Development of Improved Iron Fischer-Tropsch Catalysts

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Final Technical Report

Texas A&M Research Foundation Project 6464

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V. Udaya Rao, Project Manager (PETC)

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I. OBJECTIVE AND SCOPE OF WORK

The objective of proposed research is development of catalysts with enhanced slurry phase activity and better selectivity to fuel range products, through a more detailed understanding and systematic studies of the effects of pretreatment procedures and promoters/binders (K_2O , CuO and SiO_2) on catalyst performance. In order to accomplish this objective, the work shall be divided into several tasks which are described in the following subsections.

Task 1 – Project Management

Within 60 days of project initiation, the contractor shall prepare and submit to the DOE Project Manager a detailed project work plan covering the entire period of performance of the project. The plan shall present, in detail, all activities that will be performed to successfully complete proposed research and it shall consist of the following: (1) detailed description of the methods and technical approach that shall be used to achieve the objectives of this project; (2) a detailed project schedule for each task or other logical segment of work to be performed; (3) graphs reflecting cumulative estimated costs and person-hour expended by month for each task or other logical segment of work, and for the total project effort; (4) a project work chart showing the key personnel/groups planned to work on each task and percentage of their time devoted to the tasks; and (5) a Work Breakdown Structure (WBS) dictionary to establish the framework for contract execution and to report cost schedule and technical performance.

All project status, milestone schedule, and cost management reports, as well as topical reports, if any, shall be submitted in accordance with the DOE reporting requirements.

Task 2 – Catalyst Pretreatment Research

This task is aimed at developing optimal pretreatment conditions for precipitated unsupported (1 catalyst) and supported (or silica containing; 1-2) iron catalysts, and at providing a better understanding of the role of pretreatment on subsequent catalyst activity, selectivity and longevity during Fischer-Tropsch synthesis (FTS). This shall be accomplished by examining the effect of various activation conditions on physical and chemical properties of the catalyst as well as on catalytic behavior in fixed and slurry bed reactors. Parameters such as type of reductant (H_2 vs. CO vs. syngas), reductant flow rate, temperature and duration shall be studied. Selected catalysts shall be extensively characterized using a variety of physical, chemical and instrumental techniques with the objective to establish correlations between the physical/chemical properties of the catalysts and their observed catalytic behavior during FTS.

Task 3 – Improved Iron Silica Catalysts

The objective of this task is to determine optimal concentrations of silica and K_2O in a catalyst, and to evaluate performance of catalysts synthesized by catalyst manufacturers.

Subtask 3.1 - Baseline Catalyst Testing

In order to evaluate advances in achieved in catalyst synthesis, several baseline catalysts, synthesized by United Catalysts, Inc. (UCI) and Ruhrchemie, shall be tested in a stirred tank slurry reactor.

Subtask 3.2 - Catalysts with Varied Silica/Potassium Concentrations

Catalysts to be studied shall have a composition described by the ratio 100 Fe/x Cu/y K₂O/z SiO₂ (in parts per weight). The effect of SiO₂ and K₂O on catalytic activity, selectivity and stability shall be determined to arrive at promoter/binder concentrations for an improved catalyst performance. The screening tests shall be conducted in fixed bed reactors to obtain preliminary indication of FT activity and selectivity at different process conditions. Catalysts which show enhanced activity and/or selectivity towards transportation fuels shall be tested in slurry reactors up to 30 days on stream. Selected catalysts shall be extensively characterized, to determine relations between the physico-chemical properties of catalyst and their catalytic behavior during FT synthesis.

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 NI/g-cat/h, H₂/CO = 0.67 for 140 - 200 h.

The BET surface area of the catalyst decreased from 190 m²/g to 130 m²/g after calcination in air at 300°C for 5 hours, and further to 21-47 m²/g after pretreatments in hydrogen, carbon monoxide or syngas. The pore volume decreased upon pretreatments in H₂ 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 H₂ 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 H₂ reductions both by TEM and XRD analysis. The particle size increased with reduction temperature (e.g. 19 nm after H₂ 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 -Fe₂O₃ (~ 16 nm in diameter), which is converted to either metallic iron (α -Fe) or a mixture of α -Fe and Fe₃O₄ (magnetite) after H₂ reductions. During FT synthesis the α -Fe is carburized to iron carbides (χ -Fe₅C₂ 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 -Fe₅C₂ 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 -Fe₅C₂ carbide is the most dominant phase. During FT synthesis this carbide is partially or completely converted to ϵ' -

$\text{Fe}_{2.2}\text{C}$ carbide, Fe_3O_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_3O_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_2O_3 to Fe_3O_4 , which is followed by reduction of Fe_3O_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 NI/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 m²/g, whereas the pore volume varied from 0.31 to 0.49 cm³/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 m²/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 H₂ 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 H₂ 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 Fe₂O₃ to Fe₃O₄, followed by slow reduction of Fe₃O₄ to either metallic iron (H₂ 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 H₂ and CO at 280°C and 300°C). The amount of CO₂ 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 H₂ reductions the bulk iron is in the form of either Fe₃O₄ (magnetite) - reduction at 220°C, or a mixture of Fe₃O₄ and α -Fe (reductions at 280°C). During FT synthesis the iron carbides (χ - Fe₅C₂ or ϵ' - Fe_{2.2}C) are formed by carburization of α -Fe and/or Fe₃O₄. The used catalysts contain iron carbides and magnetite.

After CO or syngas pretreatments, the χ -Fe₅C₂ 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 Fe₃O₄. Iron carbide content is higher in samples from the top part of the reactor (reducing atmosphere), whereas Fe₃O₄ 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 catalyst reduced at 280°C for 24 hours. This is believed 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 then 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 SiO₂ 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 H₂ 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 NI/g-cat/h to 2.17 MPa and 2.2 NI/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 C₁₂₊ 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, K₂O and SiO₂ were used as promoters. The amounts of promoters (in parts per weight per 100 parts of iron) in these four catalysts were as follows: SiO₂ = 4.1-25; K = 1.1-8.7 and Cu = 1.4 - 7.5. Total BET surface area varied between 136 and 290 m²/g, and increased with the amount of silica, with the exception of two UCI catalysts having 4.1 and 9.2 g of SiO₂ 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 surface area, except for the UCI catalysts with 4.1 and 9.2 parts of SiO₂.

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 (C₂ - C₄) 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 $178 \text{ g/Nm}^3(\text{H}_2+\text{CO})$ reacted and more than $166 \text{ g C}_3^+/\text{Nm}^3(\text{H}_2+\text{CO})$ 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 $2.6 \text{ Nm}^3(\text{H}_2+\text{CO}) \text{ reacted}/(\text{kg-Fe h})$ 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.

III. PRETREATMENT EFFECT RESEARCH

Introduction

The most common catalysts for CO hydrogenation are group VIII elements: cobalt, nickel, ruthenium and iron. Before synthesis, a catalyst precursor is subjected to a pretreatment, the purpose of which is to bring the catalyst into an active form for synthesis. Cobalt, nickel, and ruthenium are almost always reduced in flowing H₂ at 200-450°C to the zero-valent metallic state. During the synthesis, under a variety of process conditions, these catalysts remain in the zero-valent state (Anderson, 1956). However, the purpose of pretreatment for iron catalysts is not so clear. Reduction with H₂ may lead to the zero-valent state, but during the synthesis, the metallic iron is rapidly converted to a carbide phase (Amelse et al., 1978; Raupp and Delgass, 1979b). At high syngas conversions, the reaction mixture becomes more oxidizing (relatively high H₂O/H₂ and CO₂/CO ratios) and magnetite (Fe₃O₄) is also formed (Anderson, 1956; Dry, 1981; Satterfield et al., 1986). Other pretreatments have also been employed, such as CO reduction (activation), synthesis gas treatment (induction), and/or H₂ reduction followed by CO or vice versa. These activations often yield a better catalyst than that obtained by H₂ reduction, but the catalyst composition still changes during synthesis.

There is a large number of studies in literature dealing with the issue of the role of iron phases in the FT synthesis. Typically, these studies were conducted with model catalyst systems (e.g. iron supported on alumina, silica and other supports), at atmospheric pressure, with H₂ rich syngas mixtures (H₂/CO = 3 or higher), over short periods of time (several hours on stream) and at low (differential) conversions. In the majority of these studies calcined catalyst precursor was completely reduced with H₂ prior to exposure to synthesis gas, and conversion of metallic iron to iron carbide

phases was followed as a function of time (usually by Mössbauer effect spectroscopy - MES), while changes in gas phase composition were monitored with an on-line GC or a mass spectrometer. In some of these studies a precarbided (e.g. Matsumoto and Bennett, 1978, Butt, 1990) and oxidized (e.g. Dwyer and Somorjai, 1978; Raymond et al., 1982; Butt, 1990) catalysts were used. In studies where the catalyst precursor was completely reduced prior to FT synthesis it was found that rate of FT synthesis as a function of time on stream passes through a maximum. Several models have been proposed to explain this type of behavior, and the two which are most frequently cited are: the carbide model (Amelse et al., 1978; Raupp and Delgass, 1979a,b) and the competition model (Niemantsverdriet and van der Kraan, 1981). In the carbide model iron is not considered to be active for the FT synthesis, but the surface carbides with its underlying iron carbide bulk structure, whereas in the competition model iron atoms at the surface are considered as the active sites. In the latter model both bulk carbidation and FT synthesis (hydrocarbon formation) have a common surface carbidic precursor. In addition to these two postulates concerning the nature of the active phase, Teichner and co-workers proposed that magnetite (Fe_3O_4) is the active phase in FT synthesis (Raymond et al., 1982, Blanchard et al., 1982). According to them, the oxide phase is more difficult to carburize and be covered by graphitic (inactive) carbon, and thus the catalyst remains in its active state during synthesis. The addition of support helps stabilize iron oxide and results in greater stability. The proposal that magnetite is the active phase for FT synthesis was questioned by Dictor and Bell (1986). However, results from recent studies by Soled et al. (1990), and Butt and co-workers (Kuivila et al., 1989; Butt, 1990) lend support to this proposal. In these studies magnetite was the only phase present in the working active catalyst. Furthermore, X-ray photoelectron spectroscopy (XPS) results strongly suggest that magnetite is active for FT synthesis (Kuivila et al., 1989).

There have been only a few systematic studies on the effect of activation parameters on subsequent catalyst activity, selectivity and stability during the synthesis. The early work was reviewed by Anderson (1956, 1984) and the key findings were summarized by Bukur et al. (1989a, b). Recently, we have completed a comprehensive study of pretreatment effects with an unsupported doubly promoted precipitated iron catalyst with nominal composition 100 Fe/ 3 Cu / 0.2 K (Bukur et al., 1989a). Major findings from this study are described below.

Eleven different pretreatment procedures were employed to study effects of: temperature (250-310°C), duration (8 vs. 24 hours), pressure (0.1 vs. 1.48 MPa, with CO only) and type of reductant (CO, H₂ and H₂/CO = 0.68 at 280°C, 0.1 MPa for 24 h) on performance of 100 Fe/ 3 Cu/ 0.2 K catalyst in a fixed bed reactor. Flow rate of reductant was 3 NI / g-cat/ h in all pretreatments. Following activation the catalyst was tested at 250°C, 1.48 MPa (200 psig), 2 NI / g-cat/ h using syngas with H₂ to CO molar feed ratio of about 1. Results showed that activation parameters have significant effect on catalyst activity, stability (deactivation) and selectivity during the FT synthesis. Activations with CO or syngas minimize production of gaseous hydrocarbons and produce more liquid and high molecular weight hydrocarbons (wax), relative to reductions with pure H₂. However, these treatments usually lead to faster deactivation during the synthesis. Good stability can be achieved with a proper combination of activation parameters (temperature and duration). Reductions with hydrogen result in a constant or gradually increasing activity over 120 h of FT synthesis. The same trends were observed in tests with a variety of precipitated iron catalysts (Bukur et al., 1989b, 1990a) after hydrogen reductions. The catalyst activity can be improved by performing reduction at relatively low temperatures (220 - 240°C). In a stirred tank slurry reactor test SB - 0458 with a precipitated catalyst having nominal composition 100 Fe/0.3 Cu/0.5 K, we were able to achieve : (1) no loss in activity over 460 h period; and (2)

desirable hydrocarbon selectivity (low methane and C₂ - C₄ selectivities and high yield of C₁₂+ products), by using hydrogen reduction (Bukur et al., 1989b).

Although, it has been shown that activation parameters have significant effect on subsequent catalyst activity, selectivity and stability, the underlying reasons for differences in catalytic behaviors during FT synthesis are still unknown. Detailed catalyst characterization studies are needed to help explain catalytic results and provide basis for development of improved catalysts.

In order to gain better understanding of the role of pretreatment on catalyst performance during FT synthesis, we have examined the effect of various pretreatment conditions (reductant type, flow rate, temperature and duration of pretreatment) with three precipitated iron catalysts with nominal compositions: 100 Fe/0.3 Cu/0.8 K, 100 Fe/5 Cu/4.2 K/25 SiO₂ (Ruhrchemie catalyst which was used initially at SASOL in their commercial fixed bed reactors) and 100 Fe/5 Cu/4.2 K/16 SiO₂. The catalysts were tested in fixed bed and stirred tank slurry reactors. Catalyst samples before and after the pretreatment were characterized by a variety of physico-chemical and instrumental techniques, such as: BET surface area and pore size distribution, X-ray powder diffraction (XRPD), Mössbauer effect spectroscopy (MES) and/or transmission electron microscopy (TEM). Catalyst samples withdrawn from the reactor during STSR tests and/or after FBR and STSR tests were characterized by XRPD and/or MES to determine bulk phases in the working catalyst. Results from these characterization and reaction studies are described in the following sections of this report.

III-1 Pretreatment Effect Research - Characterization Studies with 100 Fe/0.3 Cu/0.8 K Catalyst

III-1.1 Experimental

III-1.1.1 Catalyst Preparation Procedure

A 100 Fe/0.3 Cu/0.8 K in parts by weight catalyst was used for this study. The catalyst preparation involved two steps: preparation of the Fe-Cu precursor followed by potassium impregnation. The constant pH precipitation technique was used to prepare the Fe-Cu catalyst precursor. This technique has been described in detail elsewhere (Bukur et. al. 1989a,b). In brief, the catalyst precursor was continuously precipitated at 82 °C from a flowing aqueous solution containing Fe and Cu nitrates at the desired Fe/Cu ratio, using aqueous ammonia. The precipitate was then thoroughly washed by distilled water by vacuum filtration. After a vacuum drying step, the potassium promoter was added as aqueous KHCO_3 solution via an incipient wetness pore-filling technique. The catalyst was then dried at 120°C for 16 h in a vacuum oven. The dried catalyst was calcined in air at 300°C for 5 h. The powder so obtained was then crushed and sieved to diameter between 0.25 to 0.55 mm (30/60 mesh).

III-1.1.2 Catalyst Characterization Equipment and Procedures

The catalyst composition was verified by Atomic Absorption using a Varian SpectrAA-30 spectrophotometer. Required amount of catalyst was dissolved in 10 ml of concentrated HCl followed by dilution with distilled water to 100 ml. Portions of this sample were then tested for the composition of Cu, K, and Fe. The standard solutions for Cu, Fe, and K were obtained from Aldrich.

Catalysts were pretreated in a SS-316 fixed bed reactor (1/2 inch OD, 4 3/4 inch long). This unit was used only for characterization studies following pretreatment in

different reducing environments. The unit has two valves 2.5 inches from either end of the reactor. At the end of pretreatment, the catalyst was purged with helium and the two valves were closed to isolate the reactor from the remainder of the apparatus. The reactor was then removed without exposing the catalyst to an oxidizing atmosphere. Typically 1.5-2.5 g of catalyst was used in pretreatment studies.

Powder X-ray diffraction patterns of the catalyst samples before pretreatment, after pretreatment, and after FT reaction (used catalysts) were obtained on a Geigerflex (Rigaku, Dmax Series) system using Cu-K α radiation ($\lambda = 1.54 \text{ \AA}$) starting from $2\theta = 2^\circ$ to 85° at the rate of $4^\circ/\text{min}$. For the determination of particle size by line broadening method the region of interest was scanned at a lower scan rate of $0.5^\circ/\text{min}$. The instrumental line broadening was determined from NBS standard SRM-640 powder sample. The particle size was determined using standard Scherrer's formula with $K=0.9$ after applying the instrumental line broadening correction.

The BET surface area and the pore size distribution of the catalysts before and after pretreatment were determined by N $_2$ physisorption at 77 K using a Micromeritics Digisorb 2600 system. The samples were degassed at 150°C for 12 h prior to each measurement.

Transmission electron micrographs of the catalysts were obtained using a Zeiss transmission electron microscope (Model No.10C). The particle size range was obtained directly from the micrographs by simple observation.

Isothermal reduction experiments with H $_2$ and CO at atmospheric pressure were carried out in a fixed bed reactor system similar to that used for FT synthesis. The system was equipped with an on-line mass spectrometer (Dycor, M200; Ametek, Inc.) and a gas chromatograph (Carle, AGC Series 400). Prior to reduction by either CO or H $_2$, the catalyst was heated in a flow of helium from room temperature to 280°C . Reductant gas was admitted in the system through switch from He to either CO or H $_2$ (space velocity = 3 NI/g-cat/h). The effluent gases were monitored continuously by

mass spectroscopy. A fast rate of data acquisition (1 minute intervals) for the species of interest was achieved by the use of a computerized data acquisition system. A proper background correction was employed for all the species of interest. Care was taken to heat all the lines and the vacuum chamber in order to avoid condensation of products. The composition of gases was also determined frequently using gas chromatography.

III-1.1.3 Catalyst Handling and Sample Preparation

After each pretreatment procedure, the reactor was sealed (air-tight) in an inert gas atmosphere and then transferred to a glove box. The samples for XRD analyses were removed in an inert atmosphere and then transferred to specially designed sample holders. These sample holders could be sealed in the glove box and then placed directly in the X-ray machine. The sample holders were made out of Plexiglas which does not yield any diffraction peaks. The above procedure prevents exposure of catalyst samples to an oxidizing environment.

The used catalysts were removed from a fixed bed reactor in an inert atmosphere at the end of the reaction tests. The sample handling procedure was similar to that described above. Catalyst samples removed from the top, bottom, and/or middle portions of the reactor were analyzed separately. In addition, for the used catalysts samples from each portion of the reactor, separation from glass beads (used as a diluent during FT synthesis) was necessary. This was achieved by magnetic separation in a glove box. Such a separation was found to increase the intensity of the XRD peaks significantly.

The used catalyst samples from slurry reactor tests were separated from wax in an inert atmosphere. This was carried out in a glove box filled with He as follows: A slurry sample (about 20 g), from the slurry sampling cylinder was dissolved in warm and degassed varsol and then filtered at about 80°C. The filter cake, mostly catalyst and a small amount of wax, was then rinsed with warm degassed toluene. The wet

cake was dried in vacuum at ambient temperature in a pre-chamber of the glove box. After drying, the cake was put into an extraction thimble which was placed inside a small sealable plastic bag. The thimble was then transferred into the Soxhlet extraction apparatus in a glove bag filled with He. The extraction apparatus was then taken out of the glove bag and the extraction is carried out first with xylene for 36 h, followed by methyl ethyl ketone for 18 h. The top of the condenser unit was closed so that no air could enter the system during extraction. At the end of extraction, the catalyst was transferred again to the glove box where it was removed from the thimble and sealed in sample vials and stored or placed in specially designed sample holders for characterization by XRD.

The sample preparation for the BET/PSD analyses was also carried out in an inert atmosphere (in a glove box). The BET sample tubes were loaded with the required amount of catalyst and then sealed in the glove box in order to prevent air oxidation of the catalysts.

