EXECUTIVE SUMMARY

This report contains the results of a three year study on the preparation of high surface area iron catalysts using a continuous precipitation technique, of a detailed program designed to define the impact of three pretreatment procedures (CO only, syngas only, or hydrogen followed by syngas) on the physical and chemical changes that the catalyst undergoes during activation, and the impact of catalyst composition and pretreatment on the ultimate activity and selectivity of the catalyst during the synthesis. Overall the results of this three year study attained, or came very close to attaining, the activity, aging and selectivity targets in the Statement of Work. This report also contains a critical review of the literature on the preparation of iron catalysts and their pretreatment for use in Fischer-Tropsch synthesis. Also included is a brief review of the action of promoters in Fischer-Tropsch iron catalysts, the models for chemisorption of CO and H_2, emphasizing that which is appropriate for Fischer-Tropsch synthesis, and an over-view of the results of testing of iron catalysts for Fischer-Tropsch synthesis activity and product selectivity.

The specific objectives of the study are:

1. technology development for the production of active and stable iron Fischer-Tropsch catalysts for use in slurry phase synthesis reactors.
2. a scale-up procedure for larger scale synthesis of such catalysts for process development and long-term testing in slurry bubble column reactors, and
3. the preparation of 100 lbs of the most promising iron catalyst and delivery of the same to U.S. Department of Energy.

Preparation of Iron Oxide Catalyst

The preparation of the iron oxide catalyst was to define the impact of the following variables on the final catalyst:

1. final pH of the precipitation mixture,
2. concentration of iron and base,
3. base used ,
4. temperature of precipitation,
5. time taken to effect the precipitation,
6. length of time the precipitate is aged,
7. filtration rate,
8. method of washing,
9. fraction of the reagents contained in the hydrous precipitate, and
10. drying and calcination conditions.

The criteria for a definition of the impact that the above variables had upon the catalyst preparation was the surface area of the material following drying at 110°C or calcining in the temperature range 200-400°C. It was established that the concentration of iron and base, at least in the range of 0.1 to 1.5 M iron and 1 to 15 M base, did not have a large impact upon the surface area. In the pH range of about 5-10, there was not a major impact of pH on the surface area; aging at either lower or higher pH values increased the solubility of the iron species and led to lower surface area materials. For ammonium hydroxide as base, the final surface area decreased with an increase of the temperature at which precipitation was effected. For rates ranging from very rapid (dumping the iron and base solutions into a contained) to

precipitations with an average residence time in the precipitation vessel of up to 20 minutes, time did not impact the final surface area to a significant extent. Aging the precipitate at room temperature for periods up to two months did not cause the surface area to change from that of the un-aged sample; aging at temperatures above about 50°C did cause a decrease in surface with the ultimate decrease depending upon the length of the aging period. Since the surface area was not decreased by aging at room temperature, the rate of filtration did not materially impact the area of the final product. If the aging was at elevated temperatures, the surface area declined with the time of aging; however, the time for significant loss of surface area was a matter of hours rather than minutes. The retention of the salt formed during precipitation (ammonium nitrate) caused a decrease in the surface area of the dried and/or calcined material; the loss of area increased with the amount of salt included. The dominant factor in determining the efficiency of washing was the retention of water in the filter cake; the more water retained the less efficient the washing. After three wash cycles the material contained about 2-5 wt.% of ammonium nitrate, based upon the content of Fe_2O_3. Essentially all of the occulated ammonium nitrate decomposed during 4-24 hours of calcination at 300°C or higher.

In summary, methods were developed to prepare medium (50-150 m_2/g) surface area materials consisting of nearly pure α-, γ- or δ-FeOOH as well as α- or γ-Fe_2O_3. The highest surface area materials (about 300 m^2/g) were obtained by the rapid (average residence time of about 4-10 minutes) precipitation from a 1.2 M ferric nitrate solution by the addition of concentrated ammonium hydroxide at a rate to

maintain a pH of about 8-10. THIS PROCEDURE WAS SCALED UP TO PREPARE AT THE CAER ABOUT 160 POUNDS OF IRON OXIDE CATALYST.

Preparation of Promoted Iron Catalysts

A series of catalysts, promoted with non-reducible metal oxide, were prepared in several kilogram batches so as to contain a range of silica, alumina or zirconia contents. In addition, smaller quantities of samples containing 6 wt% of a non-reducible promoter were prepared. In general, it was observed that those metals with an ionic radius smaller than that of Fe^{3+} led to a surface area that was greater than that of the unpromoted precipitate while those promoters with an ionic radius larger than Fe^{3+} led to a surface area that was less than the unpromoted material.

