II. EXECUTIVE SUMMARY

Despite the current worldwide oil glut, the United States will ultimately require large-scale production of liquid (transportation) fuels from coal. Slurry phase Fischer - Tropsch (FT) technology, with its versatile product slate, may be expected to play a major role in production of transportation fuels via indirect coal liquefaction.

Texas A&M University (TAMU) with sponsorship from the US Department of Energy, Center for Energy and Mineral Resources at TAMU, Texas Higher Education Coordinating Board, and Air Products and Chemicals, Inc., has been working on development of improved iron FT catalysts and characterization of hydrodynamic parameters in two- and three-phase bubble columns with FT derived waxes. Our previous studies have provided an improved understanding of the role of promoters (Cu and K), binders (silica) and pretreatment procedures on catalyst activity, selectivity and longevity (deactivation).

The objective of the present contract was to develop improved catalysts with enhanced slurry phase activity and higher selectivity to liquid fuels and wax. This was accomplished through systematic studies of the effects of pretreatment procedures and variations in catalyst composition (promoters and binders). The major accomplishments and results in each of these two main areas of research are summarized here.

II-1 Pretreatment Effect Research

II-1.1 Characterization Studies with 100 Fe/0.3 Cu/0.8 K Catalyst

The unsupported, doubly promoted precipitated iron catalyst with nominal composition 100 Fe/0.3 Cu/0.8 K was characterized before and after different pretreatments, and after Fischer-Tropsch synthesis in a fixed bed reactor at 250°C, 1.48 MPa (200 psig), 2 Nl/g-cat/h, $H_2/CO = 0.67$ for 140 - 200 h.

The BET surface area of the catalyst decreased from 190 m^2/g to 130 m^2/g after calcination in air at 300°C for 5 hours, and further to 21-47 m^2/g after pretreatments in hydrogen, carbon monoxide or syngas. The pore volume decreased upon pretreatments in H$_2$ or CO, but remained unchanged after syngas pretreatment. The pore size distribution of as-prepared and pretreated catalyst was essentially monomodal, and shifted to larger pore diameters after H$_2$ or CO pretreatments. However, the syngas pretreated catalyst had a bimodal pore size distribution with maxima at 4 and 45 nm. Transmission electron micrographs of samples before and after different pretreatments reveal that particles are largely spherical. An increase in particle size was observed after H$_2$ reductions both by TEM and XRD analysis. The particle size increased with reduction temperature (e.g. 19 nm after H$_2$ reduction at 220°C, and 33 nm after reduction at 280°C).

X-ray diffraction (XRD) and Mössbauer effect spectroscopy (MES) were used to identify bulk iron phases in pretreated and used (after FT synthesis) catalyst samples. Calcined catalyst is in the form of α-Fe$_2$O$_3$ ($\sim$ 16 nm in diameter), which is converted to either metallic iron (α-Fe) or a mixture of α-Fe and Fe$_3$O$_4$ (magnetite) after H$_2$ reductions. During FT synthesis the α-Fe is carburized to iron carbides (χ- Fe$_5$C$_2$ or ε' - Fe$_{2.2}$C) or oxidized to magnetite. The gas environment is predominantly reducing at the top of the reactor (since the syngas is introduced at the top), and more oxidizing at the bottom of the reactor due to formation of water and carbon dioxide. Thus, the catalyst samples from the top part of the reactor contain relatively more iron carbides or metallic iron, whereas magnetite is found preferentially in samples from the bottom part of the reactor. Also, relative amounts of χ- Fe$_5$C$_2$ carbide are greater in the top part of the reactor than in the bottom part, whereas the opposite trend is observed for ε' - Fe$_{2.2}$C carbide.

After CO or syngas pretreatments, the χ- Fe$_5$C$_2$ carbide is the most dominant phase. During FT synthesis this carbide is partially or completely converted to ε' -

Fe$_{2.2}$C carbide, Fe$_3$O$_4$, and/or FeCO$_3$ (siderite). Again it was found that the iron carbides are dominant in samples from the top part of the reactor (reducing atmosphere), whereas Fe$_3$O$_4$ or FeCO$_3$ are dominant iron phases in samples from the bottom part.

Temporal release of reduction products (water or carbon dioxide) was monitored continuously during H$_2$ and CO pretreatments by gas chromatography and mass spectroscopy. It was found that the reduction is very rapid initially (first 5 to 10 minutes), and then continues at a much lower rate. The reduction products were detected in the effluent gas after 8 hours of reduction at 280°C. This has been interpreted as a two step reduction process. The first (fast) step is the reduction of Fe$_2$O$_3$ to Fe$_3$O$_4$, which is followed by reduction of Fe$_3$O$_4$ to either metallic iron (H$_2$ reduction) or to an iron carbide (CO pretreatment). The second step is a slow one, and the reduction is not complete (H$_2$ reduction). The amount of CO$_2$ released during the CO pretreatment was greater than the stoichiometric amount needed for complete oxygen removal and complete carburization of iron in the catalyst. It is assumed that this is due to formation of carbonaceous deposits by Boudouard reaction.