The TEM, however, was carried out in air at room temperature. This indeed exposed the samples to an oxidizing environment. However, this is not expected to change the catalyst morphology and particle size drastically. The samples were dispersed on the carbon film sample holder supported by 300 to 400 mesh specimen mounts. The probe was then mounted in the microscope and micrographs at several magnifications were obtained.

III-1.2 Results and Discussion

III-1.2.1 Atomic Absorption

The composition of the catalyst determined by Atomic Absorption Spectroscopy was found to be 100 Fe/ 0.33 Cu/ 0.84 K which is in agreement with the nominal composition of the catalyst.

III-1.2.2 X-Ray Diffraction

As-Prepared and Calcined Catalyst

XRD patterns of the as-prepared and calcined catalysts are shown in Figure III-1.1. XRD pattern exhibited by both samples is typical of Fe_2O_3 (hematite, rhombohedral) phase. The as-prepared catalyst, however, exhibited broader peaks indicating partial crystallinity of the Fe_2O_3 phase (see Figure III-1.1a). On calcination in air at 300°C the crystallinity improved considerably as seen from Figure III-1.1 b. The phases identified are listed in Table III-1.1. The average particle sizes for the as-prepared and the calcined catalyst estimated by X-ray line broadening technique using the corresponding slow scans were 16 and 14 nm respectively, and are listed in Table III-1.1.

Reduced (Pretreated) Catalyst

The XRD patterns of the catalyst obtained after pretreatment with H_2 at different temperatures and flow rates are shown in Figure III-1.2. After pretreatment with H_2 at 220°C for 1h with a flow rate of 3550 cc/min, the bulk Fe_2O_3 phase was reduced to Fe_3O_4 (Figure III-1.2a). Several peaks corresponding to metallic Fe were also detected. The phases identified are listed in Table III-1.1. The particle size of Fe_3O_4 was estimated from the corresponding slow scan and is listed in Table III-1.1. The average particle size increased on reduction with hydrogen from 14 to 19 nm. This suggests that the Fe_2O_3 particles agglomerate on reduction to form Fe_3O_4 (magnetite). It should be noted that this is not merely a result of thermal treatment since the catalyst was already calcined at 300°C .

The XRD pattern obtained after pretreatment with H_2 at 250°C for 2 h with a flow rate of 3550 cc/min is illustrated in Figure III-1.2 b. Peaks corresponding to metallic iron only could be detected indicating that Fe_2O_3 is completely reduced to Fe. The particle size increased significantly after reduction at 250°C (from 14 to 24 nm).

Figure III-1.1 XRD patterns of 100 Fe/O.3 Cu/O.8 K catalyst: a) as prepared; b) calcined in air at 300°C for 5h.

Table III-1.1 Summary of XRD and TEM Results of Pretreated 100 Fe/0.3 Cu/0.8 K Catalyst Samples.

Run No.	Pretreatment Conditions	Phases Detected by XRD ^a	Average Particle Size Determined by XRD (nm)	Particle Size Range Determined by TEM (nm)
C0308-3 (as prep)	None	Fe ₂ O ₃	16	---
C0308-3 (calcined)	Air, 300°C, 5 h	Fe ₂ O ₃	14	26-28
FA-2451	H ₂ , 220°C, 1h, 3550 cc/min	Fe ₃ O ₄ , α-Fe	19 (Fe ₃ O ₄) ^b	12-31
FA-2491	H ₂ , 250°C, 2h, 3550 cc/min	α-Fe	24	31-64
FA-2751	H ₂ , 280°C, 8h, 85 cc/min	Fe ₃ O ₄ , α-Fe	33 (α-Fe) ^b	35-61
FA-2531	CO, 280°C, 8h, 85 cc/min	χ-Fe ₅ C ₂	*	11-56
FA-2601	H ₂ /CO=0.67, 280°C, 8h, 85cc/min	χ-Fe ₅ C ₂	*	22-43
FA-2581	H ₂ /CO=2, 310°C, 6h, 1200 cc/min	χ-Fe ₅ C ₂	*	17-80

a: Phases are in decreasing order of relative intensities.

b: Indicates the phase used for particle size determination.

*: The particle sizes could not be estimated using XRD because of overlapping signals.

Figure III-1.2 XRD patterns of 100 Fe/0.3 Cu/0.8 K catalyst samples after pretreatment with H_2 at: a) 220°C for 1 h (flow rate = 3550 cc/min); b) 250°C for 2 h (flow rate = 3550 cc/min); c) 280°C for 8 h (flow rate = 85 cc/min).

Again, this can be attributed to the sintering/agglomeration of the particles on reduction.

The XRD pattern obtained after hydrogen reduction at 280°C for 8 h and at a flow rate of 85 cc/min showed the existence of Fe_3O_4 and Fe phases (see Figure III-1.2 c). It is important to note that in spite of higher reduction temperature and longer duration of reduction than in the previous cases, the reduction was incomplete. The flow rate used, however, was lower than in the previous two H_2 reduction procedures. It has been proposed earlier that water formed during reduction plays an important role in the determination of the iron phases formed (Dry, 1981; Anderson, 1984; Bukur et al., 1989a). At higher activation temperatures, water is released more rapidly and the partial pressure of water is higher than that occurring during reduction at lower temperatures. This, coupled with a low H_2 flow rate, results in high water partial pressure during reduction at 280°C. At these high partial pressures of water, partial reoxidation of the iron phases may occur. It is not clear whether mass transfer also plays an important role in such a reduction process. Low flow rate coupled with high reaction rate may result in relatively low mass transfer rates and, thus, in partial reduction of the catalyst. The particle size of metallic Fe estimated from the XRD slow scan was greater than that obtained after reduction at 250°C (33 vs. 24 nm). This may be due to the fact that higher water partial pressure enhances the rate of sintering of iron particles resulting in larger crystallite sizes.

When CO was used for pretreatment peaks at $2\theta=39, 41, 43, 45,$ and 58° appeared (see Figure III-1.3a). These peaks were assigned to Hägg carbide ($\chi\text{-Fe}_5\text{C}_2$) phase. This suggests that after 8 hours of pretreatment with CO at 280°C complete carburization of the oxide occurred. The particle sizes after pretreatment with CO could not be estimated due to overlapping signals of the Hägg carbide. The XRD patterns after pretreatment with syngas at 280°C for 8 h and 310°C for 6 h are illustrated in Figures III-1.3b and III-1.3c, respectively. The phases identified are

Figure III-1.3 XRD patterns of 100 Fe/0.3 Cu/0.8 K catalyst samples after pretreatment with CO or syngas: a) CO (85 cc/min) at 280 °C for 8h; b) syngas ($H_2/CO=0.67$, 85 cc/min) at 280 °C for 8h; c) syngas ($H_2/CO=2.0$, 1200 cc/min) at 310 °C for 6h.

summarized in Table III-1.1. It can be seen that even in the presence of H_2 no oxide/metallic iron phases could be detected. Hägg carbide was the only iron phase present after pretreatment with syngas. Since the presence of Fe/Fe_3O_4 depends on the relative rates of reduction (by H_2) followed by their carburization (by CO) it seems that the carburization of Fe or Fe_3O_4 is faster than the rate of H_2 reduction. In such a case no Fe/Fe_3O_4 would be expected after pretreatment with syngas. It is interesting to note that all the CO or syngas pretreatment procedures yield Hägg carbide regardless of the temperature, flow rate, or composition of the reducing gas. This suggests that the carburization of the iron phases is indeed rapid and may not be a strong function of the initial phase of iron. It has previously been reported that the use of promoters like Cu and K enhance the rate of carburization of precipitated iron catalysts (Vogler et al., 1984).

Used Catalyst Samples from Fixed Bed Reactor Tests

The XRD patterns of H_2 pretreated catalysts after FT synthesis in a fixed bed reactor are shown in Figure III-1.4. The used catalyst, pretreated with H_2 at $250^\circ C$ (FB-0403), from the top part of the reactor consisted of a mixture of metallic iron and iron carbide phases (Figure III-1.4 a). In the bottom part, however, iron carbides (Fe_xC) were the most dominant phase detected along with weak Fe_3O_4 signals (Figure III-1.4b). Here, Fe_xC designates either a single iron carbide phase or a mixture of two iron carbide phases (χ or ϵ'). The precise identification of these two types of carbides is rather difficult when the signal intensities are low, and other compounds with overlapping peaks are present (Fe_3O_4 , wax). Also, peak positions (2θ and the corresponding d-spacings) are sensitive to changes in height of a sample in the sample holder. In this report χ -carbide (Fe_5C_2) refers to the so called Hägg carbide, and its XRD pattern reported by Hoffer et al. (1949). Designation ϵ' -carbide ($Fe_{2.2}C$) is used to describe a pseudo-hexagonal iron carbide, which is also referred to as ϵ - Fe_2C carbide. Its XRD pattern was first reported by Barton and Gale (1964). The nature of

Figure III-1.4 XRD patterns of 100 Fe/0.3 Cu/0.8 K catalyst samples after FT synthesis and pretreatment with H_2 : a) FB-0403 (top); b) FB-0403 (bottom); c) FB-3221 (top); d) FB-3221 (bottom) (see Table III-1.2 for the pretreatment conditions used).

iron carbide phases was determined by Mössbauer effect spectroscopy. The catalyst used in run FB-0403 was completely reduced to metallic iron (α -Fe) prior to FT synthesis, whereas in the presence of CO under FTS conditions Fe_xC was the dominant phase. This is consistent with the trend observed earlier when the catalyst was pretreated with syngas, and suggests that the rate of carburization of Fe and/or oxides is higher than that of reduction of oxides to metallic Fe. The presence of Fe_3O_4 in the used catalyst has been reported earlier in the literature (Dry, 1981; Anderson, 1984; Berry and Smith, 1989; Davis and Tungate, 1991). It has been suggested that water vapor formed during FTS may influence the phase changes occurring during FTS (Anderson, 1984). Water formed during FTS is responsible for the reoxidation of Fe/ Fe_xC to Fe_3O_4 . The particle size estimated from the slow scan for the top and bottom parts of the reactor is listed in Table III-1.2. The crystallite size of the used catalyst is similar to that of the reduced catalyst.

It should be noted that effective H_2/CO ratios are different in different parts of the reactor. In addition, due to water and CO_2 formed during FTS, $\text{H}_2\text{O}/\text{H}_2$ and CO_2/CO ratios are higher in the bottom part than in the top part of the reactor. This results in a reducing environment in the top part of the reactor, and an oxidizing environment in the bottom part of the reactor. Thus phases present in the top and bottom parts of the reactor may be different depending on the differences in gas composition in the reactor. Also, differences may exist in the relative amounts of these phases in the top and bottom parts of the reactor. However, XRD measurements cannot easily yield the quantitative results (i.e. relative amounts of iron phases in the sample). The similarities/differences in the relative amounts of iron phases estimated by Mössbauer effect spectroscopy are discussed later.

The used catalyst, pretreated with H_2 at 280°C , from top part of the reactor consisted of Fe_xC and Fe phases (Figure III-1.4c). As explained earlier, the particle size of the carbide(s) could not be obtained due to overlapping signals. Also, for this

Table III-1.2 Summary of XRD Results of 100 Fe/0.3 Cu/0.8 K Catalyst Samples after FT Synthesis - Fixed Bed Reactor Tests.

Run No.	Pretreatment Conditions; Time on Stream (TOS)	Phases Detected by XRD ^a	Average Particle Size Determined by XRD (nm)
FB-0403	H ₂ , 250°C, 2h; TOS=140h	Top: α -Fe, Fe _x C ^c , Fe ₃ O ₄	19 (α -Fe) ^b
		Bottom: Fe _x C, Fe ₃ O ₄	23 (Fe ₃ O ₄) ^b
FB-3221	H ₂ , 280°C, 8h; TOS=155h	Top: Fe _x C	--
		Bottom: Fe _x C	
FB-0021	CO, 280°C, 8h; TOS=140h	Middle: Fe ₃ O ₄ , Fe _x C, FeCO ₃	31 (Fe ₃ O ₄) ^b
FB-0352	H ₂ /CO=0.67 280°C, 8h; TOS=150h	Top: Fe _x C	
		Bottom: Fe ₃ O ₄ , Fe _x C	33 (Fe ₃ O ₄) ^b
FB-0942	H ₂ /CO=2, 310°C, 6h; TOS=142h	Top: Fe _x C	
		Bottom: FeCO ₃	42 (FeCO ₃) ^b

a: Phases are in decreasing order of relative intensities.

b: Indicates the phase used for particle size determination.

c: Fe_xC denotes iron carbide phase(s).

catalyst sample, the particle size of Fe could not be obtained due to weak Fe signals (Figure III-1.4c). In the bottom part of the reactor only Fe_xC phase was detected (Figure III-1.4d) indicating that the carburization was near complete in the bottom part of the reactor.

The XRD patterns of used catalysts pretreated with CO or syngas are shown in Figure III-1.5. The XRD pattern of the used catalyst, pretreated with CO, showed peaks

Figure III-1.5 XRD patterns of 100 Fe/0.3 Cu/0.8 K catalyst samples after FT synthesis and pretreatment with CO or syngas: a) FB-0021 (middle); b) FB-0352 (top); c) FB-0352 (bottom); d) FB-0942 (top); e) FB-0942 (bottom) (see Table III-1.2 for the pretreatment conditions used).

at $2\theta = 32, 38.2, 52.5^\circ$ which were assigned to FeCO_3 (siderite). In addition, Fe_xC and Fe_3O_4 phases were also detected. The particle size of the Fe_3O_4 phase estimated from the corresponding XRD slow scan is listed in Table III-1.2. The presence of siderite in the used precipitated iron catalyst was reported earlier (Anderson, 1984). It is possible that CO_2 formed by the water gas shift reaction plays a role in the formation of siderite. The reason why this phase is formed only in some cases is unclear at this time.

When pretreated with syngas ($\text{H}_2/\text{CO}=0.7$) at 280°C for 8 h, XRD pattern of the used catalyst sample from the top portion of the reactor showed the existence of Fe_xC phase (Figure III-1.5b), whereas in a sample from the bottom part of the reactor Fe_3O_4 could also be detected (Figure III-1.5c). The average particle size of Fe_3O_4 phase is about 33 nm. The XRD pattern of the used catalyst, pretreated with syngas at 310°C for 6 h, from the top part of the reactor showed the existence of Fe_xC phase (Figure III-1.5d). However, in the bottom part of the reactor only siderite (FeCO_3) could be detected (Figure III-1.5e). The presence of siderite was confirmed by the Mössbauer effect spectroscopy. The average particle size of the FeCO_3 phase is 42 nm, which is the largest crystallite size found in used catalyst samples (see Table III-1.2).

Used Catalyst from Slurry Reactor Tests

Used 100 Fe/0.3 Cu/0.8 K catalyst samples from slurry phase FT tests were also characterized by XRPD. In order to explain the similarities/differences in the activity/selectivity of the catalysts during FT tests as a function of time on stream, information on the phase changes with time is necessary. The catalyst samples withdrawn from a slurry reactor were separated from wax as described earlier and XRD measurements were made without exposure of samples to air.

Figure III-1.6 shows XRD patterns of the used 100 Fe/0.3 Cu/0.8 K catalyst samples from two slurry runs (SB-2262 and SA-0791) at various time on stream (TOS) values. In run SB-2262, the catalyst was pretreated with syngas ($\text{H}_2/\text{CO}=0.7$) at

280°C for 12 h, whereas in run SA-0791 the catalyst was pretreated with H₂ at 250°C for 2 h. The XRD pattern of the catalyst from run SB-2262 drawn prior to the FT synthesis (TOS=0 h) exhibited major peaks at 2θ=30.1, 35.4, 41, 43, 57, and 62.5°. Some minor peaks were also found above 2θ> 70° (Figure III-1.6a). As indicated earlier, the peaks at 30.1, 35.4, 43, 57, and 62.5° were assigned to Fe₃O₄ (magnetite) phase. The peaks at 41, 43 and peaks above 70° can be assigned to carbide phase(s) designated as Fe_xC. The exact assignment of these peaks to any single carbide phase is difficult since the peaks for most of the carbide phases are at similar positions. The closest match, however, was obtained for the Fe₂C (monoclinic) phase. The phases identified are summarized in Table III-1.3.

The XRD pattern of the catalyst drawn after 54 h on stream (T=250°C, SV=2 NI/g-cat/h, P=1.5 MPa, H₂/CO=0.7) is shown in Figure III-1.6b. It can be seen that the peak at 35.4 and 62.5° have decreased considerably whereas the peak at 43° has increased with time. Since the carbide peaks and the magnetite peaks overlap at 2θ = 43 and 57°, the appearance/disappearance of the magnetite phases can be monitored by observing the peaks at 35.4 and 62.5°. Although the amounts of the phases cannot be quantitatively determined by XRD, the relative change in the intensities would at least qualitatively indicate changes in the phases with time on stream. Thus, it can be seen that the Fe₃O₄ phase decreased with time on stream whereas the Fe_xC phases seemed to have increased with time. This suggests that progressive carburization of iron oxide(s) occurred under FT conditions.

Figure III-1.6c shows the XRD pattern after 283 hours of reaction. There were two regeneration procedures carried out prior to this sampling; one after 162 h (H₂, 260°C, 4 h) and the other after 224 h (H₂, 280°C, 12 h). It can be seen from Figure III-1.6c that peaks at 35.4 and 62.5° disappeared completely while new peaks at 38, 39, 45, and 49° appeared indicating the formation of some new phase(s). Again, an unambiguous assignment of the new peaks to any particular phase was difficult.

Figure III-1.6 XRD patterns of 100 Fe/0.3 Cu/0.8 K catalyst samples after FT synthesis in slurry reactor tests: a) SB-2262; TOS=0 h; b) SB-2262; TOS=54 h; c) SB-2262; TOS=284 h; d) SA-0791; TOS=325 h.

Table III-1.3 Phases Identified by XRD and MES in 100 Fe/0.3 Cu/0.8 K Catalyst after FT Synthesis - Slurry Phase Reactor Tests.

Run No.	Pretreatment Conditions	Time on Stream (hours)	Phases Identified by XRD	Phases Identified by MESA ^a
SA-0791	H ₂ , 250°C, 2h	325	Fe _x C ^c	
SB-2262	H ₂ /CO=0.7, 280°C, 12h	0	Fe ₃ O ₄ , Fe _x C	ε'-Fe _{2.2} C (54%), Fe ₂ O ₃ (38%), Spm ^b (8%)
		54	Fe _x C, Fe ₃ O ₄	ε'-Fe _{2.2} C (86%), χ-Fe ₅ C ₂ (7%), Fe ₃ O ₄ (7%)
		284	Fe _x C	χ-Fe ₅ C ₂ (93%), Spm (7%)

a: Numbers in paranthesis indicate the relative amount of the phases.

b: Superparamagnetic (spm) iron oxide/hydroxide.

c: Fe_xC denotes iron carbide phase(s).

However, some of these peaks can be assigned to χ-carbide. These phases are listed in Table III-1.3. Thus, despite the two regeneration processes with hydrogen, the catalyst sample at 283 h contained only iron carbide(s). Thus, the complete carburization of iron oxides occurred under FT conditions.

Figure III-1.6d shows the XRD pattern of the catalyst from run SA-0791 after 325 h on stream. At the end of the run (TOS=325 h), Fe_xC was the only component detected. Comparison of the bulk phases from runs SB-2262 and SA-0791 reveals

that although different pretreatment procedures were employed in these two tests, the carbide phases were the only phases detected after 280 h of FT synthesis. This means that complete carburization of the bulk iron oxides occurred during the course of the run regardless of the pretreatment procedure used.