A series of catalysts, with or without silica, alumina or zirconia promoter, were prepared to contain varying amounts of alkali in the range 0 to 5 wt.% K_2O. In general, the addition of alkali to the catalyst led to a decrease in the surface area, and the higher the alkali content, the greater the decrease in surface area.

Process Configuration Studies

Process conditions were defined so that a precipitated iron catalyst that had a surface area of 300 m^2/g could be prepared by precipitation. The precipitated material was shown by SEM examination to consist of small spherical particles, and the nitrogen adsorption/desorption data were consistent with this particle shape. The sample with this surface area would consist of particles with approximately 3.0 nm diameter, and the SEM measurements indicate that they are of this size range. Based upon the size of particles of commercially available ultrafine iron oxide, it does not appear that it will be feasible to obtain a material with a larger surface area than

obtained by this precipitation procedure. Furthermore, it was shown by both surface area and catalytic activity measurements that repeat preparations had the same properties. Thus, it is concluded that an optimum process configuration has been defined for the preparation of precipitated iron Fischer-Tropsch catalysts, and that the process can be operated repeatedly to prepare materials with essentially the same physical and catalytic characteristics.

It was verified that drum filters could be operated on a continuous basis in the optimum process configuration to produce a slurry containing about 20 wt% solids. The filter areas required for the initial and first two washes were defined.

Novel Catalysts

The preparation of ultrafine iron carbide catalysts using a laser pyrolysis procedure was accomplished. Two large (10g) batches of iron carbide were prepared from iron carbonyl and ethylene using the laser pyrolysis technique. These batches were utilized to obtain a measure of their catalytic activity. During the first 10 days of operation, the iron carbide catalyst was shown to convert to a material that essentially consisted of bulk Fe_3O_4. The ultrafine iron carbide prepared using the laser pyrolysis procedure was not as active as a catalyst prepared by carbiding a precipitated iron catalyst with CO.

Catalyst Pretreatment

Much effort was expended to define the phases that are present during the course of the catalyst pretreatment step, and the subsequent catalyst changes that occur during the synthesis. Much of this effort was directed toward catalyst testing following a pretreatment in synthesis gas. A number of temperature and/or pressure

recipes were followed during this test, including the one that was used for the first F-T run at LaPorte and the one initially anticipated to be used during the second LaPorte F-T run. With very few exceptional runs, it was observed that the catalysts prepared by UCI did not have significant activity during activity testing at the specified conditions when the material was pretreated with synthesis gas. At the same time, a catalyst obtained by DOE personnel from Ruhrchemie was shown to exhibit adequate catalytic activity following the same pretreatment used for the UCI catalysts. It was demonstrated that all of the catalysts prepared by UCI exhibited adequate activity when the CO pretreatment was utilized.

In summary, it has been shown that a 24 hour pretreatment in CO at 270°C will produce a material that consists predominantly of iron carbide and has adequate catalytic activity for the conversion of a $H_2/CO = 0.7$ syngas flow rate of 2.4 NL/g.Fe/hr. at 270°C and 200 psig. A similar observation was made with about 100 catalyst tests conducted with materials prepared at the Center for Applied Energy Research (CAER) except that a flow of 3.4 NL/gFe/hr. was used.

In a series of studies to support the second F-T run at LaPorte, it was shown that a CO pretreatment in a 2" x 6' slurry reactor produced CO_2 at about the same rate as was obtained with the CSTR, indicating that the carbiding proceeded at the same rate in the two reactors. Furthermore, it was demonstrated that the spherical shape and the average size of the catalyst particle at the end of the 24 hour carbiding was essentially the same as that of the initial oxide form of the catalyst received from UCI. Subsequent pretreatment of the UCI catalyst in the larger slurry reactor at LaPorte with CO gave results for CO_2 production that were similar to the CAER

experience. The activity data for the second LaPorte data appears to be similar to that obtained at the CAER in the l-liter CSTRs. Thus, it is concluded that the CO pretreatment results obtained in the 1-liter CAER can be scaled with confidence to the slurry reactor used at LaPorte.