II-1.2 Reaction Studies with 100 Fe/0.3 Cu/0.8 K Catalyst

The effects of pretreatment conditions on catalyst performance (activity, selectivity and stability with time) during Fischer-Tropsch synthesis were studied in fixed bed (five different pretreatment procedures) and stirred tank slurry (two pretreatment procedures) reactors. The major findings from these tests are summarized below.

It was found that hydrogen reductions result in stable or increasing catalyst activity with time on stream. Hydrogen reduced catalyst produces more methane and gaseous hydrocarbons than CO or syngas pretreated catalyst. Secondary reactions (olefin hydrogenation and isomerization) were more pronounced in tests in which hydrogen reductions were employed. Pretreatment conditions (temperature, duration

and/or gas flow rate) have a strong effect on the subsequent catalyst activity. Differences in activity may be attributed to formation of different iron phases, variations in crystallite sizes (or surface areas) and migration of sulfur impurities to the surface of the catalyst during the reduction.

Pretreatments with carbon monoxide and syngas result in formation of Hägg χ - carbide, which is very active for FT synthesis. However, the catalyst deactivates fairly rapidly with time due to conversion of χ - carbide to less active iron oxide phases, and buildup of inactive carbonaceous species which block the active sites on the surface. The CO or syngas pretreated catalyst favors production of high molecular weight hydrocarbons, and suppresses the secondary reactions.

The above results suggest that the surface hydrogen concentration is higher after hydrogen reductions, which results in higher hydrogenation activity, production of low molecular weight hydrocarbons and better stability with time on stream.

The same qualitative trends were observed in two STSR tests, in which hydrogen and syngas pretreatments were used, with the exception that methane selectivity was higher in the test with syngas pretreated catalyst than with H_2 reduced one.

II-1.3 Characterization Studies with Ruhrchemie Catalyst

A precipitated iron catalyst with nominal composition 100 Fe/5 Cu/4.2 K/25 SiO_2, prepared by Ruhrchemie, was characterized before and after five different pretreatments, as well as after the Fischer-Tropsch synthesis, following these pretreatment procedures, in a fixed bed reactor at 250°C, 1.48 MPa (200 psig), 2 Nl/g-cat/h, $H_2/CO = 0.67$ for 100 - 426 hours.

The as-received catalyst had the BET surface area of 295 m^2/g and the pore volume of 0.58 cm^3/g, both of which remained unchanged (within experimental errors) after calcination in air at 300°C for 5 hours. After different pretreatments with H_2, CO or syngas both the BET surface area and the pore volume of the catalyst decreased, while

the average pore diameter increased. The surface area of the pretreated catalysts ranged from 100 to 180 m^2/g, whereas the pore volume varied from 0.31 to 0.49 cm^3/g. The decrease in the surface area and the pore volume is attributed to a partial collapse of the porous iron oxide/hydroxide network, which is stabilized by the presence of silica. In the absence of silica the surface areas of pretreated precipitated iron catalysts are between 10 and 40 m^2/g.The pore size distribution of as-received and pretreated catalyst was rather broad with a maximum at about 20 nm, which shifted slightly to higher values after H$_2$ or CO pretreatments. The catalyst, before and after pretreatments, also had micropores less than 1.5 nm (the lower limit of detection) in diameter.

The extent of bulk iron reduction following H$_2$ and CO pretreatments was studied by isothermal and temperature programmed reduction. The isothermal and temperature programmed reduction profiles indicate that the reduction occurs in two steps: Facile reduction of Fe$_2$O$_3$ to Fe$_3$O$_4$, followed by slow reduction of Fe$_3$O$_4$ to either metallic iron (H$_2$ reduction) or an iron carbide (CO pretreatment). The first step is completed in about 15-30 minutes, whereas the second step is not complete even after 8-10 hours (isothermal reductions with H$_2$ and CO at 280°C and 300°C). The amount of CO$_2$ released during the CO pretreatment at 280°C was greater than the stoichiometric amount needed for complete oxygen removal and complete carburization of iron in the catalyst. It is assumed that this is due to formation of carbonaceous deposits by Boudouard reaction.