III-1.2.3 Mössbauer Effect Spectroscopy (MES)

Although XRD is useful in determining the phases present in the catalyst after pretreatment and after FTS, the relative amounts of these phases cannot be easily quantified. The advantages of MES in determining the nature and the amounts of iron phases in the catalysts are well known (Amelse et al., 1978, Raupp and Delgass, 1979 a,b). In order to obtain a quantitative information on the bulk phases present in the reduced and used iron catalyst after pretreatment with H₂, CO, and syngas Mössbauer effect spectroscopy (MES) was used. The Mössbauer spectra were obtained and analyzed at the University of Kentucky (The Consortium for Fossil Fuel Liquefaction Science).

Reduced (Pretreated) Catalyst

Results of MES measurements are summarized in Table III-1.4. The Mössbauer spectrum of the catalyst sample, reduced with H₂ at 250°C for 2h, indicated the presence of metallic Fe only, which is consistent with the results from XRD analysis. Hydrogen reduction at 220°C for 1h resulted in formation of magnetite, and a small amount of superparamagnetic oxide/hydroxide phase. An upper limit to the particle size can be obtained from the occurrence of superparamagnetism. Kündig et al. (1966) have found that the critical diameter of Fe₂O₃ for superparamagnetic relaxation at room temperature is about 13.5 nm. In our case, some iron oxide particles are superparamagnetic indicating that the particle size is less than 13.5 nm. Low temperature measurements are needed to determine the exact nature of iron phases

Table III-1.4 Relative Amounts of Phases Identified by Mössbauer Effect Spectroscopy in Pretreated 100 Fe/0.3 Cu/0.8 K Catalyst Samples.

Run No.	Pretreatment Conditions	Spm ^a (%)	Magnetite (%)	χ -Carbide (%)	ϵ' -Carbide (%)	Fe-metal (%)
FA-2451	H ₂ , 220°C, 1h	11	81	—	8	—
FA-2491	H ₂ , 250°C, 2h	—	—	—	—	100
FA-2751	H ₂ , 280°C, 8h					
FA-2531	CO, 280°C, 8h	13	—	87	—	—
FA-2601	H ₂ /CO=0.67 280°C, 8h	16	—	84	—	—
FA-2581	H ₂ /CO=2, 310°C, 6h	5	—	95	—	—

a: Superparamagnetic (spm) iron oxide/hydroxide

exhibiting superparamagnetic properties. The presence of ϵ' -carbide in the reduced sample is attributed to the contamination of the sample with traces of another sample during sample preparation and handling.

The major phase in CO and syngas pretreated catalyst samples was χ -carbide (84-95%), the remainder being superparamagnetic oxide/hydroxide phase. This is in agreement with the results from XRD analysis.

Used Catalyst Samples From Fixed Bed Reactor Tests

Figure III-1.7a shows a typical Mössbauer spectrum obtained at 300 K of the used catalyst sample, pretreated with H₂ at 250°C, from the top part of the reactor (FB-0403). The spectral parameters (Isomer shift - IS; Hyperfine field - H, and Quadrupolar

split - QS) are typically obtained from such spectrum. The peak assignment is generally carried out by fitting such a spectrum to a known set of phases. For example, the spectrum shown in Figure III-1.7a could be fitted with three sets of sextets and a doublet (represented by a stick chart in Figure III-1.7a). The resultant values of H were 330 and 205 kGauss and can be assigned to Fe metal and Hägg carbide, respectively (Raupp and Delgass, 1979b). The amounts of phases identified are listed in Table III-1.5. The XRD pattern of this sample indicated the presence of Fe and Fe_xC phases which is in agreement with the MES results. However, iron oxide/hydroxide phase could not be detected by XRD either because of the low amount of this phase in the sample, or because of small particle size (less than 4 nm). Low temperature MES measurements are needed to determine the nature of superparamagnetic phase consisting of fine particles.

The relative amounts of iron phases in the catalyst sample, pretreated with H_2 at 250°C , from the bottom part of the reactor (FB-0403) are also listed in Table III-1.5. It can be seen that ϵ' -carbide (hexagonal close-packed) was the predominant phase in the bottom part of the reactor. The amount of χ -carbide, however, decreased from the top part of the reactor to the bottom part of the reactor from 64 to 7%, respectively. The phases identified are in agreement with the XRD results (Table III-1.2). It should be noted that MES results confirm the presence of Fe_3O_4 (magnetite) in the sample from the bottom part of the reactor.

The phases identified by MES for the catalyst sample, pretreated with H_2 at 280°C , from the top part of the reactor (FB-3221) are listed in Table III-1.5. Two carbide phases (χ -carbide and ϵ' -carbide) were predominant indicating that the carbiding is near complete in the top part of the reactor. The used catalyst from the bottom part of the reactor also showed the existence of ϵ' -carbide and χ -carbide phases. The relative amount of ϵ' -carbide increased from 57% in the top part of the reactor to 95 % in the bottom part, whereas that of χ -carbide decreased from 36% in

Figure III-1.7 Mössbauer spectra of 100 Fe/0.3 Cu/0.8 K catalyst samples after FT synthesis in a fixed bed reactor: a) FB-0403 (top); b) FB-0942 (bottom) (see Table III-1.2 for the pretreatment conditions used).

**Table III-1.5 Relative Amounts of Phases Identified by Mössbauer Effect Spectroscopy
in 100 Fe/0.3 Cu/0.8 K Catalyst Samples after FT Synthesis.**

Run No.	Position	Pretreatment Conditions; TOS	Spm ^a (%)	Magnetite (%)	χ -Carbide (%)	ϵ' -Carbide (%)	Fe-Metal (%)	Siderite (%)
FB-0403	Top	H ₂ , 250°C, 2h; TOS=140h	13	—	64	—	23	—
FB-0403	Bottom		8	14	7	71	—	—
FB-3221	Top	H ₂ , 280°C, 8h; TOS=155h	7	—	36	57	—	—
FB-3221	Bottom		—	—	5	95	—	—
FB-0021	Middle	CO, 280°C, 8h; TOS=140h	2	50	—	43	—	5
FB-0352	Top	H ₂ /CO=0.67 280°C, 8h; TOS=150h	6	—	94	—	—	—
FB-0352	Bottom		9	59	—	32	—	—
FB-0942	Top	H ₂ /CO=2, 310°C, 6h; TOS=142h	35	—	65	—	—	—
FB-0942	Bottom		—	—	—	—	—	100

a: Superparamagnetic (spm) iron oxide/hydroxide

the top part to 5 % in the bottom part of the reactor. In general, the measurements are consistent with results obtained from XRD analysis.

In summary, the MES results for H₂ pretreated catalyst indicate significant carbiding under FTS conditions. The type of carbide formed, however, varies along the reactor. Raupp and Delgass (1979 b) found that the type of carbide formed was

dependent on the particle size of the iron phase. Larger iron particles tend to form χ -carbide, whereas smaller iron particles form the less stable ϵ' -carbides. Also, it is possible that the gas composition in the reactor influences the phases formed during FTS. As stated earlier, the reducing atmosphere exists at the top of the reactor, whereas the oxidizing atmosphere exists at the bottom of the reactor.

For the catalyst pretreated with CO at 280°C (FB-0021), Fe_3O_4 , ϵ' -carbide, siderite, and superparamagnetic iron oxide/hydroxide phases were detected (see Table III-1.5). Several interesting observations can be noted from the MES results. Firstly, after CO pretreatment only the Hägg carbide was present in the catalyst as indicated by the XRD and MES measurements (Tables III-1.1 and III-1.4). However, in the used catalyst only the ϵ' -carbide phase was detected. Secondly, an iron carbonate (siderite) was identified by MES, which is in agreement with the XRD measurements. Finally, Fe_3O_4 is present in the used catalyst whereas none was detected initially. The reason for the formation of Fe_3O_4 was discussed earlier. However, the reason for the phase transformation from χ -carbide to ϵ' -carbide during FTS is not clear.

In the used catalyst, pretreated with syngas ($\text{H}_2/\text{CO}=0.7$) at 280°C (FB-0352), from the top part of the reactor, χ -carbide (94%) and superparamagnetic oxide (6%) were detected. The catalyst from the bottom part of the reactor consisted of Fe_3O_4 , ϵ' -carbide, and superparamagnetic iron oxide/hydroxide phases (Table III-1.5). This is consistent with the phases identified by XRD. It can be seen that a significant amount of magnetite is observed in the used catalyst from the bottom part of the reactor for reasons explained earlier. Again, the ϵ' -carbide phase is found at the bottom part of the reactor, whereas the χ -carbide is found in the upper part of the reactor.

Iron phases in the used catalyst samples, pretreated with syngas ($\text{H}_2/\text{CO}=2.0$) at 310°C (FB-0942), from the top and bottom parts are listed in Table III-1.5. In the catalyst sample from the top part of the reactor, χ -carbide and oxide/hydroxide phases

were detected. The amount of superparamagnetic iron oxides in the catalyst was relatively large (about 35%). However, no iron oxide phases were detected by XRD measurements probably because of their fine particle size (less than 4 nm). The used catalyst from the bottom part of the reactor shows only FeCO_3 (siderite). Figure III-1.7b shows the MES pattern of siderite, which is characterized by a doublet with an isomer shift of 1.21 mm/s. The presence of siderite is consistent with the XRD pattern of the catalyst shown in Figure III-1.5.

Used Catalyst From Slurry Reactor Tests

The Mössbauer spectra of the used catalyst samples from slurry reactor tests were obtained as a function of time on stream. The relative amounts of phases identified by MES are listed in Table III-1.3. In the catalyst sample withdrawn prior to FT synthesis (Run SB-2262, syngas pretreatment at 280°C, for 12 h) the following phases were identified: ϵ' -carbide (54%), $\gamma\text{-Fe}_2\text{O}_3$ (38%), and superparamagnetic iron oxide (8%). The XRD pattern for this catalyst sample indicated the presence of Fe_3O_4 and Fe_xC phases (Table III-1.3). It is possible that magnetite phase in the pretreated sample was oxidized to $\gamma\text{-Fe}_2\text{O}_3$ due to exposure of the catalyst to air before and/or during MES measurements. The composition of catalyst sample withdrawn from the reactor after 54 h on stream ($T=250^\circ\text{C}$, $\text{SV}=2 \text{ NI/g-cat/h}$, $P=1.5 \text{ MPa}$, $\text{H}_2/\text{CO}=0.7$) is given in Table III-1.3. It can be seen that the relative amount of the carbide phases (ϵ' carbide + χ -carbide) increased from 54 % to 93 %, whereas the amount of oxide phases decreased. This shows that progressive carburization of the catalyst occurs under FTS conditions. The amounts of phases identified by MES after 283 h on stream are also shown in Table III-1.3. There were two regeneration procedures carried out prior to this sampling; one after 162 h (H_2 , 260°C, 4 h) and the other one after 224 h (H_2 , 280°C, 12 h). At 283 h on stream, the catalyst consisted of χ -carbide (93%) and superparamagnetic iron oxide (7%) phases. Thus, despite the two reduction procedures at 162 and 224 h on stream, χ -carbide was the most dominant phase at

283 h indicating that complete carburization of iron phases occurred under FT conditions. This is in agreement with the results from XRD analysis.

III-1.2.4 Isothermal Reduction Experiments

Isothermal reduction, using CO as the reductant, at 280°C for 8h was carried out by switching from He to CO at 280°C and monitoring the composition of the effluent gas by mass spectrometry as a function of time on stream. Figure III-1.8a shows the relative concentration profiles of reductant CO and product CO₂ (formed during reduction) up to 150 minutes. It can be seen that CO₂ profile shows a sharp peak at about 5 minutes followed by a broad maximum after about 40 minutes of reduction (Figure III-1.8a). This means that the rate of reduction of the catalyst is very rapid initially (up to 10 minutes). Similar behavior was observed earlier during isothermal reduction with CO of a 100 Fe/1 Cu/0.2 K catalyst at 300°C (Bukur et al., 1989b). This peak is probably due to the reduction of Fe₂O₃ to Fe₃O₄. The second broad peak may be due to the reduction of Fe₃O₄ to Fe and further carburization to iron carbides. The rate of reduction, as indicated by the formation of CO₂, gradually decreased after 150 minutes. However, a small amount of CO₂ was detected even after 8 hours of reduction.

The concentrations of CO and CO₂ were also obtained by gas chromatography at 12 minute intervals. Although data could not be acquired as rapidly with a gas chromatograph as with an on-line mass spectrometer, the CO₂ profile so obtained is in qualitative agreement with the profile seen in Figure III-1.8a.

The amount of CO₂ formed during reduction up to about 8 hours was obtained from the CO₂ concentration profile shown in Figure III-1.8a. For this purpose, the data obtained by mass spectrometry were converted into absolute molar flow rates of CO₂ after proper calibration of the mass spectrometer using several known concentration values obtained by gas chromatography and the total flow effluent flow rate.

Figure III-1.8 Isothermal reduction profiles for 100 Fe/0.3 Cu/0.8 K catalyst at 280°C as a function of duration of reduction: a) CO reduction; b) H_2 reduction.

Integration of the CO₂ molar flow rate profile yielded the total amount of CO₂ formed up to 8 hours of reduction as 47 mmol/g of catalyst. It should be noted that the total amount of CO₂ that can be accounted for assuming complete reduction of the catalyst is 18.7 mmol/g. Whereas, the total amount of CO₂ that can be formed assuming complete carbiding of the catalyst (to Fe_{2.2}C) is 5.6 mmol/g. This means that the total amount of CO₂ formed far exceeds the amount of CO₂ that can be accounted for by both reduction as well as carburization. The excess CO₂ is presumably due to the formation of carbonaceous deposits on the catalyst.

Isothermal reduction profile obtained for H₂ reduction of the catalyst at 280°C for 8 hours, as seen by the formation of water, is illustrated in Figure III-1.8b. A sharp peak at about 10 minutes of reduction indicates rapid initial reduction. However, the rate of reduction decreases gradually after about 30 minutes. Similar reduction behavior was observed with 100 Fe/3 Cu/0.2 K catalyst during reduction with H₂ at 300°C (Bukur et al., 1989b). The sharp peak can attributed to the reduction of Fe₂O₃ to Fe₃O₄ whereas the slow reduction, i.e., after about 30 minutes, can be attributed to the reduction of Fe₃O₄ to metallic Fe. Quantitative information that could be obtained was limited due to lack of proper calibration methods for H₂O observed by mass spectrometry. However, the weight loss due to reduction was estimated at about 25 % of the total expected weight loss for reduction of Fe₂O₃ to Fe. Incomplete reduction of Fe₂O₃ after H₂ reduction under the above conditions was confirmed by XRD results, wherein Fe₃O₄ was detected (Table III-1.1). The incomplete reduction was also observed earlier (Bukur et al., 1989b) during the isothermal reduction of 100 Fe/3 Cu/0.2 K catalyst at 300°C.

III-1.2.5 BET Surface Area and Pore Size Distribution

The BET surface areas of as-prepared, calcined, and reduced samples are listed in Table III-1.6. The BET surface area was found to decrease after calcination

from 190 m²/g to 130 m²/g. This is probably caused by the collapse of pore structure due to removal of water of hydration from the highly porous FeOOH/Fe₂O₃ structure. Figure III-1.9 shows the pore size distribution of as-prepared and calcined samples. It can be seen that the distribution is fairly uniform with a maximum at approximately 6 nm. The average pore diameter calculated from measured values of the surface area and the pore volume are in good agreement with the pore diameter corresponding to the maximum in the pore size distribution curve (see Table III-1.6).

On pretreatment with H₂ at 220°C, the BET surface area decreased significantly (from 130 to 48 m²/g). Likewise, the pore volume obtained by N₂ physisorption also decreased significantly after reduction with H₂ (Table III-1.6). The decrease in the surface area after H₂ reductions at 250 and 280°C was even larger than that at 220°C.

It is known that as-prepared precipitated iron catalysts have high surface areas (Dry, 1981; Bukur et al., 1990b). A majority of the area is due to a highly porous iron network formed from small iron oxide particle agglomerates (about 15 nm; see Table III-1.6). The interparticle pores so formed are small in size and the network remains fairly stable even after low temperature calcination (300°C). On reduction, however, the porous structure collapses (in the absence of a suitable binder) resulting in sintering of iron particles (Dry, 1981). The fine pore structure disappears and the particles agglomerate to form larger clumps of particles. This increase in particle size translates into lower surface areas upon reduction. Similar behavior was observed by McCartney et al. (1950) and Hall et al. (1950). The decrease in the surface area due to increase in the particle size (as a result of sintering) can be calculated theoretically using a simple model which consists of uniform spherical particles. The surface area of such a model iron oxide system consisting of uniform spherical particles of size d can be expressed as: SA (per unit mass basis) = $6 / (\rho \times d)$; where ρ is the density of the particle.

Figure III-1.9 Pore size distribution of 100 Fe/0.3 Cu/0.8 K catalyst:
 a) as prepared; b) calcined in air at 300°C for 5h.

Table III-1.6 Summary of BET Results of Pretreated 100 Fe/0.3 Cu/0.8 K Catalyst Samples.

Run No.	Pretreatment Conditions	Surface Area (m ² /g)		Pore Volume (cc/g)		Pore Diameter (nm)	
		BET	Calc ^a .	BET	Calc ^b .	BET ^c	Calc ^c
As prepared	None	190	72 (Fe ₂ O ₃)	0.33	0.496 (Fe ₂ O ₃)	7	27.5
Calcined	Air, 300°C, 5h	130	82 (Fe ₂ O ₃)	0.36	0.496 (Fe ₂ O ₃)	11	24
FA-2451	H ₂ , 220°C, 1h	48	60 (Fe ₃ O ₄)	0.25	0.502 (Fe ₃ O ₄)	21	33
FA-2491	H ₂ , 250°C, 2h	21	32 (Fe)	0.20	0.330 (Fe)	38	41
FA-2751	H ₂ , 280°C, 8h	21	23 (Fe)	0.28	0.330 (Fe)	54	57
FA-2531	CO, 280°C, 8h	44	*	0.25	0.350 (Fe _x C)	23	*
FA-2501	H ₂ /CO=0.7, 280°C, 8h	34	*	0.30	0.350 (Fe _x C)	35	*
FA-2581	H ₂ /CO=2, 310°C, 6h	47	*	0.36	0.350 (Fe _x C)	31	*

a: Surface area = $6/(\text{density} \times \text{diameter})$; diameter from XRD measurements (Table III-1.1); phases used for density values are indicated in parenthesis.

b: Pore volume = $2.602/(\text{density})$; phases used for density values are indicated in parenthesis.

c: Pore diameter = $4 \times \text{pore volume}/\text{surface area}$; for BET pore diameters, measured BET surface areas and measured pore volumes were used, whereas for calculated pore diameters calculated values of surface area and pore volumes were used.

* The particle sizes could not be estimated using XRD because of overlapping signals.

The surface areas calculated using the above formula and the diameter of the particle determined by XRD are listed in Table III-1.6. The calculated surface area of the as-prepared and calcined samples is not in agreement with the measured surface area. However, the surface areas after H₂ reduction are in agreement with the measured BET surface areas. A possible reason for apparent disagreement between calculated and measured values of the surface area for the calcined and as-prepared catalysts is that in a real system the pore structure can be highly irregular (non-uniform particle sizes, interconnecting 3-dimensional pores; non spherical particles etc.).

This simple model can also be used to estimate the pore volume of the catalyst before and after reduction. Assuming particles of size d in a cubic closed packed (ccp) geometry (analogous to face centered cubic crystal structure) the pore volume per unit mass, V_p , is given by $V_p = 2.602/\rho$. The pore volume depends on the density of the particle only and is independent of the particle size. It should be noted that the phase change on reduction leads to the formation of iron which is more dense than the corresponding oxides. The calculated pore volumes are listed in Table III-1.6. It can be seen that the calculated pore volumes are in fair agreement with the observed pore volumes considering the simplicity of the model involved.

