1.0.0 Executive Summary

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

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

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

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

Promotion with copper lowered the reduction temperature and increased FTS activity, regardless of the activation gas used. Carbon monoxide activation gave the highest activity for a 100Fe/4.4Si/5.2K catalyst (atomic percent, relative to iron) while syngas activation was superior for a 100Fe/4.4Si/2.6Cu/5.2K catalyst. Selectivity of the FTS product was not affected by the activation gas employed or copper promotion; however, potassium promotion increased wax and alkene selectivity. A syngas activated 100Fe/4.4Si/2.6Cu/5.2K catalyst gave the best overall performance at 230°C. Alkene selectivity was greater than 75% for the C_2-C_{11} fraction, methane selectivity was below 3 wt% and C_{12}+ selectivity was above 70 wt%.

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

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

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

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

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

Slurry phase Fischer-Tropsch Synthesis (FTS) was conducted with two precipitated iron catalysts (100Fe/3.6Si/0.71K and 100Fe/4.4Si/1.0K, atomic % relative to Fe) at 543K, 1.31MPa and a synthesis gas (H_2/CO=0.7) space velocity of 3.1 NL h^{-1} g Fe^{-1}. The impact of activation gas (CO, H_2/CO=0.7 or H_2/CO=0.1), temperature (543K or 573K) and pressure (1.31MPa or 0.10 MPa) on the long term (>500 h) activity and selectivity of the catalysts were explored. Pretreatment with CO under the conditions employed gave highly active and stable catalysts. Catalyst performance when synthesis gas activation was used was found to be dependent upon the partial pressure of hydrogen in the activating gas with low hydrogen partial pressures resulting in the highest catalyst activity. X-ray diffraction results indicate that carbon monoxide activations and synthesis gas activations with low hydrogen partial pressure result in the formation of the carbides χ-Fe_5C_2 and ϵ'-$Fe_{2.2}C$ while activation with synthesis gas with high hydrogen partial pressure results in the formation of only Fe_3O_4. It was found that treating the 100/3.6Si/0.71K catalyst activated with synthesis gas at 1.31 MPa and 543K, with carbon monoxide caused the activity to increase dramatically and the Fe_3O_4 to be partially converted to iron carbides. It is concluded that Fe_3O_4 is relatively inactive for FTS while the presence of some bulk iron carbide is necessary for high FTS activity to be achieved.

CO pretreatment of precipitated Fe/Si/K catalysts consistently results in high FTS activity because active carbide phases are readily formed. In the case of syngas activation, there is a relationship between the hydrogen partial pressure in the activation gas and the initial FTS activity. During activation with syngas, the catalyst is exposed to carbon dioxide and water as well as carbon monoxide and hydrogen. It has been found that during activations with high partial pressures of hydrogen, enough water is formed to prevent the catalyst from being reduced to active iron carbide phases and only relatively inactive Fe_3O_4 is formed. The results of this study indicate that the formation of an iron carbide (χ-Fe_5C_2 and/or ϵ'-$Fe_{2.2}C$) is necessary for high FTS activity; however, based on previous Mössbauer spectroscopy experiments, the activity of iron catalysts is not related to the amount of bulk iron carbide present [3]. These results indicate that a layer of surface carbide may be responsible for FTS activity.

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

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

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

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

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

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

The solvent used for start-up may have impact upon the subsequent performance of the catalyst. Our study using a light (average molecular weight 420) and a heavy (average molecular weight 3000) start-up solvent produced the same results, indicating that the viscosity and/or molecular weight do not impact the catalyst performance (activity and aging).

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

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

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

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

2.0.0 Introduction

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

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

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

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

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

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

- Role of precursor particle size on activity.

- Role of Cu in precipitated catalysts.
- Define attrition resistance.

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

- Define optimum SiO_2.
- Define optimum Al_2O_3.

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

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

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

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

2.1 Determine the Role of Cu in the Activation of Precipitated Low- and High-Alpha, Iron-Based Fischer-Tropsch Catalysts.

2.2 Determine the Effect of K Content on Activation Procedures and Determine if the Method of Addition has any Effect on Catalyst Activity and Life.

2.3 Determine the Physical and Chemical Changes that Occur during Catalyst Pretreatment and Use and Determine how these Changes Effect the Strength of the Catalysts.

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

c. Task 3.0 Catalyst Structure and Characterization.

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

d. Task 4.0 Catalyst Testing.

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

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

4.2 Measure Catalyst Performance.

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

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