

Technology Development for Iron and Cobalt Fischer-Tropsch Catalysts

Final Technical Report

June 30, 2002

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DE-FC26-98FT40308

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## Abstract

### CAER

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

### UC/B

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

preventing the collapse of the Fe oxide matrix during high temperature pretreatment. K promotes CO chemisorption, increases reduction/carburization of Fe oxides, increases product molecular weight, olefin content and minimizes secondary hydrogenation and isomerization reactions. Cu and Ru promote the reduction rates of Fe oxide by providing H<sub>2</sub> dissociation sites, and also enhance the carburization process. These faster reduction and carburization rates result in smaller Fe<sub>x</sub>C crystallites that lead to a greater active site density. A similar effect was also achieved via synthesis of high surface area Fe-Zn precursors by employing a solvent (isopropanol) with a lower surface tension than water to wash the precipitates. A Fe-Zn-Cu<sub>8</sub>-K<sub>4</sub> catalyst thus prepared compares well with a typical Co/SiO<sub>2</sub> catalyst in terms of hydrocarbon productivities.

In this project, attempts were also made to study the enhancement of FTS rates, product molecular weight and olefin content caused by water during FTS reactions on Co-based catalysts. Reactions with CO-H<sub>2</sub> and CO-D<sub>2</sub> mixtures showed that the kinetic isotope effect was unchanged with changes in water partial pressure in the reactor, which indicates that water does not participate in the kinetically relevant steps in FTS. In addition, the total CO-binding site density monitored using *in situ* IR spectroscopy was unchanged during H<sub>2</sub>O addition, which indicated that the rate enhancement did not reflect a change in the site density. Similarly, transient experiments performed by switching from synthesis gas to H<sub>2</sub>, showed that the total carbon determined from the CH<sub>4</sub> evolution transient did not change significantly with added H<sub>2</sub>O, which showed that either the total carbon measured thus was a combination of active and inactive carbon during FTS or that the total amount of active carbon did not change sufficiently to account for the observed increase in FTS rates with water addition.

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## Executive Summary

### CAER

#### Iron Catalysts

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

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



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

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

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

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

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

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

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

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

### Cobalt Catalysts

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

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

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

#### UC/B

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

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

Zn when present as a promoter maintains the structural integrity of Fe oxide matrix and prevents its collapse during high temperature pretreatment, hence increase in Zn loading results in higher surface areas. However, this also results in the formation of a less reducible, less active  $\text{ZnFe}_2\text{O}_4$  phase, which results in optimum Zn/Fe ratios ( $\sim 0.1$ ) being responsible for the highest FTS rates. K promotes CO chemisorption and decreases hydrogen chemisorption, and increases carburization rates of Fe oxides. This results in higher FTS rates, higher product molecular weight, minimization of secondary hydrogenation and isomerization reactions, and increased olefin content. Cu and Ru reduce at lower temperatures, and hence by providing  $\text{H}_2$  dissociation sites promote the reduction and carburization rates of Fe oxides. These faster reduction and carburization rates result in shorter diffusion distances and hence lead to the formation of smaller  $\text{Fe}_x\text{C}$  crystallites that in turn lead to a greater active site density for FTS.

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

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

treatment. A Fe-Zn-Cu<sub>8</sub>-K<sub>4</sub> catalyst thus prepared, showed nearly two-fold increase in FTS rates with unchanged product selectivities when compared to its low surface area counterpart. Furthermore, we have also successfully tested this high surface area sample at conditions typically employed for Co-FTS catalysts and rare for Fe catalysts (473 K and 2 MPa) and our results show that this catalyst compares well with a typical Co/SiO<sub>2</sub> catalyst in terms of hydrocarbon productivities. Hence Fe catalysts when prepared in a highly dispersed form can provide selective and active alternative to Co catalysts.

In this project, studies were also conducted with FTS reactions on Co/SiO<sub>2</sub> to investigate the mechanism and the effect of water on the reaction in detail. Water enhances FTS rates, decreases CH<sub>4</sub> and increases C<sub>5+</sub> selectivities, and also increased olefin content. Reactions with CO-H<sub>2</sub> and CO-D<sub>2</sub> mixtures showed an inverse kinetic isotope effect and this was a combination of kinetic and equilibrium effects. The kinetic isotope effect was unchanged with changes in water partial pressure in the reactor, which effectively ruled out the participation of water in the kinetically relevant steps in the reaction mechanism.

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

In a parallel study, we performed switch transient experiments, in which FTS reaction was carried out on a Co/TiO<sub>2</sub> catalyst at steady state and the flow was switched to H<sub>2</sub>. The resulting CH<sub>4</sub> transient evolution, which gave information on the total active carbon hydrogenated during this switch, was monitored with and without the addition of water. These studies showed that the total carbon determined thus did not change significantly with added

H<sub>2</sub>O, which showed that either the total carbon measured thus was a combination of active and inactive carbon during FTS or that the total amount of active carbon did not change significantly to account for the large increase in FTS rates under the same conditions.