Figure III-1.10 shows the pore size distribution after pretreatment with H₂. Although the pore size distribution is fairly uniform, i.e. with a single maximum (unimodal), the pore size corresponding to the maximum is considerably higher than that for the calcined catalyst. In fact, the position of maximum shifted to higher values with increase in the reduction temperature (from 15 nm at 220°C to 46 nm at 280°C; see Figure III-1.10). The average pore diameter calculated from the pore volume and the surface area is also listed in Table III-1.6, and is in reasonable agreement with that corresponding to the maximum of the pore size distribution curves. The average pore diameter was also estimated from the calculated values of surface areas and pore volumes (using the model described above). Although the calculated pore diameters

Figure III-1.10 Pore size distribution of 100 Fe/0.3 Cu/0.8 K catalyst after pretreatment with H₂ at: a) 220°C for 1 h (flow rate = 3550 cc/min); b) 250°C for 2 h (flow rate = 3550 cc/min); c) 28°C for 8 h (flow rate = 85 cc/min).

are over estimated for the calcined and as-prepared catalyst samples, the pore diameters after reduction are in agreement with the average pore diameter calculated from observed values of surface area and pore volume.

The surface area after pretreatment with CO or syngas also decreased significantly (see Table III-1.6). This may be attributed to particle sintering and collapse of the porous iron network as explained earlier. The surface areas could not be estimated from the model described earlier since the particle size was not determined by XRD. The pore volume decreased after pretreatment with CO. However, no significant change in the pore volume was observed when the catalyst was pretreated with syngas. In order to explain this, it is necessary to examine the pore size distribution of the catalyst.

Figure III-1.11 shows the pore size distribution (PSD) of the catalyst after pretreatments with CO and syngas. The pore diameter corresponding to the maximum in the PSD increased from 6 nm for the calcined catalyst to 13 nm after CO pretreatment (Figure III-1.11a). However, upon pretreatment with syngas the pore size distribution became increasingly bimodal as seen from a small shoulder in Figure III-1.11b, and from two distinct peaks (4 nm and 45 nm) in Figure III-1.11c. This suggests that on reduction with syngas smaller pores are also created, in addition to the formation of larger pores. The higher pore volume observed after syngas pretreatment is due to the formation of smaller pores. XRD analysis indicated the formation of carbide on reduction with syngas. It is possible that the carbide particle agglomerates have smaller pores whereas the large pore originate from the agglomerates of the oxide and/or bulk Fe particles. Also, it has been postulated earlier (Davis and Tungate, 1991) that a carbon overlayer is formed on pretreatment with CO or syngas. This overlayer is known to be porous and may possess fine pore structure. These small pores are probably responsible for higher pore volume after reduction with syngas.

Figure III-1.11 Pore size distribution of 100 Fe/0.3 Cu/0.8 K catalyst after pretreatment with CO or syngas: a) CO (85 cc/min) at 280 °C for 8h; b) syngas ($H_2/CO=0.67$, 85 cc/min) at 280 °C for 8h; c) syngas ($H_2/CO=2.0$, 1200 cc/min) at 310 °C for 6h.

The BET surface area and the pore size distribution of the used catalyst samples were not obtained, since the catalyst was mixed with glass beads to maintain isothermal conditions during FTS and complete separation of catalyst particles from glass beads is difficult. Also, the used catalysts are covered with wax and possibly carbonaceous deposits, both of which would need to be removed before BET measurements.

III-1.2.6 Transmission Electron Microscopy

Figure III-1.12 shows the TEM micrographs of the calcined catalyst under two different magnifications. It can be seen that the particle morphology is essentially spherical. The particle size is approximately 26 nm. The micrographs of the reduced (pretreated) 100 Fe/0.3 Cu/0.8 K catalyst samples are shown in Figures III-1.13 and III-1.14. The particle size ranges obtained by TEM are summarized in Table III-1.1. After reduction with H₂, the particles exhibited a broader size range (Figure III-1.13). It should be noted that the large particles observed in these micrographs may in fact be aggregates of smaller particles. Generally, an average particle size can be determined from the electron micrographs only after careful statistical procedure and multiple sampling. In this case a precise estimation of average particle size was not obtained due to a broad distribution of particle sizes observed in these micrographs. In general, however, the particle size seems to have increased after reduction with H₂. In particular, after pretreatment with H₂ at 250°C, the particle size has increased significantly. Particles as large as 64 nm could be observed (Figure III-1.13b). The morphology, however, still remained essentially spherical. After pretreatment with H₂ at 280°C a similar increase in particle size was observed. This is consistent with the XRD results wherein a similar increase in the particle size was observed. As stated earlier, the increase in the particle size after H₂ reduction is probably due to the

Figure III-1.12 TEM micrographs of calcined 100 Fe/0.3 Cu/0.8 K catalyst at different magnifications: a) 108,000 X; b) 140,000 X.

Figure III-1.13 TEM micrographs of 100 Fe/0.3 Cu/0.8 K catalyst samples after pretreatments with H_2 at: a) 220 °C for 8 h (flow rate = 3550 cc/min); b) 250 °C for 2 h (flow rate = 3550 cc/min); c) 280°C for 8 h (flow rate = 85 cc/min).

collapse of the highly porous Fe_2O_3 network. This behavior is also consistent with the observed decrease in the surface area on reduction.

Figure III-1.14 shows TEM micrographs after pretreatment with CO and syngas. The estimated particle sizes are listed in Table III-1.1. After CO or syngas pretreatment, the TEM micrographs indicate the presence of aggregates of small particles (10 nm) as well as those of large particles (>25 nm). The morphology of the catalyst remained largely spherical after CO or syngas pretreatment.

TEM micrograph of the used catalyst sample, reduced with H_2 at 250°C , is shown in Figure III-1.15. Both large (> 80 nm) and small (3-10 nm) particles were detected in this catalyst sample. Although some large particles may be aggregates of smaller particles, individual particles with sizes greater than 50 nm can be clearly distinguished. It is interesting to note that small particles are present after the FT synthesis reaction, even though large Fe or Fe_3O_4 particles were observed after H_2 reduction. The smaller particles were essentially spherical. However, the larger particles were either plate like (hexagonal) or needle shaped.

A comparison of the particle size determined by XRD and by TEM indicates that XRD underestimates the average particle size. Similar observations were made wherein the particles sizes (even single crystals) determined by XRD were smaller than those determined by TEM (Butt, 1990). This was attributed to the presence of faults (imperfections) in these particles. Imperfections cause the particle to diffract more or less like two (or many) smaller particles. Also, care should be taken when interpreting TEM data. The large particles may in fact be aggregates of smaller particles. The presence of carbonaceous deposits may also mask the original particle size. There have been hypotheses that a carbon overlayer (or filamentous carbon) is generally formed during FTS (Tungate and Davis, 1991; Vogt et al., 1987). Although this overlayer is believed to be porous, the particle size estimated from TEM may be overestimated. Such an overlayer can be seen in Figure III-1.15.

Figure III-1.14 TEM micrographs of 100 Fe/0.3 Cu/0.8 K catalyst samples after pretreatments with CO or syngas: a) CO (85 cc/min) at 280 °C for 8h; b) syngas ($H_2+CO=0.67$, 85 cc/min) at 280 °C for 8h; c) syngas ($H_2+CO=2.0$, 1,200 cc/min) at 310°C for 6h.

Figure III-1.15 TEM micrograph of 100 Fe/0.3 Cu/0.8 K catalyst after FT synthesis in the fixed bed reactor Run FB-0403.

III-1.3 Summary

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 NI/g-cat/h, H₂/CO = 0.67 for 140 - 200 h.

The BET surface area of the catalyst decreased from 190 m²/g to 130 m²/g after calcination in air at 300°C for 5 hours, and further to 21-47 m²/g after pretreatments in hydrogen, carbon monoxide or syngas. The pore volume decreased upon pretreatments in H₂ 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 H₂ 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 H₂ reductions both by TEM and XRD analysis. The particle size increased with reduction temperature (e.g. 19 nm after H₂ 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 -Fe₂O₃ (~ 16 nm in diameter), which is converted to either metallic iron (α -Fe) or a mixture of α -Fe and Fe₃O₄ (magnetite) after H₂ reductions. During FT synthesis the α -Fe is carburized to iron carbides (χ -Fe₅C₂ 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 -Fe₅C₂ 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 -Fe₅C₂ carbide is the most dominant phase. During FT synthesis this carbide is partially or completely converted to ϵ' -Fe_{2.2}C carbide, Fe₃O₄, and/or FeCO₃ (siderite). Again it was found that the iron carbides are dominant in samples from the top part of the reactor (reducing atmosphere), whereas Fe₃O₄ or FeCO₃ are dominant iron phases in samples from the bottom part.

Temporal release of reduction products (water or carbon dioxide) was monitored continuously during H₂ 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 Fe₂O₃ to Fe₃O₄, which is followed by reduction of Fe₃O₄ to either metallic iron (H₂ reduction) or to an iron carbide (CO pretreatment). The second step is a slow one, and the reduction is not complete (H₂ reduction). The amount of CO₂ 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.

III-1.4 References

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III-2 Pretreatment Effect Research - Reaction Studies with 100 Fe/0.3 Cu/0.8 K Catalyst

In this section we report our studies on pretreatment effect using a precipitated, unsupported iron catalyst with nominal composition 100 Fe/0.3 Cu/0.8 K in parts per weight. Pretreatment parameters investigated were: gas composition, temperature, duration and flowrate. Five pretreatment procedures were used to study their effect on subsequent catalyst performance in a fixed bed reactor. Two additional tests were carried out in a stirred tank slurry phase reactor. Test identifications and pretreatment conditions are listed in Table III-2.1.

Table III-2.1 Pretreatment Conditions and Test Designations

Test (ID)	Temp. (°C)	Reductant	Duration (h)	Pressure (MPa)	Flowrate (cm ³ /min)
FB-0403	250	H ₂	2	0.1	4,000
FB-3221	280	H ₂	8	0.1	175
FB-0352	280	H ₂ /CO=0.7	8	0.1	150
FB-0942	310	H ₂ /CO=2.0	6	0.1	1,200
FB-0021	280	CO	8	0.1	175
SA-0791	250	H ₂	2	0.8	7,500
SB-2262*	280	H ₂ /CO=0.7	12	0.8	343

FB = Fixed bed reactor test; SA, SB = Slurry phase reactor test;

* Different catalyst batch used in this test

III-2.1 Experimental Procedure

In fixed bed reactor tests, about 3.0 to 3.5 g of calcined catalyst was diluted 1:8 by volume with glass beads of the same size range (32/60 mesh) and loaded into the reactor. Helium was fed through the reactor at a gas space velocity of 3.0 NI/g-cat/h during heating-up. For the pretreatments using hydrogen, hydrogen was introduced to the reactor at a temperature about 10 °C below the desired pretreatment temperature, whereas for the pretreatments using CO or syngas, the activation gas was introduced usually at 20 - 30°C below the desired temperature. Such precaution is needed to prevent a temperature runaway. Following the catalyst pretreatment, flow was switched to helium and the reactor temperature was decreased to 190-200°C. The reactor system was then pressurized to 1.48 MPa (200 psig), the helium flow was stopped, and synthesis gas ($H_2/CO = 0.67$) was introduced at gas space velocity of 2.0 NI/g-cat/h (2.9 NI/g-Fe/h). The reactor temperature was then increased to 250°C according to a time-temperature schedule shown in Table III-2.2 (conditioning period). A gradual increase in reaction temperature was used to prevent development of hot spots within the reactor. After achieving desired process conditions of 250°C, 1.48 MPa, 2.0 NI/g-cat/h and $H_2/CO = 0.67$, the catalyst was tested over a period of 100 to 150 h, during which two or three mass balances were made at approximately 70, 90 and 140 h on stream (including 30 h conditioning period). Tail (exit) gas was analyzed frequently during the entire test. Detailed description of our fixed bed reactors, product analysis system and operating procedures is provided in Appendix A.

III-2.2 Results

Activity and Stability

Catalyst activity, measured by volumetric gas contraction, as a function of temperature and time during the conditioning period is shown in Figure III-2.1. Volumetric contraction, defined as $100 \times (\text{inlet flowrate} - \text{outlet flowrate}) / \text{inlet flowrate}$,

Table III-2.2 Start-up/Temperature Schedule Used during Conditioning Period following Catalyst Pretreatment

Time on stream, h	Temperature, °C	Duration, h
	reduction - 190	1
0	190 - 200	1
1	200	1
2	200 - 210	1
3	210	2
5	210 - 220	1
6	220	3
9	220-230	1
10	230	12
22	230-240	1
23	240	4
27	240-250	2

is a convenient measure of catalyst activity, since it changes nearly linearly with syngas (H_2+CO) conversion. It can be seen that the gas contraction increases with temperature and reaches different values at the end of the conditioning period. Results during the conditioning period are indicative of initial catalyst activity. During the first ten hours on stream the data are scarce and erratic due to non uniformity of reactor temperature and fluctuations in outlet gas flow rate. At temperatures of 230 °C and above (10 - 30 h on stream) the activity of hydrogen reduced catalysts was lower than that of the CO or syngas pretreated catalysts. Hydrogen reduction at 280 °C resulted in the lowest gas contraction (catalyst activity).

Figure III-2.1 Volumetric contraction during conditioning period.

Catalyst activity and stability, at the process conditions, as a function of time-on-stream (TOS) is shown in Figure III-2.2. The activity is represented by (H₂+CO) conversion (defined as mole of syngas consumed per mole of syngas fed). The catalyst exhibited similar activity behavior after pretreatments with carbon monoxide (280°C for 8 h) or syngas (both H₂/CO = 0.7 at 280°C for 8 h and H₂/CO = 2.0 at 310°C for 6 h). Initial (H₂+CO) conversion was between 85 and 93%. However, the catalyst deactivated with time-on-stream, following a similar time-dependent behavior in all three cases. The (H₂+CO) conversion decreased to about 55 % at 150 h on stream.

Catalyst activity after reduction with hydrogen was clearly dependent on the reduction conditions employed (temperature, duration and flowrate). After reduction at 250°C, flowrate 4000 cc/min (which corresponds to a linear gas velocity of 150 cm/s) for 2 h, the initial (H₂+CO) conversion was 77 %; whereas after reduction at higher temperature of 280°C, flowrate 175 cc/min (which corresponds to a gas space velocity of 3.0 NI/g-cat/h) for 8 h the (H₂+CO) conversion was only about 50 %. During the FT synthesis, the (H₂+CO) conversion increased steadily with time reaching 85 and 58 %, respectively. Such time-dependent behavior is in contrast to that observed following CO or syngas pretreatment.

Water gas shift (WGS) activity of the catalyst is related to H₂ to CO usage ratio (UR), and partial pressure quotient ($K_p = P_{CO_2} P_{H_2} / P_{CO} P_{H_2O}$). Lower values of the usage ratio, or higher values of the K_p imply higher WGS activity. In both tests, after hydrogen reduction, the usage ratios were similar, about 0.60-0.61, and stable with time on stream (Table III-2.3). For the catalyst pretreated with CO and H₂/CO = 2, the usage ratio was 0.61 - 0.64, whereas for the catalyst pretreated with syngas H₂/CO = 0.7 the usage ratio was 0.59. In the latter three cases, even though the overall catalyst activity decreased continuously, the usage ratio did not change with time. Hydrogen reduced catalyst had higher K_p values, than either CO or syngas pretreated catalyst. In

Figure III-2.2 Effect of pretreatment conditions on conversion and catalyst stability.

Table III-2.3. Summary of Results for Pretreatment Effect Study with 100 Fe/0.3 Cu/0.8 K Catalyst - Fixed Bed Reactor Tests

Test designation	FB-0403		FB-3221		FB-0352		FB-0942		FB-0021	
Time-on-stream, h	67	116	72	149	72	144	62	134	68	92
CO conversion, %	86.4	89.5	56.0	61.0	76.8	59.7	72.8	57.9	73.0	70.1
(H ₂ +CO) conversion, %	81.4	84.3	54.1	58.2	70.7	55.7	70.7	56.6	70.0	67.6
STY, mmol/g-cat/h	73	75	48	52	63	50	63	50	63	60
k, mmol/g-Fe/h/MPa ^a	218	229	134	142	177	134	190	142	180	171
(H ₂ /CO) usage ratio	0.61	0.61	0.60	0.60	0.59	0.59	0.64	0.64	0.61	0.61
(H ₂ /CO) exit ratio	1.30	1.54	0.74	0.80	1.18	0.86	0.79	0.74	0.82	0.81
$K_p = P_{CO_2}P_{H_2}/P_{CO}P_{H_2O}$	77.0	78.1	46.1	48.0	20.0	17.8	5.60	4.10	18.0	15.0
mmol CH ₄ /g-Fe/h	2.44	2.44	1.23	1.35	1.11	1.00	1.21	1.00	1.00	0.89
Hydrocarbon selectivity, wt%										
CH ₄	9.1	8.4	6.8	6.8	4.3	5.0	4.4	4.8	3.1	3.7
C ₂ -C ₄	26.5	24.4	23.0	22.4	18.6	20.6	18.8	19.5	18.1	18.2
C ₅ -C ₁₁	41.3	41.7	37.8	30.2	23.1	24.0	24.6	24.0	23.5	22.5
C ₁₂ +	23.1	25.5	32.4	40.6	54.0	50.4	52.2	51.7	55.3	55.5
Chain growth parameter, α_{1-10} ^b	0.73	0.75	0.72	0.70	0.72	0.70	0.75	0.73	0.77	0.75
Olefin content, wt%										
C ₂ -C ₄	75.2	73.2	77.3	76.3	79.8	78.0	81.3	80.2	81.3	81.5
C ₅ -C ₁₁	73.0	72.7	70.9	71.8	85.2	84.6	86.1	85.6	80.6	82.1

Process conditions: 250°C, 1.48 MPa (200 psig), 2.0 NI/g-cat/h, H₂/CO=0.67

^a Apparent reaction rate constant for a first order reaction in hydrogen, based on measured usage ratio.

^b Parameter estimated from products in the carbon number range C₁ - C₁₀.

general, the pretreatment procedure had small effect on WGS activity under the conditions studied.

Selectivity

Hydrocarbon product distribution and the fraction of olefins in hydrocarbons obtained during two mass balances for each of the five pretreatment procedures are given in Table III-2.3. Hydrocarbon selectivity remained relatively stable in tests in which hydrogen reductions were employed. After CO or syngas pretreatment, hydrocarbon selectivity usually shifted towards lower molecular weight hydrocarbons, especially methane, as the catalyst deactivated with time. For example, methane selectivity gradually increased from 4.3 to 5.0 wt % between 70 to 150 h on stream in test FB-0352 (i.e. the increase of about 16 %). However, such changes with time on stream for a given pretreatment procedure were small in comparison to more profound differences in selectivity resulted from the use of different pretreatment procedures. Therefore, the average values from two and/or three balances (not shown in Table III-2.3) were used to compare the effect of pretreatment procedures on selectivity.

Figure III-2.3 compares hydrocarbon product selectivity, lumped into four groups of products C_1 (methane), C_2-C_4 (light gases), C_5-C_{11} (gasoline fraction), and $C_{12}+$ (diesel fuel and hydrocarbon wax). Low methane and gaseous hydrocarbon selectivities, and high $C_{12}+$ selectivities were obtained when CO and/or syngas pretreatments were employed. CO pretreated catalyst had the lowest methane selectivity, less than 4 %. On the other hand, hydrogen reduced catalyst produced more methane and other low molecular weight products. The highest methane selectivity, about 9 %, was obtained following reduction with H_2 at $250^\circ C$.

