74% and of CO_2 about 9%. During this period CO_2 was converted to CO so that these two gases exiting the reactor had essentially the same radioactivity/mole (1.7×10^2 for CO and 1.3×10^2 for CO_2). Thus there was certainly interchange between these two compounds toward a similar specific radioisotope label.

The analysis of the C_4 - C_{10} hydrocarbons indicates that all hydrocarbons have radioactivity (figure 2). This is a not a surprising result. A similar result was obtained when the $^{14}\text{CO}_2$ was added as a tracer but at a low chemical composition (0.2 mole% of the CO). The result that was obtained with low concentration of CO_2 is the one expected when the $^{14}\text{CO}_2$ serves to initiate but that the chain growth is due to the unlabeled CO. The surprising result is the shape of the curve in figure 2.

If there was significant WGS conversion and it occurred at a rate that was similar to or exceeded that of the hydrocarbon synthesis, one would expect the CO to contain significant ^{14}C as well as the CO_2 . If the CO and CO_2 served to initiate chain growth and the CO to cause chain growth, the radioactivity/mole should increase with carbon number. Furthermore, the slope of the line should be equal to the ^{14}C content of the CO. Thus, if the WGS reaction had attained equilibrium prior to the beginning of the FTS, the radioactivity of C_1 should be the same as that of the CO_2 (and, in this case, the same as CO) that initiates the reaction and the slope of the line defining the radioactivity/mole versus the carbon number should have had a slope that is defined by the radioactivity of the CO. This is exactly the result that is obtained for the hydrocarbons in the carbon number range C_1 to C_4 but the trend does not apply for carbon numbers higher than 4.

One of the puzzling features of the earlier tracer studies was the result that the low isotopic distribution for the lower carbon number compounds was consistent with chain initiation by either an added alcohol or alkene; however, the C^{14} /mole for the higher carbon number compounds decreased with increasing carbon number (figure 3). The slope of the line for the higher carbon number compounds for many runs that utilized different alcohols and alkenes were in the range of -0.06 to -0.24 and appeared to depend upon the operating conditions (Davis, B. H., "Mechanism of Promotion of Fischer-Tropsch Catalysts", DOE/PC/70029-T1, Final Report, December 1987). Originally the reason advanced for the decrease in the radioactivity/mole for the higher hydrocarbons was that two independent FTS chains contributed to the FTS reaction mechanism. However, more recent work indicates that the accumulation of hydrocarbons may also impact the ASF plot and even give the appearance of a two-alpha mechanism (Raje, A. and Davis, B. H., submitted).

The slope of the line, based on the log (radioactivity/mole) as was done in figure 3, is -0.06, in agreement with the lower values obtained earlier. Thus, it appears that the accumulation of hydrocarbons in the CSTR prior to the addition of the $^{14}CO_2$ dilutes the products in the C_4 - C_9 hydrocarbon range sufficiently to cause the apparent decline in the radioactivity/mole.

The present data together with our earlier data are consistent with the high partial pressure of CO inhibiting the adsorption of CO_2 and this, combined with the low H_2/CO ratio, caused CO_2 to only initiate chain growth. However, the lower CO partial pressure in the present study together with the higher H_2/CO ratio caused significant WGS to occur. Thus, the synthesis was conducted with the added ^{14}C about equally distributed between the CO and the CO_2 , and this caused a linear

increase in the radioactivity/mole for the C_1 - C_4 hydrocarbons, as seen in figure 2. The accumulation of unlabeled hydrocarbons causes the radioactivity to be diluted for the higher carbon number hydrocarbons and the observed decline in the radioactivity/mole versus carbon number plot.

Oxygenate Production Runs

The amount of oxygenates that are present in the aqueous layer depends upon the level of alkali in the catalyst (figure 4). In general, the alumina containing catalysts produce as much or more oxygenates than the silica containing catalyst. This is a surprising observation since alumina is known to be a much more active catalyst for the dehydration of alcohols than silica is. For an iron ammonia synthesis catalyst, it is generally accepted that the aluminum is present predominantly, or completely, as islands of alumina that cover a significant fraction of the iron surface (V. Solbakken, A. Solbakken and P. H. Emmett, *J. Catal.*, **15** (1969) 90). Thus, if the aluminum in the Fischer-Tropsch catalysts was present as alumina islands on the surface, it is anticipated that it should function as an alcohol dehydration catalyst (B. H. Davis, *J. Org. Chem.*, **37** (1972) 1240; B. H. Davis, *J. Catalysis*, **26** (1972) 348; D. J. Collins, R. Miranda and B. H. Davis, *J. Catal.*, **88** (1984) 542). However, the experimental data differ from this expectation. This implies that the aluminium is present in Fischer-Tropsch catalysts in a form that differs from that of three-dimensional islands of alumina supported on the iron/iron oxide/iron carbide catalyst surface.