In summary, for a program that involves the preparation and testing of many catalysts, it appears that a pretreatment in CO is preferable. This should not be taken to mean that pretreatment in a synthesis gas to produce an active catalyst is not possible; on the contrary, it seems certain that a procedure can be developed that will produce a material with an activity following a syngas pretreatment that is similar to that of a material pretreated in CO. It is believed, based primarily upon the literature and the CAER experience, that the syngas pretreatment conditions must be defined much more closely than is the case for the CO pretreatment, and that much effort will usually be required to find the optimum temperature, pressure and syngas flow conditions to produce the catalyst with a suitable activity and selectivity.

Catalyst Characterization

Samples were withdrawn directly from the reactor during the pretreatment step and at intervals during the activity testing. Samples, following extraction of the wax, were characterized to define the surface area and porosity as well as by XRD and Mössbauer spectroscopy to define the phases of iron present. During the three year program, characterization of the materials from about 50 runs was accomplished.

The general conclusion is the surface area rapidly declines during the pretreatment, whether this be in CO only, a syngas, or first in H_2 and then syngas, and that the surface area declines slowly, if at all, during the subsequent synthesis

period. The pretreatment step is therefore considered to be the step that has the dominant impact upon the physical properties of the catalyst during the synthesis period; in other words, the changes in physical properties are very rapid during the pretreatment step(s) but occur much more slowly during normal synthesis conditions.

A more surprising conclusion is that, during an initial (up to 10 days) period of the synthesis, the bulk phase of the catalyst may undergo essentially complete transformation from the iron carbide(s) form to that of Fe_3O_4 without a detectable change in either the catalytic activity or selectivity. It is therefore concluded that the bulk phase of the catalyst does not make a significant impact on the catalytic activity and/or selectivity during F-T synthesis. Since pretreatment does influence the synthesis activity and selectivity, and the bulk phase does not, it is concluded that the composition of the surface layers control these properties.

Interaction with CAER-UCI Personnel

During the course of this work, the PI interacted frequently with UCI personnel. It was an exceptional period when there was not a discussion between the PI and UCI personnel during each week. In addition, CAER personnel traveled to UCI to meet with UCI personnel as well as to work with UCI personnel on several aspects of the catalysts preparation studies. All of the studies on spray drying were conducted by a team consisting of UCI and CAER personnel, using UCI equipment and know-how. During the plant design period, there was frequent interaction between UCI and CAER personnel. In summary, the UCI Vice-President for Research considered the interaction between the two groups to be essentially the same as if the work had been conducted by a single organization.

Catalyst Testing

During the contract period eight 1-liter stirred autoclave reactors were placed into operation. This involved ordering equipment, remodeling a laboratory, and installing the needed auxiliary equipment. In addition, analytical equipment was installed and operated to permit detailed analysis of the gaseous and liquid (eventually to about C_{80} hydrocarbon carbon number) product streams. These eight reactors were operated at the same time, and on essentially a continuous time basis. Approximately 120 runs of 1,000 to 2,000 hours duration were conducted during the three years. Many of these runs were conducted to support the LaPorte plant, and were frequently accomplished under a severe time constraint in order to meet targeted milestones for the LaPorte run.

A number of problems were encountered during the operation of the reactors. One of the first problems encountered was the loss of liquid level during the longer-term testing. This was primarily a result of operating with a low-alpha catalyst with the high gas flows required by the combination of high activity for CO conversion and high slurry catalyst loadings (20 wt.%). In addition, the material produced by the low-alpha catalysts had a propensity to form a foam, and this accelerated the rate of loss of the liquid level in the reactor. Placing a stirrer blade at the top of the reactor, in the gas-phase space of the reactor, helped to eliminate much of the foaming problem. However, even with this added stirrer blade, some catalysts produced products that caused foaming problems, and this has not been solved to date.

A model, developed to account for liquid level and compositional changes during the reaction, was verified by the experimental data generated when octacosane

(C_{28}) was used as the start-up solvent. The model verified that the low alpha catalysts used in the CAER studies produced a product with sufficient vapor pressure so that the liquid level could not be maintained during extended runs. The model correctly predicts the shape of the Anderson-Schulz-Flory plots and the changes that occur during the course of the reaction; the only deviation between the experimental and predicted distribution is that the positive deviation from the linear Anderson-Schulz-Flory plot occurs as a lower carbon number for the experimental data than is predicted by the model.