Rate of methane formation as a function of time on stream for different pretreatment procedures is shown in Figure III-2.4. The catalyst pretreated with CO or syngas produces significantly less methane than the one reduced with hydrogen at

Figure III-2.3 Effect of pretreatment conditions on hydrocarbon product distribution.

Figure III-2.4 Methane formation rate vs. time on stream following different pretreatment conditions.

250°C. The methane formation rate of the catalyst reduced by hydrogen at 280°C was much lower than that obtained following hydrogen reduction at 250 °C, and slightly higher than those obtained following CO or syngas pretreatment. It is interesting to note that methane formation rate per gram of iron in the catalyst decreases with time for CO and syngas pretreatments, but methane selectivity (expressed as weight percent of methane in hydrocarbons) increases with time (Table III-2.3). These opposite, and seemingly contradictory trends, are due to catalyst deactivation. In this case the rates of production of other hydrocarbons also decrease with time, but at a faster rate than the rate of methane formation, and as a result the methane selectivity increases with time. The opposite trend is observed with the catalyst after hydrogen reduction at 250°C, where methane production rate increases with TOS (Figure III-2.4), but the methane selectivity decreases with time (Table III-2.3). In this case the rate of FT synthesis, and rates of production of other hydrocarbons also increase with time but at the faster rate than the methane production. Similar trends were observed for the rate of formation of light gases, but are not shown here.

Primary products of Fischer-Tropsch synthesis are 1-olefins, which are converted to paraffins and 2-olefins via secondary reactions. The olefin content, defined as $100 \times \text{olefin} / (\text{olefin} + \text{paraffin})$, is a measure of hydrogenation activity. Weight percent olefin content in C₂-C₄, and C₅-C₁₁ hydrocarbons is given in Table III-2.3, whereas its variation with carbon number (up to C₁₅) is illustrated in Figure III-2.5. For each pretreatment the ethene content is always low, since it readsorbs and undergoes secondary hydrogenation more readily than other low molecular weight olefins. The olefin content has a maximum at C₃, and then decreases with carbon number. The olefin contents are generally lower after hydrogen reductions than after CO or syngas pretreatments (Figure III-2.5). These results are not due to differences in conversions. The two hydrogen reductions resulted in nearly the same olefin

Figure III-2.5 Effect of pretreatment conditions on olefin selectivity.

selectivities, in spite of differences in conversions (Figure III-2.2). Also for CO and syngas reductions, the olefin selectivity did not vary with time on stream, in spite of catalyst deactivation.

Ratio of 2-olefin/(1+2) olefins is indicative of olefin isomerization activity. This ratio usually increases with carbon number, especially for hydrocarbons in the liquid phase (C₈+). The 2-olefin content is higher after H₂ reductions, and is the lowest after the CO pretreatment (Figure III-2.6). In general, the 2-olefin selectivity (i.e. 1-olefin isomerization activity) is low for this catalyst, which is due to its relatively high potassium content.

Carbon number product distributions, after two pretreatment procedures, are shown in Figure III-2.7 in the form of Anderson-Schulz-Flory (ASF) plots (mole fraction vs. carbon number). It can be seen that mole fractions of high molecular weight products are significantly smaller on the catalyst reduced with hydrogen. It was found that whenever all products collected were analyzed, including those in the high-pressure trap, two chain growth probabilities were needed to characterize the product distribution. A three parameter model of Huff and Satterfield (1984) was found to adequately represent these data:

$$x_n = (1 - \alpha_1) \alpha_1^{n-1} + (1 - \beta)(1 - \alpha_2) \alpha_2^{n-1}$$

where x_n is the mole fraction of products containing n carbon number atoms (hydrocarbons and oxygenates), β is the fraction of type 1 sites on the catalyst, and α_1 and α_2 are the chain growth probabilities associated with the type 1 and type 2 sites, respectively. The model parameters were estimated by a nonlinear regression, and their numerical values for all pretreatment procedures are summarized in Table III-2.4 together with 95% confidence interval limits for these parameters.

Figure III-2.6 Effect of pretreatment conditions on 2-olefin selectivity.

Figure III-2.7 Anderson-Schultz-Flory distribution for selected pretreatment conditions. a) Run FB-0403; b) Run FB-0352

Table III-2.4 Chain Growth Probability Factors for Different Pretreatment Procedures^a

Test	TOS, h	α_1 (95% CI) ^b	α_2 (95% CI) ^b	β (95% CI) ^b
FB-0403	67	0.74 (0.73-0.75)	0.88 (0.87-0.90)	0.98 (0.97-0.99)
FB-3221	120	0.61 (0.57-0.65)	0.86 (0.85-0.87)	0.75 (0.71-0.79)
FB-0352	72	0.63 (0.61-0.65)	0.92 (0.91-0.93)	0.73 (0.71-0.75)
FB-0942	62	0.68 (0.67-0.69)	0.92 (0.91-0.93)	0.77 (0.76-0.78)
FB-0021	88	0.68 (0.64-0.72)	0.90 (0.89-0.91)	0.74 (0.69-0.79)

^a Parameters estimated from products with carbon number in the range C₁-C₄₀.

^b 95% confidence interval.

III-2.3 Discussion

Five different pretreatment procedures were employed in the present study, and their effects on catalyst activity, stability and selectivity during the Fischer-Tropsch synthesis may be summarized as follows: (1) After CO or syngas pretreatments, the catalyst achieved high initial activity, which then decreased with time on stream. The catalyst behavior with time-on-stream, and product selectivities were similar after CO and syngas pretreatments. Initial activities of CO and syngas pretreated catalysts were higher than those of hydrogen reduced catalysts. (2) After H₂ reductions, catalyst activity was stable or gradually increased with time on stream. Activity of the catalyst reduced at 250°C for 2 h was significantly higher than that of the catalyst reduced at 280°C for 8 h. (3) CO and syngas activations favored production of higher molecular weight and more olefinic hydrocarbons, in comparison to H₂ reductions. (4) Olefin isomerization activity was low for all pretreatments, but relatively higher after hydrogen reductions. (5) Water gas shift activity was high, and did not vary markedly with pretreatment conditions.

The first three observations listed above are in agreement with our results from the study with a precipitated iron catalyst of nominal composition 100 Fe/3 Cu/0.2 K (Bukur et al., 1989a). A possible explanation for these observations is based on the fact that catalysts achieve different bulk structures after different pretreatment procedures, and in turn these structure differences affect CO and H₂ activation (chemisorption) during synthesis. Differences in bulk structures and surface concentrations of reactants result in different activity as well as selectivity trends.

After the pretreatment with CO or syngas, the dominant phase is the Hägg carbide. Surface areas and pore volumes of the catalyst were similar, too. During the subsequent FT synthesis reaction, the catalyst activity, and selectivity were also similar. This represents a strong correlation between the catalytic behavior and the structural properties of the catalyst after the pretreatment. Decline in catalyst activity may be attributed to conversion of Hägg carbide (the most active phase) to inactive (or less active) phases such as magnetite and/or siderite. An alternative explanation for the catalyst deactivation with time, due to blocking of active sites by carbonaceous deposits, is provided below.

In FT synthesis, carbon monoxide undergoes dissociative adsorption (chemisorption) on the catalyst surface, forming a highly active species (Krebs and Bonzel, 1980; Ponec, 1982). The reactions of this surface carbon, C_s^{*}, proceed competitively with iron and hydrogen, or with itself, leading to: (1) formation of surface metal carbide, and then bulk carbide by carbon diffusion; or (2) hydrogenation to methyl species (synthesis of hydrocarbons); and (3) formation of inactive carbon. (Niemantsverdriet and van der Kraan, 1981). The competition depends on the concentration of hydrogen on the catalyst surface (Machocki, 1991).

The initial activity over carbided catalyst (CO or syngas pretreatment) is high, as shown in Figures III-2.1 and III-2.2. This indicates that the concentration of the surface carbon (formed from the synthesis gas) is high initially, and the dominant reaction is

hydrogenation to form hydrocarbons since the bulk of the catalyst has been already carbided. High synthesis rate implies that consumption of the surface hydrogen species is also high and on the surface of carbided catalyst, the abundant species is carbon rather than hydrogen. As a consequence of this, the rate of removal of surface carbon by hydrogenation is lower than the rate of CO dissociation. Then some of the C_s^* forms carbonaceous deposit, which eventually converts to inactive (graphitic) carbon. This inactive carbon can further block hydrogen chemisorption sites, lowering surface hydrogen concentration and leading to decrease in the rate of FT synthesis, i.e. catalyst deactivation. The formation of inactive carbon deposits on the surface of iron based FT catalysts is considered to be the major cause of catalyst deactivation (e.g., Krebs et al., 1979; Niemantsverdriet et al., 1980; Dwyer and Handenbergh, 1984).

The observation that the CO or syngas activated catalyst has higher initial activity than H_2 reduced catalyst is consistent with the competition model of Niemantsverdriet and van der Kraan (1981). During FT synthesis with H_2 reduced catalyst some of the active surface carbon is consumed to form bulk carbides, and thus the rate of FT synthesis is initially lower relative to the precarbided catalyst. In terms of bulk iron phases present after different pretreatments, these results could be interpreted as to imply that Hägg carbide is more active for FT synthesis than the metallic iron and/or magnetite.

Two different reduction procedures with H_2 were employed and they led to different degrees of catalyst reduction and different levels of stable catalyst activity. After reduction at 250°C , 4000 cc/min for 2h the catalyst was completely reduced to metallic iron and was very active in the subsequent synthesis. After reduction at higher temperature (280°C , 175 cc/min for 8h) the reduction was incomplete (mostly magnetite) and the catalyst activity was much lower. It is known that water vapor inhibits the reduction of iron oxides in H_2 . High flowrate of H_2 during reduction

decreases the water vapor pressure and facilitates the reduction. Surface area of the calcined catalyst was 130 m²/g, after H₂ reduction at 250°C and 280°C, it drops to only 21 m²/g in both cases, which indicates that sintering of Fe₂O₃ particles to Fe or Fe₃O₄, though very severe, is similar at two temperatures. Therefore, the difference in catalyst activity is mainly related to the initial degree of iron reduction. Completely reduced catalyst is more active for FT synthesis. Used catalyst samples contain two types of iron carbides (χ and ϵ'), and superparamagnetic oxides/hydroxides (probably magnetite, based on XRD results). The more active catalyst (H₂ reduction at 250°C) also has some α -Fe (Table III-1.5), whereas the less active catalyst does not contain metallic iron.

Another explanation for the observed differences in catalyst activity has been proposed by Sault (1991), on the basis of surface composition measurements by Auger Electron Spectroscopy. This study was conducted at Sandia National Laboratory using a catalyst synthesized in our Laboratory with nominal composition 100 Fe/3 Cu/0.2 K. In this study it was found that H₂ reductions are accompanied by sulfur migration to the surface of the catalyst. The sulfur arises from bulk sulfate impurities present in the metal nitrates used to prepare the catalyst. Sulfur coverage increases with both activation time and temperature, due to an increase in the rate of sulfur diffusion with temperature. Since sulfur is known to act as a poison for FT synthesis, the catalyst reduced at higher temperature and/or longer duration is expected to have lower FT activity, which is indeed observed in our studies with both 100 Fe/3 Cu/0.2 K and 100 Fe/0.3 Cu/0.8 K catalysts.

Catalyst stability with time-on-stream after hydrogen reductions, and the observed differences in product distributions resulting from the use of different reductants can be explained in terms of differences in surface concentrations of active carbon and hydrogen species.

When a catalyst reduced by hydrogen is exposed to a synthesis gas, the surface carbon species is formed which diffuses into the bulk to form bulk iron carbides. However, the catalyst can maintain a stable activity over a long period of time, in contrast to the precarbided catalyst (after CO or syngas pretreatment). A possible explanation for this observation is that concentration of surface hydrogen during the synthesis plays an important role in stabilizing the catalyst activity. We postulate that the hydrogen concentration on the surface is higher on an H₂ reduced catalyst than on a fully carbided catalyst following CO or syngas pretreatment. This could be due to a larger number of sites available for H₂ adsorption, or due to differences in strength of sites for hydrogen adsorption. Metallic iron (hydrogen reduced catalyst) is known to promote dissociative adsorption of hydrogen. When the concentration of surface hydrogen is sufficiently high the rate of removal of surface carbon through hydrogenation is higher than or equal to the rate of CO dissociation. In other words, the rates of surface carbon formation and removal are properly balanced, and the formation of carbonaceous, or inactive carbon, deposits is prevented or limited. Consequently, the catalyst does not deactivate, and its activity may increase as a result of continued creation of active sites.

Differences in selectivity obtained after H₂ and CO or syngas pretreatments may be due to differences in surface hydrogen concentrations during the FT synthesis. For example, the olefin contents in hydrocarbons were lower after H₂ reductions (Figure III-2.5). This is consistent with the assumption that the surface hydrogen concentration is higher on H₂ reduced than on CO or syngas reduced catalysts. Higher hydrogen concentration enhances hydrogenation of olefins. Similarly, higher methane selectivity and shorter chain length hydrocarbons (Figure III-2.3) obtained with H₂ reduced catalysts are the consequence of higher surface hydrogen concentration, since it favors methanation and chain termination reactions.

It was found that the use of different pretreatment procedures did not have marked effect on secondary olefin isomerization and water-gas-shift reactions. This may be attributed to relatively high potassium content of the catalyst used in the present study. Potassium is known to promote the rate of WGS reaction (Anderson et al., 1952; Arakawa and Bell, 1983; Bukur et al., 1990a), and to suppress the olefin isomerization (Dictor and Bell, 1986; Herzog and Gaube, 1989; Bukur et al., 1990a). Thus the catalyst behavior was largely determined by its potassium content rather than by differences arising from the use of different pretreatment procedures.

III-2.4 Stirred Tank Slurry Reactor Tests

The study in slurry phase was conducted in an one liter stirred tank reactor (Autoclave Engineers). Catalyst was sieved through 270 mesh (53 μm) and was placed in the reactor containing n-octacosane as the initial medium. There was no conditioning period, and process conditions were achieved in 1 h after a pretreatment. A detailed description of the slurry phase reactor system used in this study is given in Appendix A.

Two tests were conducted in the slurry reactor in order to determine whether the trends found in fixed bed reactor tests remain the same during FT synthesis in slurry phase. After reduction with H_2 at 250°C, 0.8 MPa and a flowrate of 7,500 cc/min for 2 h (SA-0791), the catalyst activity was stable during 250 h of testing at 260°C, 1.48 MPa, 2 NI/g-cat/h and $\text{H}_2/\text{CO} = 0.67$, and the syngas ($\text{H}_2 + \text{CO}$) conversion was about 80 % (Figure III-2.8). The usage ratio was about 0.60, and the partial pressure quotient for WGS reaction was greater than 30 (The equilibrium value of the reaction quotient at 250°C is 83.6). Both of these measures are indicative of high WGS activity. Hydrocarbon product distribution shifted gradually towards lower molecular weight products with time on stream, as indicated in Table III-2.5. Selectivities of methane and

Figure III-2.8 Effect of pretreatment procedures on conversion and catalyst stability in slurry reactor tests.

Table III.2-5 Summary of Slurry Reactor Test Results for Pretreatment Effect Study with 100 Fe/0.3 Cu/0.8 K Catalyst

Test designation	SA-0791					SB-2262				
Temperature, °C	260	260	260	260	260	250	260	260	260	260 ^a
Pressure, MPa	1.48	1.48	1.48	1.48	1.48	1.48	1.48	1.48	1.48	1.48
SV, NI/g-cat/h	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Time-on-stream, h	39	111	159	266	278	44	92	140	212	268
CO conversion, %	86.1	86.8	86.6	82.4	79.0	30.0	32.8	29.8	38.8	39.4
(H ₂ +CO) conversion, %	81.8	82.6	82.4	78.7	75.3	28.7	31.3	28.2	36.7	37.3
STY, mmol/g-cat/h	72.7	73.5	73.0	69.5	60.3	26.1	28.0	25.0	33.2	33.1
k, mmol/g-Fe/h/MPa	347	365	362	326	286	68.6	77.0	67.6	93.0	94.5
(H ₂ /CO) usage ratio	0.60	0.60	0.60	0.61	0.61	0.61	0.60	0.58	0.57	0.58
(H ₂ /CO) exit ratio	1.20	1.22	1.22	1.04	0.98	0.71	0.72	0.72	0.73	0.72
$K_P = P_{CO_2} P_{H_2} / P_{CO} P_{H_2O}$	33.2	42.2	38.5	39.6	80.6	26.0	10.4	9.48	12.7	12.8
mmol CH ₄ /g-Fe/h	1.66	1.86	1.88	1.88	1.86	0.64	0.85	0.84	0.90	1.02
Hydrocarbon selectivity, wt%										
CH ₄	5.5	6.0	6.5	6.8	7.2	6.2	7.4	8.2	7.0	7.4
C ₂ -C ₄	19.0	21.3	23.1	24.0	25.9	15.6	19.9	23.3	20.5	18.2
C ₅ -C ₁₁	30.0	38.5	38.4	41.0	40.6	14.5	14.8	17.3	15.3	14.0
C ₁₂ +	45.5	34.2	32.0	28.2	26.3	63.7	57.9	51.2	57.2	60.4
Chain growth parameter, α_{1-10}^b	0.76	0.76	0.76	0.75	0.75	0.70	0.69	0.63	0.61	0.61
Olefin content, wt%										
C ₂ -C ₄	75.2	74.1	73.2	70.5	69.7	80.1	79.3	79.7	81.4	79.5
C ₅ -C ₁₁	73.5	73.2	73.5	72.8	73.1	74.7	76.4	76.6	78.5	79.2

H₂/CO=0.67 for all tests. ^a: Following H₂ regeneration. ^b: Parameter estimated from products with carbon number in the range C₁-C₁₀.

gaseous hydrocarbons ($C_2 - C_4$) varied between 5.5 - 6.5 and 19 - 23 wt%, respectively. The olefin selectivity was stable with time (Figure III-2.9a), whereas the 2-olefin selectivity increased steadily with time (Figure III-2.10).

Catalyst from a different batch of preparation was used in the second slurry phase test designated SB-2262. After pretreatment with syngas ($H_2/CO = 0.67$) at $280^\circ C$, 1.16 MPa (155 psig), 2.0 NI/g-Fe/h for 12 h, during the first 80 h on stream the catalyst was tested at $250^\circ C$, 1.48 MPa, and 2 NI/g-cat/h with $H_2/CO = 0.67$. (The same baseline process conditions as used in fixed bed reactor tests). The catalyst deactivated rapidly with time on stream (Figure III-2.8). (H_2+CO) conversion decreased from initial value of 49 % to 28 %, during the first 60 h of testing. Reaction temperature was then increased to $260^\circ C$, which was accompanied by increase in conversion followed by continued, but slower, deactivation. The catalyst was regenerated with H_2 at $260^\circ C$, 1.48 MPa, 5,000 cc/min for 4 h at about 162 h on stream, and again using more severe reduction conditions of $280^\circ C$ for 12 h at 224 h. Temporary improvements in catalyst activity were observed after each of these two regenerations, followed by deactivation. The syngas conversion after the second regeneration was about 37 % shortly before the test was terminated at 300 h on stream. WGS activity of the catalyst was high throughout the test. The usage ratio varied between 0.58 and 0.60, and the reaction quotient between 9.5 and 26. Methane selectivity was 6.2 wt % at $250^\circ C$, and it increased to 7.3 - 8.2 % during testing at $260^\circ C$ before the regeneration (80 - 140 h on stream). Hydrocarbon product distributions at $260^\circ C$ were similar before (92 h on stream) and after hydrogen regenerations (268 h) , as can be seen from Table III-2.5. The olefin selectivity was also stable as shown in Figure III-2.9, despite catalyst deactivation with time. The 2-olefin selectivity was low (4-12%) and did not vary much with time on stream.