For the catalyst that contains 4.4 atomic ratio of Al, there is a dramatic increase in the amount of oxygenates that are formed as small amounts of potassium are incorporated into the catalyst; however, increasing the potassium content above about

0.5 wt.% produces only a slight, if any, increase in the amount of oxygenates that are formed. For a given potassium content in the alumina containing catalyst, it appears that about 0.5 wt.% more oxygenates are produced at 230°C than at 270°C.

For the same potassium content, the catalyst containing silica produces about half as much oxygenates at 270°C as the alumina containing catalyst at the same reaction conditions (figure 4). At 230°C the oxygenate production for the silica containing catalyst presents a different dependence on potassium content than for the alumina containing catalyst. Thus, the maximum oxygenates are obtained for the catalyst containing 0.5 wt.% potassium, and the amount of oxygenates decline to a low value as the potassium loading is increased beyond 0.5 wt.%.

The CO conversions for the runs that produced the data shown in figure 4 are indicated in figure 5. For the alumina containing catalyst the shape of the CO conversion curves resemble in general those of the oxygenates production that were obtained at the same reaction temperature. The data for the alumina containing catalyst without alkali were obtained at an earlier reaction time than for the other catalysts and may therefore be somewhat higher than it would have been obtained at later times on stream. For the particular silica containing catalysts utilized for generating the data shown in figures 4 and 5 at 270°C, the CO conversion pattern is just opposite that of the oxygenates production curve. These silica containing catalysts are not the ones that produce the optimum CO conversion, and the results for the high activity silica containing catalysts are discussed below. For the silica catalysts, the maximum CO conversion at 230°C is obtained for a catalyst that contains about 3 wt.% potassium; the shape of the curve shown in figure 5 for the silica containing catalyst has been verified by repeat runs at 230°C. Again, it is noted

that the CO conversion/potassium content curve is essentially the mirror image of the oxygenates production/potassium content curve.

The relative amount of oxygenates usually increase as the catalyst remains on stream. This is illustrated by the data in figure 6, and indicates that the amount of each oxygenate formed increases as the catalyst ages to provide a gradual decrease in CO conversion.

In general, the water-gas-shift reaction occurs to a greater extent with the alumina containing catalyst than with the silica containing catalyst. This, combined with the higher production of oxygenates with the alumina containing catalyst, causes the weight percent of oxygenates to be much higher in the water fraction for the alumina containing catalyst (figures 6 and 7).

The amount of potassium in the catalyst impacts the oxygenate distribution as well as the total amount of oxygenates formed. Thus, for the silica containing catalyst, the amount of methanol declines continuously from about 30% to less than 10% as the potassium level is increased from 0 to 5 wt.% (figure 8). As the potassium loading is increased the amount of ethanol (and ethanal) and propanol (and propanal) increased up to a loading of about 1 wt.% potassium and then declines with further increases in potassium content. The dominant change in the oxygenate composition in going from 1 to 3 wt.% potassium is the dramatic increase in the amount of propanal that is formed. Whereas the propanal concentration dramatically increased to become the dominant oxygenate in the aqueous phase for the 3 wt.% potassium catalyst, the amount of ethanal (acetaldehyde) did not increase significantly. A partial explanation for this is that the ethanal undergoes condensation reactions to produce higher carbon number components that have been identified as components in the oil

fraction (A. W. Fort, D. J. Houpt and B. H. Davis, unpublished results). The oxygenates distribution for the alumina (4.4 atomic fraction) containing catalyst was very similar to that shown in figure 9 for the silica catalyst except that the maximum for the fraction represented by ethanol and 1-propanol was attained at about 0.5 wt.% alkali, a lower basic promoter level than was needed to obtain the maximum for the silica containing catalyst. The dependence of the oxygenates distribution, as well as the maximum for ethanol and 1-propanol, was essentially the same at 230°C and 270°C for the alumina containing catalyst. However, it appears that there are differences in the patterns obtained for the silica containing catalyst at 230°C and 270°C. At 230°C, the fraction of ethanol and 1-propanol are essentially constant as the potassium content varies from 1 to 5 wt.% (figure 9). Again, the amount of ethanal is small compared to that of ethanol (about 20 times more ethanol). Ethanol is present at about 4 times the weight fraction of 1-propanol; however, the weight fraction of ethanol plus ethanal is about equal to that of 1-propanol plus propanal. Propanal is a dominant oxygenate product in the aqueous phase, and the amount of propanal remains essentially constant over the potassium range of 1 to 5 wt.%.

A number of repeat preparations of the catalyst that contains $\text{Si/Fe} = 0.044$ and $\text{K/Fe} = 0.71$ (0.5 wt.% K) has been carried out and these have been utilized in long-term activity/selectivity studies. A representative conversion versus time curve is shown in figure 10 for a catalyst that was activated in synthesis gas for 24 hours at 270°C and at 14.7 psia total pressure. The catalyst exhibits long-term stability of activity, declining at a rate that is less than 1% CO conversion/week. Also included in this figure is the fraction of oxygenates (based on total oxygenates plus hydrocarbons) that are formed during the more than 2500 hours of run time. It is