X-ray diffraction (XRD) and Mössbauer effect spectroscopy (MES) were used to identify bulk iron phases in pretreated and used (after FT synthesis) catalyst samples. After H$_2$ reductions the bulk iron is in the form of either Fe$_3$O$_4$ (magnetite) - reduction at 220°C, or a mixture of Fe$_3$O$_4$ and α-Fe (reductions at 280°C). During FT synthesis the iron carbides (χ- Fe$_5$C$_2$ or ε' - Fe$_{2.2}$C) are formed by carburization of α-Fe and/or Fe$_3$O$_4$. The used catalysts contain iron carbides and magnetite.

After CO or syngas pretreatments, the χ-Fe_5C_2 carbide and superparamagnetic oxides are the only phases present. The latter is probably in the form of small magnetite particles, which needs to be confirmed by MES measurements at low temperatures. During FT synthesis this carbide is partially converted to Fe_3O_4. Iron carbide content is higher in samples from the top part of the reactor (reducing atmosphere), whereas Fe_3O_4 and superparamagnetic oxides are the dominant iron phases in samples from the bottom part (more oxidizing atmosphere).

II-1.4 Reaction Studies with Ruhrchemie Catalyst

The effects of pretreatment conditions on the Ruhrchemie catalyst performance (activity, selectivity and stability with time) during Fischer-Tropsch synthesis were studied in fixed bed (six pretreatment procedures) and stirred tank slurry (two pretreatment procedures) reactors. The major findings from these tests are summarized below.

It was found that hydrogen reductions (four different pretreatments) result in stable or increasing catalyst activity with time on stream. Pretreatment conditions (temperature, duration and/or gas flow rate) have some effect on subsequent catalyst activity. Activity of the catalyst reduced at 220°C was about 20% higher than that of the catyalyst reduced at 280°C for 24 hours. This is beleived to be due to higher surface area (smaller crystallite size) of the catalyst reduced at low temperature, and differences in catalyst composition during the FT synthesis. In tests following hydrogen reductions at 280°C (three different procedures) the catalyst produced more methane and gaseous hydrocarbons than the catalyst reduced at 220°C, and CO or syngas pretreated catalyst. Secondary reactions (olefin hydrogenation and isomerization) were more pronounced in tests in which hydrogen reductions were employed.

Pretreatments with carbon monoxide and syngas result in formation of Hägg χ-carbide, which is very active for FT synthesis. The CO pretreated catalyst deactivated

with time on stream due to conversion of χ - carbide to less active iron oxide phases, and buildup of inactive carbonaceous species which block the active sites on the surface. Activity of the syngas pretreated catalyst was stable during 130 h of testing at the baseline conditions. The apparent rate constant of the syngas pretreated catalyst was about 10% less than that of the catalyst reduced with H_2 at 220°C, even though its surface area after the pretreatment was significantly smaller than that of the H_2 reduced catalyst (99 vs. 179 m^2/g). Hydrogenation activity of the syngas pretreated catalyst is slightly greater than that of the CO pretreated catalyst.

Two pretreatment procedures (H_2 reduction at 220°C, and CO pretreatment at 280°C) were employed in stirred tank slurry reactor tests. These tests were of much longer duration than the corresponding fixed bed reactor tests, and they lasted over 700 hours. The activity of the H_2 reduced catalyst increased by about 10% during the first 360 h on stream and than remained stable for the remainder of the test, whereas the apparent rate constant of the CO pretreated catalyst was fairly stable during the first 390 h but declined sharply by 36% at 420 h on stream. After this unexpected step change in activity, it remained stable during the next 300 h of testing. The activity of the CO pretreated catalyst during the first 360 h on stream (before the abrupt drop in activity) was about 25% higher than that of H_2 reduced catalyst. This is attributed to incomplete reduction in the case of the latter, and higher FT activity of χ - carbide relative to magnetite. In both tests the catalyst selectivity changed with time on stream. Hydrocarbon product distribution shifted toward lower molecular weight products, and the secondary reactions (olefin hydrogenation and isomerization) increased with time.

II-1.5 Reaction Studies with 100 Fe/5 Cu/4.2 K/16 SiO2 Catalyst

The effect of three pretreatment procedures, using H_2, CO and $H_2/CO = 0.7$ as reductants, on performance of 100 Fe/5 Cu/4.2 K/16 SiO_2 catalyst during Fischer-

Tropsch synthesis was studied in stirred tank slurry reactors. The test duration was between 340 and 720 h of continuous operation.