Figure III-2.9 Effect of time on stream on olefin selectivity in slurry reactor tests.

a) Run SA-0791; b) Run SB-2262

Figure III-2.10 Variation of 2-olefin selectivity with time on stream after H₂ reduction (Run SA-0791).

III-2.5 Comparison between FBR and STSR Tests

The effect of the nature of the pretreatment gas on the catalyst stability was qualitatively the same in both the fixed bed and slurry bed reactors. After hydrogen reduction at 250°C for 2 h in tests FB-0403 and SA-0791, the catalyst activity remained stable with time on stream, whereas following pretreatment with $H_2/CO = 0.67$ at 280°C in tests FB-0352 and SB-2262, the catalyst deactivated in both type of reactors (Figures III-2.2 and III-2.8). However, the rate of deactivation was faster and the catalyst activity lower in the STSR (Run SB-2262) than in the FBR (Run FB-0352).

Comparisons of catalyst activities in terms of $(H_2 + CO)$ conversion or reactor space-time-yields (STY) are not meaningful when the reaction conditions are not the same and/or when the experiments are done in different types of reactors. In such cases an apparent reaction rate constant provides a better basis for comparison of catalyst activity. In this study the apparent reaction rate constant was calculated assuming that the reaction rate has a first-order dependence on hydrogen partial pressure and its units are : mmol $(H_2 + CO)$ converted/h/g-Fe/MPa of H_2 . In the STSR the STY is proportional to the rate of FTS reaction, and the apparent rate constant is obtained by dividing STY with the partial pressure of hydrogen at the reactor exit. On the other hand, in the FBR the reaction rate varies with position along the reactor and estimation of the apparent rate constant is not so straightforward. In this case, the rate constants were estimated using a procedure described by Zimmerman et al. (1989). Calculated values are listed in Table III-2.3 (FBR tests) and Table III-2.5 (STSR tests). Data obtained at 260°C (STSR) were converted to 250°C by using the activation energy of 90 kJ/mol, which is typical for FTS over iron catalysts (Zimmerman and Bukur, 1990). The average values of the apparent rate constants for H_2 reductions in FBR and STSR reactors are: 233 and 247 (mmol/h/g-Fe/MPa), respectively. This indicates that the intrinsic catalyst activity is nearly the same in both types of reactors.

With syngas pretreated catalysts the corresponding values were: 134 - 177 (FBR), and 46 - 68 mmol/h/g-Fe/MPa (STSR). The intrinsic catalyst activity was lower in the STSR than in the FBR, which is probably due to the use of catalysts from two different batches and differences in the pretreatment procedures (duration and reductant flow rate per gram of Fe in the catalyst).

Hydrocarbon selectivities (average values from several mass balances) are compared in Figure III-2.11. Reaction temperature in the fixed bed tests was 250°C, but mostly 260°C in the slurry reactor tests. Higher temperature is known to favor the formation of methane and lower molecular weight hydrocarbons. The reactor type did not have a strong effect on hydrocarbon product distribution with syngas pretreated catalyst (tests FB-0352 and SB-2262), if the difference in reaction temperature is taken into account. However, when H₂ reduction was employed, methane selectivity in the slurry reactor (SA-0791) varied from 5.5 to 6.5 % (before operational incident), and was markedly lower than that in the fixed bed reactor (about 9%), even though the reaction temperature was 10°C higher in the STSR. This is probably due to a better temperature control in the STSR, and/or due to differences in the catalyst composition (iron phases) after the reduction.

The effects of pretreatment conditions and the reactor type on olefin selectivity are shown in Figure III-2.12. The average values from multiple mass balances are used in this comparison, since olefin selectivity generally does not change with time on stream. In both FBR and STSR, the olefin content was higher with syngas pretreated catalyst than with H₂ reduced catalyst. This indicates that higher hydrogenation activity of H₂ reduced catalyst is related to the catalyst structure determined by the pretreatment, but not to the reaction environment (conversion, reactor type, etc.). Hydrogenation activity was slightly higher in the slurry reactor than in the fixed bed reactor after the syngas pretreatments.

Figure III-2.11 Comparison of hydrocarbon selectivities in fixed bed and slurry reactor tests.

Figure III-2.12 Comparison of olefin selectivities in fixed bed and slurry reactor tests.

Figure III-2.13 Comparison of 2-olefin selectivities in fixed bed and slurry reactor tests.

The initial (first 100 h) 2-olefin selectivity was also independent of the reactor type, as illustrated in Figure III-2.13 for the two tests using H₂ reduction. The 2-olefin selectivity continually increased with time on stream during the slurry reactor test (Figure III-2.10), however, this was not observed in the corresponding fixed bed reactor test during 120 h of testing.

The above results show that the effects of pretreatment procedures on the catalyst performance were similar in both FBR and STSR. This is probably due to the fact that the change in surface structure of catalyst induced by different pretreatment procedures plays a more important role than the reaction environment (reactor type) in influencing the catalytic activity and selectivity.

III-2.6 Summary

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 H₂ reduced one.

III-2.7 References

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III-3 Pretreatment Effect Research - Characterization Studies of Ruhrchemie Catalyst

III-3.1 Experimental

A sample of commercial catalyst synthesized by Ruhrchemie, designated as LP 33/81, with nominal composition of 100 Fe/5 Cu/4.2 K/24 SiO₂ was obtained for this study. The catalyst was calcined in air at 300°C for 5 h prior to any pretreatment.

III-3.1.1 Catalyst Characterization Techniques

Experimental procedures for characterization of the Ruhrchemie catalyst by AA, XRD, BET/PSD, MES, and TEM techniques were similar to those described in Section III-1 of this report. In addition, temperature programmed/isothermal reduction and X-ray photoelectron spectroscopy (XPS) techniques were used to characterize the Ruhrchemie catalyst.

Temperature programmed (TPR) and isothermal reduction studies were performed using both 5% H₂/N₂ and 5% CO/He as reductants. The reactive gas streams were first directed at a constant rate and pressure through the reference compartment of a thermal conductivity detector (TCD) cell via a two-way injection valve, through the catalyst sample, and finally, via a cold trap, through the other compartment of the TCD. Consumption of the CO or H₂ was monitored by a change in the thermal conductivity of the effluent gas stream. A dry ice/acetone bath was used to remove water formed during hydrogen reductions, and a liquid nitrogen bath was used to remove CO₂ formed during the CO reductions. Catalyst sample weights of 10 to 15 milligrams and the reductant flow rates of 12 cc/min were used in all experiments. A temperature ramp of 20°C/min from room temperature to 900°C was used in all temperature-programmed reduction experiments. In isothermal reductions, a ramp of 20°C/min was used until a temperature of 300°C was reached, the latter temperature

then being maintained for either 12 h for H₂, or 8 h for CO reduction.

X-ray photoelectron spectroscopy (XPS) was used to study the surface compositions and oxidation states of iron catalysts following reduction in H₂ and CO. Samples used in the XPS measurements were pressed into thin wafers to fit the copper sample holder and the sample probe of the spectrometer. After either reduction, samples were evacuated for one hour and were transferred without exposure to air, to the antechamber of the glove box attached to the spectrometer. The antechamber was back filled with dry N₂ before transferring the sealed reactor into the main glove-box chamber for sample mounting on the instrument probe. Typical pressure in the XPS analysis chamber during measurement was 10⁻⁹ Torr. The monochromatic X-ray beam power was maintained at 600 W, and an electron flood gun was used to eliminate sample charging effects. The C1s peak at 284.6 eV, due to adventitious surface carbon, and the O 1s peak at 531.6 eV were used as internal references.

III-3.2 Results and Discussion

III-3.2.1 Atomic Absorption

The amounts of Fe, Cu, and K were determined by Atomic Absorption Spectroscopy using a standard procedure described in Section III-1 of this report. The amount of SiO₂ in the catalyst was estimated indirectly knowing the actual amounts of Fe, Cu, and K and by assuming that the elements were in the form of Fe₂O₃, CuO, and K₂CO₃. The amount of SiO₂ was calculated from the equation:

$$W_{\text{SiO}_2} = W_0 - W_{\text{Fe}} \cdot \frac{1}{2} \cdot \frac{\text{Fe}_2\text{O}_3}{\text{Fe}} - W_{\text{Cu}} \cdot \frac{\text{CuO}}{\text{Cu}} - W_{\text{K}} \cdot \frac{1}{2} \cdot \frac{\text{K}_2\text{CO}_3}{\text{K}}$$

$$= W_0 - 1.43 W_{\text{Fe}} - 1.25 W_{\text{Cu}} - 1.77 W_{\text{K}}$$

where: W_0 is the weight of the sample, and W_i 's are the weight of elements

determined by AA.

The composition of the catalyst was found to be 100 Fe/5.6 Cu/5.1 K/31 SiO₂. The catalyst composition was also determined at Sandia National Laboratories as 100 Fe/5 Cu/4 K/27 SiO₂ which is in reasonable agreement with our results, and is closer to the nominal catalyst composition.

III-3.2.2 X-ray Diffraction

As-Prepared and Calcined Catalyst

XRD patterns of the Ruhrchemie catalyst were obtained before and after calcination and are shown in Figure III-3.1. The as-prepared and the calcined catalyst exhibited broad Fe₂O₃ signals indicating that the catalyst was nearly amorphous in nature.

Reduced (Pretreated) Catalyst

The XRD patterns obtained after H₂ reduction are shown in Figure III-3.2. The Ruhrchemie catalyst, after reduction with H₂ at 220°C for 1 h, exhibited weak signals at $2\theta=35.4$ and 62.5° which correspond to Fe₃O₄ (Figure III-3.2a). Weak XRD signals seen in Figure III-3.2 are due to the presence of silica in the catalyst which is believed to be of amorphous nature. The particle size estimated from the corresponding slow scan using X-ray line broadening technique was 50 Å (Table III-3.1).

The XRD pattern obtained after reduction with H₂ at 280°C for 1 h is shown in Figure III-3.2b. In addition to Fe₃O₄, peaks corresponding to metallic Fe were identified. It should be noted that due to the amorphous silica background only the strongest peaks (maximum intensity) corresponding to Fe₃O₄ or Fe could be clearly observed. The particle size of Fe was estimated to be 80 Å. It can be seen that the particle size increased with an increase in reduction temperature. This increase in the particle size can be attributed to a partial collapse of the iron pore structure on reduction. Sintering of the iron particles is expected to be higher at higher reduction

Figure III-3.1 XRD patterns of Rurhchemie catalyst: a) as prepared; b) calcined in air at 300°C for 5h.

Figure III-3.2 XRD patterns of Ruhrchemie catalyst samples after pretreatment with H_2 at: a) 220°C for 1 h (flow rate = 3550 cc/min); b) 280°C for 1 h (flow rate = 3160 cc/min); c) 280°C for 8 h (flow rate = 125 cc/min).

Table III-3.1 Summary of XRD and TEM Results of Pretreated Ruhrchemie Catalyst Samples.

Run No.	Pretreatment Conditions	Phases Detected by XRD ^a	Average Particle Size Determined by XRD (Å)	Particle Size Range Determined by TEM (Å)
As prepared	None	Fe ₂ O ₃	--	--
Calcined	Air, 300°C, 5 h	Fe ₂ O ₃	--	35
FA-2351	H ₂ , 220°C, 1h, 3550 cc/min	Fe ₃ O ₄	50	35
FA-2391	H ₂ , 280°C, 1h, 3160 cc/min	Fe ₃ O ₄ , α-Fe	80 (α-Fe) ^b	--
FA-1821	H ₂ , 280°C, 8h, 125 cc/min	Fe ₃ O ₄ , α-Fe	100 (α-Fe) ^b	--
FA-1801	CO, 280°C, 8h, 125 cc/min	Fe _x C ^c	*	--
FA-2511	CO, 280°C, 12h, 125 cc/min	Fe _x C	*	39
FA-2551	H ₂ /CO=2, 310°C, 6h, 1200 cc/min	Fe _x C	*	--

a: Phases are in decreasing order of relative intensities.

b: Indicates the phase used for particle size determination.

c: Fe_xC denotes iron carbide phase(s).

*: The particle sizes could not be estimated using XRD because of overlapping signals.

temperatures which was also observed with the unsupported iron catalysts of nominal composition 100 Fe/0.3 Cu/0.8 K (Section III-1).

The XRD pattern obtained after hydrogen reduction at 280°C for 8h and at a flow rate of 125 cc/min showed the presence of Fe₃O₄ and Fe phases (Figure III-3.2 c). It is important to note that despite the time of reduction being higher than in the previous case, the reduction was incomplete. The flow rate, however, was lower than that used in the previous H₂ reduction procedures indicating that flow rate of H₂ plays a role in the catalyst reduction. Similar behavior was also observed for the unsupported iron catalyst (100Fe/0.3Cu/0.8K) as described in Section III-1. There, it has been proposed that water formed during reduction plays an important role in the determination of the iron phases formed. At low H₂ flow rate partial pressure of water is high. At these high partial pressures of water, the complete reduction of Fe₂O₃ is not possible. As stated in the Section III-1, it is not clear whether mass transfer also plays an important role in such a reduction process. Lower flow rates coupled with higher reaction rates may indeed yield relatively low mass transfer rates resulting in the partial reduction of the catalyst. The particle size of Fe, estimated from the XRD slow scan, was 100 Å indicating that the average particle size increased further on reduction under these conditions. This can be explained by the fact that high water partial pressure enhances the rate of sintering of the iron particles resulting in larger crystallites (Anderson, 1984; Bukur et al., 1989a).

When the catalyst was pretreated with CO at 280°C for 8 h and 12 h, peaks corresponding to carbide(s) (designated as Fe_xC) phase(s) were identified. The identification of a particular iron carbide in our samples was rather difficult by XRD, since the most intense peaks corresponding to these carbides are close to each other. However, χ -Fe₅C₂ (Hägg carbide), and ϵ' -Fe_{2.2}C are the most likely carbides present. Fe_xC designates one or more of these carbides. In addition to the carbide peaks, the catalyst pretreated with CO at 280°C for 8 h exhibited sharp peaks at $2\theta = 38, 45,$

64.7, and 78°. These were assigned to aluminum which was used in our earlier design of the sample holder. The particle sizes after pretreatment with CO were not estimated due to overlapping signals of the carbides. The XRD pattern for the catalyst sample, pretreated with syngas at 310°C for 6 h, is shown in Figure III-3.3c. It can be seen that even in the presence of H₂ no oxide/metallic Fe could be detected. Iron carbide(s) was the only iron phase detected after pretreatment with syngas. Since the presence of Fe/Fe₃O₄ depends on the relative rates of reduction followed by their carburization (by CO) it seems that the rate of carburization of Fe or Fe₃O₄ is faster than the rate of H₂ reduction. It is interesting to note that all the CO or syngas pretreatment procedures yield carbide(s) regardless of the temperature or flow rate of the reducing gas. This suggests that the carburization of the iron phases is indeed rapid and may not be a strong function of the initial phase of iron. Earlier, it has also been reported that the use of promoters like Cu and K enhances the rate of carburization of iron catalysts (Vogler et al., 1984).

Used Catalysts

XRD patterns of H₂ pretreated catalysts after reaction in a fixed bed reactor were obtained and are illustrated in Figures III-3.4 and III-3.5. The XRD pattern of the used catalyst from run FA-0113 (pretreated with H₂ at 220°C for 1 h) from the top part of the reactor showed the presence of bulk Fe₃O₄ and Fe_xC phases (Figure III-3.4a). The presence of Fe_xC suggests that some carburization occurred under FTS conditions. Recently, Lox et al. (1988) reported a study on characterization of Ruhrchemie catalyst (pretreated with H₂ at 220°C for 3 h) after 200 h of reaction using XRD. Their study has also shown the presence of oxides (other than Fe₂O₃) and a mixture of carbides after 200 h of reaction. The used catalyst from the bottom part of the reactor showed the presence of only Fe_xC phase(s) (Figure III-3.4b). It should be noted that some Fe₃O₄ in the form of fine particles (< 40 Å) may be also present in the sample, but could not be detected by XRD.

Figure III-3.3 XRD patterns of Rurhchemie catalyst samples after pretreatment with CO or syngas: a) CO (125 cc/min) at 280 °C for 8h; b) CO (125 cc/min) at 280 °C for 12h; c) syngas ($\text{H}_2/\text{CO}=2.0$, 1200 cc/min) at 310 °C for 6h.

Figure III-3.4 XRD patterns of Ruhrchemie catalyst samples after FT synthesis and pretreatment with H_2 : a) FA-0113 (top); b) FA-0113 (bottom); c) FB-0183 (top); d) FB-0183 (bottom) (see Table III-3.2 for the pretreatment conditions used).

The XRD patterns of used catalyst pretreated with H_2 at $280^\circ C$ for 1 h from the top and the bottom parts of the reactor are shown in Figures III-3.4 c and d. Bulk Fe_xC phase(s) were present in both, top and bottom parts of the reactor. However, the catalyst sample from the bottom part of the reactor also showed the presence of Fe_3O_4 phase. Although some Fe_3O_4 was present in the reduced catalyst, the formation of Fe_3O_4 in the used catalyst sample from the bottom part of the reactor due to oxidation of Fe_xC by water formed during FTS cannot be ruled out (Dry, 1981; Anderson, 1984).

The XRD patterns of the used catalyst, pretreated with H_2 at $280^\circ C$ for 8 h, from the top and bottom parts of the reactor are shown in Figures III-3.5a and b. The phases identified are listed in Table III-3.2. It should be noted that only Fe_xC phase(s) could be detected in the used catalyst samples by XRD. However, some bulk Fe_3O_4 was present in the reduced catalyst. It seems that most of the bulk Fe_3O_4 , with particle sizes greater than 40 Å, is carburized under FTS conditions.

The XRD patterns of the used catalyst, pretreated with H_2 at $280^\circ C$ for 24 h, from the top and bottom parts of the reactor are shown in Figures III-3.5 c and d. The phases identified are listed in Table III-3.2. Again, Fe_xC phase was the only phase present in both, the top part and the bottom parts of the reactor.

The used catalysts pretreated with CO at $280^\circ C$ exhibited only bulk Fe_3O_4 phase (see Figure III-3.6 a). It should be noted that the catalyst after CO pretreatment consisted of Fe_xC phases only. The formation of Fe_3O_4 in the used catalyst can be attributed to the oxidation of the carbide(s) by water formed during FTS (Berry and Smith, 1989; Davis and Tungate, 1991). The used catalyst pretreated with syngas from the top part of the reactor exhibited weak Fe_xC signals (Figure III-3.6 b). However, the main phase in the catalyst from the bottom part of the reactor is Fe_3O_4 (Figure III-3.6c; Table III-3.2). This means that the position of the catalyst in the reactor also has effect on the phases present. Generally, the reaction atmosphere is more oxidizing in the bottom part of the reactor due to the formation of CO_2 and H_2O during FTS (Dry, 1981).

Figure III-3.5 XRD patterns of Ruhrchemie catalyst samples after FT synthesis and pretreatment with H_2 : a) FB-1593 (top); b) FB-1593 (bottom); c) FB-1733 (top); d) FB-1733 (bottom) (see Table III-3.2 for the pretreatment conditions used).

Figure III-3.6 XRD patterns of Ruhrchemie catalyst samples after FT synthesis and pretreatment with CO or syngas: a) FB-1588; b) FB-2290 (top); c) FB-2290 (bottom) (see Table III-3.2 for the pretreatment conditions used).

Table III-3.2 Summary of XRD Results of Ruhrchemie Catalyst Samples after FT Synthesis - Fixed Bed Reactor Tests.