The conditions specified in the contract for the catalyst testing are summarized in the following table together with the target activity and product selectivities:

Process conditions

H_2/CO ratio in the feed	0.7
Synthesis temperature	270°C
Pressure, bar	12
Syngas flow rate(NL/hr/gFe)	3.4

Desired activity and selectivity

CO conversion, %	90
CO + H_2 conversion, %	88
Total CO + H_2 used per kg Fe (Nm^3/hr.)	2.6
Hydrocarbons produced per Nm^3 syngas used:	
Total, g.	178
C_{3+}, g	166
STY of C_{3+} in 24 hr (kg/m^3 of reaction chamber)	900

The above reaction conditions, catalyst activity and productivity are the same as reported by Kölbel and Ralek (Catal. Rev.-Eng. Sci., 21, 225 (1980)) except that the gas flow rate is 3.4 NL/hr/gFe rather than the 2.4 NL/hr/gFe that was used in the

German work. In other words, the targeted activity for the catalyst to be developed during the CAER work is about 1.5 times greater than reported for the German slurry phase work.

Several catalyst formulations (at least 15 catalyst preparations) produced the targeted 90%, or greater, CO conversion during a 400 hour test period, and frequently for even longer times. Thus, catalysts have been developed that have the initial activity.

It was found that the use of a heavy start-up solvent would greatly decrease, or eliminate, the problem of loss of liquid level during the long-term testing. Two start-up solvents that were found to give satisfactory operation were a hydrogenated hard Fischer-Tropsch wax and the higher boiling fraction (bottom 50%) of an oil provided by Allied-Signal that had an average molecular weight corresponding to C_{50}.

A metal filter (0.5 micron) was found to be suitable for use with the low-alpha iron catalysts. Thus, runs could be made for up to 2,000 hours without encountering problems with withdrawing reactor-wax. However, it is emphasized that the reactor-wax production is low, even during long-term testing of these low alpha catalysts.

The role of diffusion was not evaluated during the current studies using the CSTR. A primary reason for this was the demonstration that large particles (average size of 50 microns) of the low-alpha catalysts, containing a low level of non-reducible metal oxide promoter, did not survive during testing in the CSTR. It was shown that the agitator of the autoclave would cause disintegration of the larger particles to produce smaller (1-3 micron or smaller size) particles, and that this was due to the mechanical agitation rather than the carbiding of the catalyst.

Catalyst Aging Studies

Using the reactor conditions defined above, selected catalysts were to be subjected to aging studies. The aging studies were to be for 60 days or longer. The target was to show no more than 1% activity loss per week, starting with 88% H_2 + CO conversion.

Catalysts with very long-term stability were prepared during the course of the study. However, after about 400-600 hours of testing, with the CO conversion at or above 90%, there would very frequently be a sudden (during 1-3 days) drop in activity, and this would be followed by an activity increase. Following a recovery of a catalyst to a 60-70% CO conversion level, the catalyst could be utilized during a 1500 hour period with essentially constant activity. Thus, in these instances catalyst stability was demonstrated at the 60-70% CO conversion level that exceeded the target value.

The activity/aging characteristics were determined for the 100 pound batch of catalyst that was prepared using a procedure that included continuous precipitation and spray drying. Unfortunately, operational problems were encountered during much of the spray drying step. Even so, a sample of this catalyst, following pretreatment in CO, produced an activity that resulted in a CO conversion level of 85%. This activity declined to about 70% during 2,000 hours of operation. This results in an activity decline of about 1.1% CO conversion per week, and is very close to the target value.

None of the catalysts tested, including the iron catalyst that did not have alkali promoter, had a sufficiently low water-gas-shift activity to permit attainment of the target productivity (178 g hydrocarbons per NM^3/hr/kg Fe); the productivity for the

active CAER catalysts was about 173 g of hydrocarbons per NM^3/hr/kg Fe. The selectivity for C_{3+} hydrocarbons (93%) of total hydrocarbons was approached but not attained.

In summary, several catalyst formulations were prepared that met or exceeded the target CO conversion. The target aging rate was essentially met. Because of excess water-gas-shift activity, hydrocarbon productivity per unit of syngas was approached closely but was not attained. Likewise, hydrocarbon selectivity was approached closely but was not attained.

Preliminary Design and Cost Estimate of a Catalyst Synthesis Facility

A design for a plant to produce 100 pounds a week of iron F-T catalyst was completed. The design was based on results obtained in a plant with the capacity to produce 100 pounds during a week of operation. Thus, no scale-up of either the procedure nor of the equipment is needed. Thus, the design and cost estimate are the final plans for the plant, and not a preliminary design.