The synthesis gas conversion was high in all three tests, and varied between 64 and 87%. Deactivation rates were low and the loss of activity was less than 1% per day in all three tests. Activity of the syngas pretreated catalyst was about 25% higher than that of H_2 or CO pretreated catalyst. Beneficial effects of operation at higher reaction pressure on the reactor productivity (space-time-yield) were demonstrated in all three tests. By simultaneously increasing the reaction pressure and the gas space velocity in the same proportion (from 1.48 MPa and 1.5 Nl/g-cat/h to 2.17 MPa and 2.2 Nl/g-cat/h) in order to keep the gas contact time constant as at the baseline conditions, the STY was increased by 32% to 47%. The latter value is proportional to increase in reaction pressure, and confirms some of the earlier literature findings that space-time-yield is proportional to pressure. Obviously, one would want to operate at as high synthesis pressure as possible, however, the catalyst deactivation rate also increases with pressure, and there is an optimum value of reaction pressure which is largely influenced by process economics.

In general, catalyst selectivity did not vary markedly with time on stream. During the operation at high pressure a slight decrease in secondary olefin hydrogenation and isomerization reactions was observed, as well as a shift in selectivity toward higher molecular weight hydrocarbons. However, the magnitude of these changes was small in all cases. Methane selectivity was low (2.9-4.6 wt%) and C_{12+} selectivity was high (57-64 wt%) after hydrogen and CO pretreatments, whereas the syngas pretreated catalyst had unexpectedly high methane (10-11 wt%) selectivity. The olefin content was higher after CO and syngas pretreatments, than that of hydrogen reduced catalyst.

II-2 Development of Improved Iron-Silica Catalysts

II-2.1 Baseline Catalyst Testing

In order to evaluate advances achieved in catalyst synthesis four catalysts prepared by two catalyst manufacturers (United Catalysts, Inc. and Ruhrchemie) were tested in stirred tank slurry reactors to determine their performance during Fischer-Tropsch synthesis. Precipitated iron was used as the active metal in all catalysts, and CuO, K_2O and SiO_2 were used as promoters. The amounts of promoters (in parts per weight per 100 parts of iron) in these four catalysts were as follows: SiO_2 = 4.1-25; K = 1.1-8.7 and Cu = 1.4 - 7.5. Total BET surface area varied between 136 and 290 m^2/g, and increased with the amount of silica, with the exception of two UCI catalysts having 4.1 and 9.2 g of SiO_2 per 100 g of Fe (see Table IV-1.1).

The Ruhrchemie and two of the UCI's catalysts (Runs SA-3391 and SA-2052) had low deactivation rates, whereas the UCI catalyst with low silica content (Run SA-1532) deactivated more rapidly. The intrinsic activity of the low silica catalyst, measured by apparent first order reaction rate constant, was the lowest, whereas the Ruhrchemie catalyst had the highest activity (on per gram of iron basis). Activity of the Ruhrchemie catalyst was higher after CO pretreatment. than after hydrogen reduction. The intrinsic activity of catalysts correlates with total su. ace area, except for the UCI catalysts with 4.1 and 9.2 parts of SiO_2.

The low silica catalyst favored production of high molecular weight products. Methane selectivity in Run SA-1532 was only 2.2 - 2.4 wt%, and that of gaseous (C_2 - C_4) hydrocarbons 10 - 11 %. This catalyst also had low olefin hydrogenation and olefin isomerization activity. However, it was the least active and stable catalyst among the four catalysts tested. The Ruhrchemie and the other two UCI catalysts had similar hydrocarbon and olefin selectivities. Methane selectivity in tests with these three catalysts varied between 4.1 and 4.7 wt%, during the first 360 h of testing.

II-2.2 Testing of Iron-Silica Catalysts Synthesized at TAMU

Eight of iron FT catalysts synthesized in our laboratory have met specified performance targets for hydrocarbon selectivity, i.e. total hydrocarbon production greater than 178 g/Nm^3(H_2+CO) reacted and more than 166 g C_3^+/Nm^3(H_2+CO) reacted. Four of the catalysts have met the requirement that methane + ethane + ethylene selectivity be less than 8 wt% of total hydrocarbons. Initial synthesis gas conversions in five tests were higher than 81%, and the catalyst deactivation rate in three tests was moderate, between 0.9 and 1.4% per day. Catalyst productivity target of greater than 2.6 Nm^3(H_2+CO) reacted/(kg-Fe h) has been met in two tests, whereas in several other tests this target was not met by a small margin only. The activity targets for syngas conversion ($\geq$ 88%) and catalyst productivity are very difficult to achieve in a stirred tank slurry reactor (nearly perfectly mixed reactor), but it is expected that some of our catalysts would exceed these targets in a bubble column slurry reactor. Several of our catalysts are more active than any other known iron FT catalysts developed for maximization of production of high molecular weight hydrocarbons.