Run No.	Pretreatment Conditions; TOS	Phases Detected by XRD ^a	
FA-0113	H ₂ , 220°C, 1h; 125h	Top:	Fe _x C ^b , Fe ₃ O ₄
		Bottom:	Fe _x C, Fe ₃ O ₄
FB-0183	H ₂ , 280°C, 1h; 100h	Top:	Fe _x C
		Bottom:	Fe _x C, Fe ₃ O ₄
FB-1593	H ₂ , 280°C, 8h, 154h	Top:	Fe _x C
		Bottom:	Fe _x C
FB-1733	H ₂ , 280°C, 24h;124h	Top:	Fe _x C
		Bottom:	Fe _x C
FB- 1588	CO, 280°C, 12h; 427h	Average:	Fe ₃ O ₄
FB-2290	H ₂ /CO=2, 310°C, 6h; 160h	Top:	Fe _x C
		Bottom:	Fe ₃ O ₄ , Fe _x C

a: Phases are in decreasing order of relative intensities.
b: Fe_xC denotes iron carbide phase(s)

III-3.2.3 Mössbauer Effect Spectroscopy

Reduced Catalysts

Although XRD is useful in determining the phases present in the catalyst after pretreatment and after FTS, the relative amounts of these phases cannot be easily quantified. The advantages of MES in determining the nature and the amounts of iron phases in the catalysts are well known (Raupp and Delgass, 1979 a, b). In order to obtain quantitative information on bulk phases present in the reduced and used catalyst after pretreatments with H₂, CO, and syngas Mössbauer effect spectroscopy

(MES) was used. The Mössbauer spectra were obtained and analyzed at the University of Kentucky (The Consortium for Fossil Fuel Liquefaction Science).

Table III-3.3 shows results of MES analysis of the reduced Ruhrchemie catalyst samples. The catalyst, reduced with H_2 at $220^\circ C$ for 1 h consisted of only the superparamagnetic iron oxide/hydroxide phase. This phase is probably magnetite. The XRD analysis of the used catalyst indicated the presence of Fe_3O_4 with an average particle size of about 50 Å. The positive identification of such small magnetite particles could not be achieved by MES at room temperature. The catalyst reduced with H_2 , at $280^\circ C$ for 1 h contained superparamagnetic iron oxide/hydroxide (87%) and metallic Fe (13%) phases. The major component of the superparamagnetic phase is probably magnetite based on the results from XRD analysis. In the catalyst, reduced with H_2 at $280^\circ C$ for 8 h, some iron carbide (8%) was also detected in addition to superparamagnetic iron oxide hydroxide (80%), Fe (7%), and Fe_3O_4 (5%) phases (Table III-3.3). The existence of iron carbide phase is attributed to the sample contamination during preparation and/or handling.

The compositions of CO and syngas pretreated catalyst samples, determined by MES, were the same: 54 % of χ -carbide and 46% of superparamagnetic oxide/hydroxide (Table III-3.3). This is in agreement with results obtained with the 100 Fe/0.3 Cu/0.8K catalyst (Section III-1 of this report) where it was found that these two pretreatment procedures yield the same bulk iron phases. The carbide phase was the only phase determined by XRD analysis after these two pretreatments (Table III-3.1). The lack of iron oxide/hydroxide phases by XRD analysis, indicates that crystallites are less than 4 nm in diameter (limit of detection by XRD). Low temperature MES measurements are needed to determine composition of the superparamagnetic phase (probably mostly magnetite - Fe_3O_4 , and some unreduced Fe_2O_3).

Table III-3.3 Relative Amounts of Phases Identified by Mössbauer Effect Spectroscopy in Pretreated Ruhrchemie Catalyst Samples.

Run No.	Pretreatment Conditions	Spm ^a (%)	Magnetite (%)	Fe (%)	χ -Fe ₅ C ₂ (%)
FA-2351	H ₂ , 220°C, 1h, 3550 cc/min	100	---	---	---
FA-2391	H ₂ , 280°C, 1h, 3160 cc/min	87	---	13	---
FA-1821	H ₂ , 280°C, 8h, 125 cc/min	80	5	7	8
FA-2511	CO, 280°C, 12h, 125 cc/min	46	---	---	54
FA-2551	H ₂ /CO=2, 310°C, 6h, 1200 cc/min	46	---	---	54

a: Spm=superparamagnetic iron oxide/hydroxide.

Used Catalysts

Table III-3.4 summarizes the available results of MES measurements at 300K of some used Ruhrchemie catalyst samples. For the used catalyst, pretreated with CO at 280°C for 12 h, magnetite (68%), superparamagnetic iron oxides (27%) and χ -carbide (5%) were the phases detected. This is in agreement with the XRD results (Table III-3.2). The presence of Fe₃O₄ in the used catalyst is attributed to the reoxidation of the iron carbide(s) by water.

Table III-3.4 Relative Amounts of Phases Identified by Mössbauer Effect Spectroscopy in Ruhrchemie Catalyst Samples after FT Synthesis.

Run No.	Pretreatment Conditions; TOS	Spm ^a (%)	Magnetite (%)	χ -Carbide (%)
FB-1588 (Middle)	CO, 280°C, 12h; 427h	27	68	5
FB-2290 (Top)	H ₂ /CO=2, 310°C, 6h; 160h	63	--	37
FB-2290 (Bottom)		45	38	17

a: Spm=superparamagnetic iron oxide/hydroxide.

The phases identified by MES for the catalyst, pretreated with syngas, from the top and bottom parts of the reactor are listed in Table III-3.4. The top part consisted of the χ -carbide and the superparamagnetic iron oxide. MES results for the catalyst sample from bottom part of the reactor, show the presence of χ -carbide, magnetite, and superparamagnetic oxides. These results are in agreement with those obtained by XRD analysis.

III-3.2.4 BET Surface Area and Pore Size Distribution

The BET surface area and the pore volume of the as prepared catalyst obtained by N₂ physisorption were 295 m²/g and 0.58 cc/g, respectively (Table III-3.5). After calcination the BET surface area and the pore volume were found to be 290 m²/g and 0.62 cc/g, respectively (Table III-3.5). The BET surface area and the pore volume did not change significantly after calcination, indicating that the porous iron network is resistant to high temperatures. This is due to the presence of silica in the catalyst. The

Table III-3.5 Summary of BET Results of Pretreated Ruhrchemie Catalyst Samples.

Run No.	Pretreatment Conditions	Surface Area (m ² /g)	Pore Volume (cc/g)	Pore Diameter ^a (Å)
Ruhrchemie (as prep)	None	295	0.58	79
Ruhrchemie (calcined)	Air, 300°C, 5 h	290	0.62	86
FA-2351	H ₂ , 220°C, 1h, 3550 cc/min	179	0.46	103
FA-2391	H ₂ , 280°C, 1h, 3160 cc/min	136	0.42	124
FA-1821	H ₂ , 280°C, 8h, 125 cc/min	160	0.49	122
FA-1801	CO, 280°C, 8h, 125 cc/min	118	0.34	115
FA-2551	H ₂ /CO=2, 310°C, 6h, 1200 cc/min	99	0.31	125

a: Pore diameter=(4 x Pore volume)/Surface area.

presence of silica is known to maintain the porous iron oxide/hydroxide network (Bukur et al., 1990b; Dry, 1981). Silica enters the pores of the original network of the catalyst thus providing a rigid matrix which helps prevent a complete collapse of the pore structure of the catalyst.

However, after reduction with H_2 at $220^\circ C$ for 1 h the BET surface area decreased to $179\text{ m}^2/\text{g}$. This is in agreement with results reported by Dry (1981) and Lox et al. (1988), where a similar decrease in the surface area was observed after a reduction with hydrogen. The decrease in the surface area and pore volume can be attributed to a partial collapse of the porous $Fe_2O_3/FeOOH$ network. Hydrogen reduction at $280^\circ C$ for 1 and 8 hours led to further decrease in surface area to $136\text{ m}^2/\text{g}$ and $160\text{ m}^2/\text{g}$ respectively. The pore volumes also decreased significantly after H_2 reduction (Table III-3.5). It is important to note that in the absence of silica, after H_2 reduction, the surface areas decrease to about $40\text{ m}^2/\text{g}$ (see Section III-1).

The BET surface area decreased from $290\text{ m}^2/\text{g}$ to $118\text{ m}^2/\text{g}$ and $99\text{ m}^2/\text{g}$ after pretreatment with CO and syngas, respectively. The decrease in the BET surface area was higher for the CO or syngas reduced catalysts than for the H_2 reduced catalysts. Similar trends were seen when the pore volumes of the H_2 and the syngas reduced catalysts were compared. This may be due to the formation of carbonaceous deposits (formed only in the presence of CO) causing blocking of the pores of the catalyst, and resulting in lower surface area than with the H_2 reduced catalyst. Several studies have reported on the formation of carbonaceous deposits (probably in the form of graphitic carbon) on the catalyst after FTS (Vogt et al., 1987; Tungate and Davis, 1991). Although the carbonaceous deposits were reported to be present after FTS, it is likely that these deposits may be formed during CO or syngas pretreatment. Our CO reduction studies (Section III-3.2.6) indicate that there is a possibility of formation of such deposits on the pretreated catalyst.

The pore size distribution for the as prepared and the calcined catalyst obtained

by N₂ physisorption is shown in Figure III-3.7. It can be seen that both, the as prepared and the calcined catalyst exhibited a relatively broad pore size distribution (< 15-300 Å; 15 Å was the limit of detection) with a maximum at 200 Å. The pore size distribution for the H₂ reduced catalysts is shown in Figure III-3.8. The pore size distribution of the catalyst reduced with H₂ at 220°C exhibited a bimodal distribution; with maxima at 20 Å and 200 Å. The pore size distributions of the catalyst pretreated with H₂ at 280°C for 1 and 8 hours exhibited a maximum at 200 Å. However, pores with diameters < 15 Å were also present (Figures III-3.8 b and c).

The pore size distributions of the CO and the syngas pretreated catalysts are shown in Figure III-3.9. Although the pore size distribution profiles for the H₂, CO, and syngas reduced catalysts seem similar to that of the calcined catalyst, some differences in the average pore diameter obtained from the surface area and the pore volume were observed. It can be seen that the average pore diameter increased slightly on pretreatment with H₂, CO, or syngas (Table III-3.5). Dry (1981) reported that the average pore size increases after H₂ reduction, and after FT synthesis.

III-3.2.5 Transmission Electron Microscopy

Figure III-3.10 shows the TEM micrographs of the calcined sample under two different magnifications. Particles smaller than 100 Å are distinctly visible from these micrographs. It is, however, difficult to identify the iron phases from these micrographs. Silica being amorphous is unlikely to diffract the electron beam in TEM and hence cannot be clearly seen by TEM. Nonetheless, it can be seen that the particle morphology is essentially spherical. A number average particle size was estimated after measuring the sizes of particles from different portions of the sample. This procedure yielded the particle size to be approximately 35 Å and is listed in Table III-3.1.

Figure III-3.7 Pore size distribution of Rurhchemie catalyst: a) as prepared; b) calcined in air at 300°C for 5h.

Figure III-3.8 Pore size distribution of Ruhrchemie catalyst after pretreatment with H₂ at: a) 220°C for 1 h (flow rate = 3550 cc/min); b) 280°C for 1 h (flow rate = 3160 cc/min); c) 280°C for 8 h (flow rate = 125 cc/min).

Figure III-3.9 Pore size distribution of Ruhrchemie catalyst after pretreatment with CO or syngas: a) CO (125 cc/min) at 280 °C for 12h; b) syngas (H₂/CO=2.0, 1200 cc/min) at 310 °C for 6h.

Figure III-3.10 TEM micrographs of calcined Ruhrchemie catalyst at different magnifications: a) 169,000 X; b) 292,000 X.

The micrographs of the reduced (pretreated) Ruhrchemie catalysts (H_2 at 220°C and CO at 280°C) were also obtained and are illustrated in Figures III-3.11. The particle sizes were obtained by the procedure described above and are listed in Table III-3.1. Slight discrepancy is seen in the particle sizes obtained by XRD and TEM which is well within experimental and sampling errors. The morphology of the catalysts remained spherical even after pretreatment by CO or H_2 . The average particle size estimated by TEM after H_2 or CO pretreatment is similar to that of the calcined catalyst.

III-3.2.6 Temperature Programmed Reduction/Isothermal Reduction

The reduction behavior of the Ruhrchemie catalyst was also studied by temperature programmed reduction (TPR) and isothermal reduction. The H_2 TPR profile of the precalcined Ruhrchemie catalyst, determined at a temperature program rate of $20^\circ\text{C}/\text{min}$, is shown in Figure III-3.12. The peak at 340°C is due to the first step of iron reduction ($\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4$) while the smaller peak at $\sim 300^\circ\text{C}$ arises from the reduction of copper oxide ($\text{CuO} \rightarrow \text{Cu}$). The broad peak centered at 650°C is due to the reduction of Fe_3O_4 to metallic iron. Thus, it can be seen that the reduction of Fe_3O_4 to Fe is a more difficult step requiring temperatures greater than 600°C for its reduction in temperature programmed mode.

In order to better simulate the reduction conditions followed in FTS, isothermal reduction profiles at 300°C were obtained. Two types of experiments were performed for this purpose. The first involved monitoring the consumption of reductants H_2 and CO using TCD, while the second involved monitoring the formation of products H_2O and CO_2 using mass spectrometry. The former involved use of smaller amounts of catalysts (10-15 mg) and lower flow rates (12 cc/min; also see Section III-3.1.2 for details) whereas in the latter experimental conditions similar to those employed during pretreatment prior to FT synthesis ($\text{SV} = 3 \text{ NI/g-cat/h}$; see Section III-1 for details) were used.

Figure III-3.11 TEM micrographs of Ruhrchemie catalyst samples after pretreatment with H₂ or CO: a) H₂ at 220°C for 1 h; b) CO at 280°C for 12 h.

Figure III-3.12 TPR profile in H₂ at 20 °C/min of calcined Ruhrchemie catalyst (16h in air at 300°C).

The isothermal reduction profile at 300°C of the Ruhrchemie catalyst in H₂ monitored using TCD is shown in Figures III-3.13. The sharp peak in the H₂ isothermal reduction profile (Figure III-3.13) corresponds to the reduction of Fe₂O₃ to Fe₃O₄ and CuO to Cu. The broad peak corresponds to the reduction of Fe₃O₄ to Fe. In the earlier studies it was found that the level of silica influences reduction of Fe₃O₄ to Fe but does not influence the reduction of Fe₂O₃ to Fe₃O₄ and CuO to Cu significantly (Li, 1988, Bukur et al., 1990b). The H₂ isothermal reduction profile indicates that even after reduction at 300°C for over 10 h the reduction to metallic iron is incomplete. This is consistent with the XRD and MES results discussed previously.

Isothermal reduction profile was also obtained by switching from He to H₂ at 280°C and monitoring the composition of the effluents by mass spectrometry as a function of time on stream. The profile obtained for H₂ reduction of the catalyst at 280°C for 8 hours, as seen by the formation of water, is illustrated in Figure III-3.14a. A sharp peak at about 20 minutes of reduction, indicates rapid initial reduction. However, the rate of reduction decreases gradually after about 50 minutes. This is consistent with the H₂ reduction profile shown in Figure III-3.13. As stated earlier, this sharp peak can be attributed to the reduction of Fe₂O₃ to Fe₃O₄ whereas the slow reduction, i.e., after about 50 minutes, can be attributed to the reduction of Fe₃O₄ to metallic Fe. Quantitative information that could be obtained was limited due to lack of proper calibration methods for H₂O observed by mass spectrometry. However, the total amount of water formed during the reduction was collected in a trap and weighed. This amount corresponded to 30% reduction of Fe₂O₃ to Fe. Incomplete reduction of Fe₂O₃ after H₂ reduction under the above conditions was confirmed by XRD results, wherein Fe₃O₄ was detected (Table III-3.1).

The isothermal reduction profile in CO at 300°C obtained by monitoring CO consumption using TCD is shown in Figure III-3.15. A sharp maximum at around 20 minutes can be seen in Figure III-3.15 followed by decrease with time which levels

Figure III-3.13 Isothermal reduction profile in H_2 of calcined Ruhrchemie catalyst
(16h in air at $300^\circ C$).

Figure III-3.14 Isothermal reduction profiles of Ruhrchemie catalyst at 280°C as a function of duration of reduction: a) in H_2 ; b) in CO .

Figure III-3.15 Isothermal reduction profile in CO of calcined Ruhrchemie catalyst (16h in air at 300°C)

after around 300 minutes. The sharp peak corresponds to the reduction of Fe_2O_3 to Fe_3O_4 . A small shoulder visible on the left side of these peaks results from reduction of the copper promoter, which subsequently facilitates the onset and increases the rate of iron reduction (Bukur et al., 1989b). The portion of profile which shows decrease with time corresponds to subsequent reduction of Fe_3O_4 to metallic Fe.

Isothermal reduction, using CO as the reductant, at 280°C for 8h was also carried out by switching from He to CO at 280°C and monitoring the composition of the effluent gas by mass spectrometry as a function of time on stream. Figure III-3.14b shows the relative concentration profiles of reductant CO and product CO_2 (formed during reduction) up to 150 minutes. It can be seen that the CO_2 formation profile is very similar to the CO consumption profile shown in Figure III-3.15. An initial sharp peak is followed by a gradual decrease after about 30 minutes of reduction (Figure III-3.14b). As stated earlier, the sharp peak corresponds to the reduction of Fe_2O_3 to Fe_3O_4 , whereas further CO_2 is formed due to the reduction of Fe_3O_4 to Fe and subsequent carbiding. Small amount of CO_2 was seen even after 8 hours of reduction.

The concentrations of CO and CO_2 were also obtained by gas chromatography at 20 minute intervals. Although data could not be acquired as rapidly with a gas chromatograph as with an on-line mass spectrometer, the CO_2 profile so obtained is in qualitative agreement with the profile seen in Figure III-3.14b. Some CO_2 was also detected in the effluent gas by gas chromatography after 8 hours of reduction.

The amount of CO_2 formed during reduction up to about 8 hours was obtained from the CO_2 concentration profile shown in Figure III-3.14b. For this purpose, the data obtained by mass spectrometry was converted into absolute molar flow rate of CO_2 after proper calibration of the mass spectrometer using several known concentration values obtained by gas chromatography and the total flow effluent flow rate. Integration of the CO_2 molar flow rate profile yielded the total amount of CO_2 formed during 8 hours of reduction as 27.5 mmol/g of catalyst. It should be noted that the total

amount of CO_2 that can be accounted for assuming complete reduction of the catalyst is 15.7 mmol/g. Whereas, the total amount of CO_2 that can be formed assuming complete carbiding of the catalyst (to $\text{Fe}_{2.2}\text{C}$) is 3.5 mmol/g. This means that the total amount of CO_2 formed exceeds the amount of CO_2 that can be accounted for by both reduction as well as carburization. The excess CO_2 is presumably due to the formation of carbonaceous deposits on the catalyst.

III-3.2.7 X-ray Photoelectron Spectroscopy

The programmed/isothermal reduction studies described above reveal overall bulk-phase reduction behaviors of the iron catalysts. In order to obtain additional information about the extent of iron reduction and the catalyst composition in the near surface region, where adsorption and catalysis occur, XPS spectra were obtained after reduction with CO and H_2 . Figure III-3.16 shows the XPS spectra in the Fe 2p region after calcination and after CO and H_2 reductions. It has been shown that the Fe 2p_{3/2} peak at 711.2 eV with a characteristic satellite peak at 719.5 eV corresponds to Fe^{3+} ; peak at 709.7 eV with a characteristic satellite at ~715 eV corresponds to Fe^{2+} species, whereas the one at 706.0 eV corresponds to metallic Fe (Kuivila et al., 1988). The spectrum for Fe_3O_4 is essentially a weighted average of Fe^{2+} and Fe^{3+} spectra, with binding energy of 710.8 eV (Kuivila et al., 1988). Figure III-3.16 a shows a peak at 710.5 eV with a shake-up satellite peak at 719 eV. The binding energy of 710.5 eV indicates the presence of Fe_3O_4 whereas the satellite peak at 719 eV confirms the presence of some Fe_2O_3 . Reduction in CO for 16h at 300°C (Figure III-3.16 b) yields peaks at approximately 707.0 and 710.5 eV. Recently, Kuivila et al. (1988) reported that it was possible to distinguish metallic Fe from iron carbides using a rigorous fitting technique resulting in binding energies of 707.0 eV and 707.3 eV for metallic Fe and carbidic Fe respectively. Such a rigorous procedure was not applied in this case. Thus, it is not possible to distinguish between the nature of various reduced iron

Figure III-3.16 XPS spectra of Ruhrchemie catalyst samples in Fe 2p region: a) following calcination for 16 h at 300°C; b) following exposure of (a) to CO at 300°C; c) following exposure of (a) to H₂ at 300°C.

species that exist after CO reduction. Nonetheless, the presence of a peak at 710.5 eV indicates that most of the surface iron remained in the form of unreduced $\text{Fe}^{3+}/\text{Fe}^{2+}$ species. By contrast, reduction in H_2 under the same conditions resulted in much greater percentage of reduced iron, as shown by the sharp peak at 707-708 eV (Figure III-3.16 c) which is characteristic of metallic Fe.

Figure III-3.17 shows XPS spectra after calcination and after CO and H_2 reductions in the K 2p and C 1s regions. A peak at C 1s binding energy of 284.6 eV corresponds to "graphitic" or "surface carbon", whereas the one at 283.2 eV corresponds to carbidic carbon (Kuivila et al., 1988). After calcination a small peak at ~ 284 eV is observed (Figure III-3.17 a) which is due to residual surface carbon. However, after pretreatment with CO at 300°C, the large peak at ~ 284 eV was observed (Figure III-3.17b). It is not clear whether the peak is due to the presence of surface carbon or carbidic carbon. XRD and MES measurements after CO pretreatment at 280°C have indicated the presence of bulk carbide species. However, the presence of surface carbon species cannot be completely ruled out. As expected, after H_2 reduction the peak corresponding to carbon is absent (see Figure III-3.17 c). In all cases, a small K 2p peak at a binding energy of 293 eV was observed indicating that the concentration of surface potassium is low.

Figure III-3.18 shows XPS spectra after calcination and after CO and H_2 reductions in the O 1s regions. The O 1s binding energy for all iron oxides is 530.3 eV. Thus it is not very useful for discriminating between compounds. Nonetheless, the characteristic peak observed for the iron oxides at 530.3 eV decreases in intensity after CO reduction (see Figures III-3.18 a and b) indicating that CO is responsible for at least partial reduction of the oxides. After H_2 reduction, however, a peak at ~ 532 eV is observed (Figure III-3.18 c) which is characteristic of the adsorbed OH group. This means that H_2 reduction is near complete which is consistent with the appearance of the metallic Fe peak in the Fe 2p region. The adsorbed OH groups may originate from

Figure III-3.17 XPS spectra of Ruhrchemie catalyst samples in C 1s and K 2p region:
a) following calcination for 16 h at 300°C; b) following exposure of (a)
to CO at 300°C; c) following exposure of (a) to H₂ at 300°C.

Figure III-3.18 XPS spectra of Ruhrchemie catalyst samples in O 1s region:
a) following calcination for 16 h at 300°C; b) following exposure of (a)
to CO at 300°C; c) following exposure of (a) to H₂ at 300°C.

the water formed during reduction of the iron oxides.

III-3.3 Summary

A precipitated iron catalyst with nominal composition 100 Fe/5 Cu/4.2 K/25 SiO₂, 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 NI/g-cat/h, H₂/CO = 0.67 for 100 - 426 hours.

The as-received catalyst had the BET surface area of 295 m²/g and the pore volume of 0.58 cm³/g, both of which remained unchanged (within experimental errors) after calcination in air at 300°C for 5 hours. After different pretreatments with H₂, 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 m²/g, whereas the pore volume varied from 0.31 to 0.49 cm³/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 m²/g (Bukur et al., 1989b, also see Section III-1 of this report). 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 H₂ or CO pretreatments. The catalyst, before and after pretreatments, also had micropores less than 1.5 nm (the lower limit of detection) in diameter.

Transmission electron micrographs of calcined sample and samples after pretreatments with either H₂ at 220°C or CO at 280°C reveal that particles are small and spherical (~ 3.5 nm). An increase in particle size was observed after H₂ reductions by X-ray line broadening method. The particle size increased with reduction temperature (e.g. 5 nm after H₂ reduction at 220°C, and 10 nm after

reduction at 280°C for 8 hours). The particle size of Hagg carbide, formed during CO or syngas pretreatments, was not determined due to low intensity of the peaks and /or their close proximity.

The extent of bulk iron reduction following H₂ 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 Fe₂O₃ to Fe₃O₄, followed by slow reduction of Fe₃O₄ to either metallic iron (H₂ 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 H₂ and CO at 280°C and 300°C). The amount of CO₂ 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.

The catalyst composition in the near surface region, where adsorption and catalysis occur, after H₂ and CO pretreatments was studied by X-ray photoelectron spectroscopy (XPS). Results indicate that H₂ reduction leads to a greater degree of iron reduction than that obtained after the CO pretreatment. However, in both cases a significant fraction of the surface iron remained in the form of unreduced Fe³⁺/Fe²⁺ species. After the CO pretreatment we were not able to positively identify the nature of the surface iron species due to close proximity of binding energies of metallic iron (707.0 eV) and surface carbide (707.3 eV).

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 H₂ reductions the bulk iron is in the form of either Fe₃O₄ (magnetite) - reduction at 220°C, or a mixture of Fe₃O₄ and α-Fe (reductions at 280°C). During FT synthesis the iron carbides (χ- Fe₅C₂ or ε' - Fe_{2.2}C) are formed by carburization of α-Fe and/or

Fe₃O₄. The used catalysts contain iron carbides and magnetite.

After CO or syngas pretreatments, the χ -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 Fe₃O₄. Iron carbide content is higher in samples from the top part of the reactor (reducing atmosphere), whereas Fe₃O₄ and superparamagnetic oxides are the dominant iron phases in samples from the bottom part (more oxidizing atmosphere).

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III-4 Pretreatment Effect Research - Reaction Studies with Ruhrchemie LP 33/81 Catalyst

Results from catalytic studies with the state-of-the-art Ruhrchemie catalyst LP 33/81 (100 Fe/5 Cu/4.2 K/25 SiO₂, in parts per weight) are reported in this section. Six different pretreatment procedures were employed in fixed bed reactor (FBR) tests, and two in stirred tank slurry reactor (STSR) tests. Test identifications and pretreatment conditions are listed in Table III-4.1. Tests FB-1588 and SA-0888 were completed earlier (Bukur et al. 1989b, 1990c), but the results are included here for the sake of completeness.

Table III-4.1 Pretreatment Conditions and Test Designations
Catalyst: Ruhrchemie LP 33/81

Test (ID)	Temp. (°C)	Reductant	Duration (h)	Pressure (MPa)	Flowrate (cm ³ /min)
FA-0113	220	H ₂	1	0.1	4,000
FB-0183	280	H ₂	1	0.1	4,000
FB-1593	280	H ₂	8	0.1	175
FB-1733	280	H ₂	24	0.1	175
FB-2290	310	H ₂ /CO=2.0	6	0.1	1,200
FB-1588	280	CO	12	0.1	170
SA-0888	280	CO	16	0.8	1,730
SB-1370	220	H ₂	1	0.8	7,500

FA, FB = Fixed bed reactor test.

SA, SB = Slurry phase reactor test.

Catalyst loading, dilution and other experimental procedures were the same as described in Section III-2. After the pretreatment, the catalyst was tested at baseline process conditions: 250°C, 1.48 MPa (200 psig), 2.0 NI/g-cat/h (3.8 NI/g-Fe/h) with syngas H₂:CO ratio of 2:3 in both fixed bed and slurry phase reactors. Results from the fixed bed reactor tests will be discussed first.

III-4.1 Fixed Bed Reactor Results

Table III-4.2 summarizes selected results from six tests in fixed bed reactors. Test FB-1588 lasted over 630 h under various reaction conditions (Bukur et al., 1990c). Only the results obtained from the first 160 h at the baseline conditions are discussed here. A power failure occurred at 100 h on stream during test FB-0183, and the test was terminated prematurely after completing only one mass balance.

Activity and Stability

Change in catalyst activity during the conditioning period is shown in Figure III-4.1. Activity of the H₂ reduced catalyst, measured by volumetric contraction, varied with reduction conditions and increased in the following order: 280°C, 8 h < 280°C, 24 h < 280°C, 1 h < 220°C, 1 h. Such differences in initial catalyst activity were observed at 220°C, and higher reaction temperatures. The CO pretreated catalyst had higher activity (since 220°C) than the H₂ reduced catalyst, regardless of reduction conditions, during the conditioning period. However, the CO pretreated catalyst started to deactivate upon reaching the steady state process conditions.

During the steady state FT synthesis, the catalyst was the most active after it was reduced according to the manufacturer's procedure, i.e. H₂ at 220°C, superficial gas velocity of 150 cm/s (corresponding to 4,000 cc/min) for 1 h. The syngas (H₂+CO) conversion was about 72-73% (Figure III-4.2). After reduction at higher temperature of 280°C for 1h, but maintaining the same H₂ flowrate, the syngas conversion was significantly lower, 63 % . When the catalyst was reduced at 280°C using a markedly

Table III-4.2 Summary of Results for Pretreatment Effect Study with Ruhrchemie LP 33/81 Catalyst --
Fixed Bed Reactor Tests

Test designation	FA-0113		FB-0183	FB-1593		FB-1733		FB-2290		FB-1588	
	68	117	71	72	144	71	116	73	157	71	167
Time-on-stream, h											
CO conversion, %	74.9	73.8	66.4	61.2	64.9	58.7	60.7	61.1	57.9	56.4	51.6
(H ₂ +CO) conversion, %	71.9	71.5	64.7	59.2	62.5	57.3	58.7	63.3	60.9	58.6	54.4
STY, mmol/g-cat/h	64.0	64.1	58.2	53.0	55.9	51.0	52.1	56.8	55.0	52.0	49.1
k, mmol/g-Fe/h/MPa ^a :	241	243	215	192	205	187	190	225	216	201	187
(H ₂ /CO) usage ratio	0.61	0.61	0.67	0.64	0.63	0.66	0.64	0.75	0.78	0.76	0.78
(H ₂ /CO) exit ratio	0.95	0.82	0.79	0.78	0.81	0.75	0.78	0.60	0.57	0.60	0.60
$K_p = P_{CO_2} P_{H_2} / P_{CO} P_{H_2O}$	12.7	9.9	12.5	13.0	16.0	11.1	11.0	2.28	1.71	2.20	2.00
mmol CH ₄ /g-Fe/h	1.99	2.01	2.98	2.43	2.69	2.33	2.36	2.04	1.94	1.41	1.33
Hydrocarbon selectivity, wt%											
CH ₄	6.1	6.4	10.4	9.4	10.0	9.0	8.6	7.0	6.9	5.6	5.6
C ₂ -C ₄	16.8	18.0	24.2	22.5	23.2	25.3	23.0	22.7	23.3	22.7	22.8
C ₅ -C ₁₁	19.8	21.7	32.8	29.6	31.7	32.9	31.6	22.4	31.7	18.6	20.2
C ₁₂ +	57.3	53.9	32.6	38.5	35.1	32.8	36.8	47.9	38.1	53.1	51.4
Chain growth parameter, α_{1-10}^b	0.59	0.61	0.68	0.69	0.70	0.69	0.69	0.65	0.64	0.65	0.67
Olefin content, wt%											
C ₂ -C ₄	64.3	66.1	64.7	63.8	63.3	65.6	65.5	75.9	76.8	77.6	80.8
C ₅ -C ₁₁	66.7	68.6	68.1	68.6	68.7	69.4	69.5	80.4	62.0	77.2	77.1

Process conditions: 250°C, 1.48 MPa (200 psig), 2.0 NI/g-cat/h, H₂/CO=0.67

^a: Apparent reaction rate constant for a first order reaction in hydrogen, based on measured usage ratio.

^b: Parameter estimated from products with carbon number in the range C₁-C₁₀.

Figure III-4.1 Volumetric contraction during conditioning period.

Figure III-4.2 Effect of pretreatment conditions on conversion and catalyst stability.

lower H_2 flowrate (corresponding to a gas space velocity of 3.0 NI/g-cat/h) for 8 h and 24 h, respectively, the syngas conversion decreased further. After 8 h reduction the initial syngas conversion (1 h at the process conditions) was only 47 %; it then continued to increase with time, reaching 62 % at 154 h on stream. After 24 h reduction the initial syngas conversion was somewhat higher, 54 %, and it increased with time to stabilize at about 58 %. Thus, the steady state activities after 8 h and 24 h H_2 reductions at 280°C were similar. The corresponding values of the apparent reaction rate constant are listed in Table III-4.2, and they follow the same trend as syngas conversions. All four H_2 reduction procedures led to either a stable or gradually increasing activity during the synthesis.

After CO pretreatment (280°C, 12 h) the initial (H_2 +CO) conversion was 66 %, it then gradually decreased with time to 55 % at 160 h on stream. Though not shown here, the conversion was 50 % after 460 h testing. The rate of deactivation was moderate with the conversion loss of 0.9 % per day. The activity of the syngas pretreated catalyst (H_2 :CO = 2, at 310°C, flowrate 1,200 cc/min for 6 h) was fairly stable between 50 and 160 h on stream, and the (H_2 +CO) conversion was about 62%. The apparent reaction rate constant (220 mmol/g-Fe/h/MPa) of the syngas pretreated catalyst was slightly greater than the corresponding rate constants of H_2 reduced catalyst at 280°C (187 - 215 mmol/g-Fe/h/MPa), but smaller than the apparent rate constant of H_2 reduced catalyst at 220°C (242 mmol/g-Fe/h/MPa).

The effects of pretreatment procedures on WGS activity, measured by H_2 to CO usage ratio and partial pressure quotient K_p , are illustrated in Table III-4.2. The K_p values during FT synthesis following H_2 reductions were about one order of magnitude greater than those obtained after CO and syngas pretreatments (Table III-4.2). The usage ratio was stable with time on stream in all tests (0.62 - 0.65 after H_2 reductions, and 0.76 - 0.78 following CO and/or syngas pretreatments). Thus, the

WGS activity of the Ruhrchemie catalyst was higher (smaller usage ratio, greater K_p) after H_2 reductions than after CO and/or syngas activation.

Selectivity

The effect of pretreatment conditions on hydrocarbon product distribution is illustrated in Table III-4.2 and Figure III-4.3. The catalyst selectivity remained relatively stable between 70 and 170 h on stream. Therefore, the average values from 2-3 mass balances were used in Figure III-4.3 for comparison of different pretreatment procedures. The CO activated catalyst had the lowest methane selectivity (~5.6 %). The catalyst reduced with H_2 at 220°C for 1 h also had relatively low methane selectivity (6.2 %), and had the lowest selectivity to C_2 - C_4 hydrocarbons (17.4 %). These two pretreatment procedures resulted in high C_{12+} selectivities, about 55.6% (H_2 at 220°C) and 52.2 % (CO activation). Hydrocarbon selectivities were similar following three procedures using hydrogen reduction at 280°C with different flowrates and/or durations. In all three cases, methane selectivity was high (8.8 to 10.4 %), whereas C_{12+} selectivity was low, only 32 to 36 %. The syngas pretreatment gave an intermediate behavior: 7 % methane selectivity and 43 % C_{12+} selectivity.

Methane formation rate (per gram of iron in the catalyst) as a function of time on stream for different pretreatment procedures is shown in Figure III-4.4. Methane formation rate follows the same trends as methane selectivity, with the exception of H_2 reduction at 220 °C and the syngas pretreatment. Methane formation rates for these two pretreatments are the same (Figure III-4.4), whereas methane selectivity after H_2 reduction is about 10% less than that after the syngas pretreatment. This is caused by differences in conversions, i.e. differences in total hydrocarbon production rates. After H_2 reduction, both the syngas conversion and the total hydrocarbon production rate are higher than after the syngas pretreatment. Thus methane selectivity (mass fraction

Figure III-4.3 Effect of pretreatment conditions on hydrocarbon product distribution.

Figure III-4.4 Methane formation rate as a function of time on stream following different pretreatment conditions.

of methane in total hydrocarbons) is lower with the former pretreatment procedure, even though the methane formation rates are the same.

Representative carbon number product distributions are presented in Figure III-4.5 in the form of Anderson-Shulz-Flory plots. The two ASF plots were fitted well using the three parameter (double alpha) model of Huff and Satterfield (1984). The model parameters (chain growth parameters - α_1 and α_2 , and the fraction of type 1 sites - β) were estimated by nonlinear regression.

Olefin selectivity following different pretreatment conditions is plotted in Figure III-4.6 for carbon numbers up to C_{15} . Catalyst pretreated with CO had higher olefin selectivity than the catalyst reduced with H_2 . For example, the olefin content in C_2 - C_4 and C_5 - C_{11} ranges were about 10 - 15 wt % higher after the CO pretreatment (Table III-4.2). Different temperatures, flowrates and/or durations used during H_2 reductions did not have a marked effect on olefin selectivity. The olefin selectivity obtained after the syngas pretreatment, was, in general, between values obtained after CO and H_2 pretreatments.

Olefin isomerization activity, measured by 2 - olefin content, varied markedly with pretreatment conditions. As shown in Figure III-4.7 (the average values from multiple mass balances were used in this plot) the isomerization of C_8+ olefins was significantly higher after H_2 reductions than after CO or syngas pretreatments. The 2 - olefin content of C_{15} hydrocarbons reached 80 % after H_2 reduction at 220°C for 1h, whereas it was about 30 % after CO or syngas pretreatment. The 2-olefin selectivity was also influenced by different H_2 activation conditions and increased in the same order as the overall catalyst activity. Reduction at high flowrate of H_2 and low temperature, which resulted in the highest activity, also yielded the highest olefin isomerization activity.

Figure III-4.5 Carbon number product distribution for selected pretreatment conditions: (a) FA-0113 (68 h on stream); (b) FB-0183 (71 h on stream).

Figure III-4.6 Effect of pretreatment conditions on olefin selectivity.

Figure III-4.7 Effect of pretreatment conditions on 2-olefin selectivity.

III-4.2 Discussion

The major findings from catalytic tests following six different pretreatment procedures are: (1) After CO pretreatment the catalyst activity was high initially, and then gradually decreased with time. Catalyst deactivation rate was moderate. (2) Reduction using high flowrate of H_2 , low temperature ($220^\circ C$) and short duration resulted in high activity and relatively low methane selectivity. (3) Reductions using low flowrate of H_2 at $280^\circ C$ resulted in low catalyst activity, and relatively high methane selectivity. (4) Catalyst activity was either stable or gradually increasing with time on stream (up to 140 h) after all H_2 reductions. (5) Secondary reactions (olefin hydrogenation and isomerization) were higher after hydrogen reductions. (6) CO and syngas pretreatments favored production of higher molecular weight products, in comparison to H_2 reductions at $280^\circ C$. However, the catalyst reduced with H_2 at $220^\circ C$ produced less gaseous hydrocarbons (C_1 - C_4) and more C_{12+} hydrocarbons than either the CO or syngas pretreated catalyst.

These observations are in a qualitative agreement with those made in our previous studies with precipitated iron catalysts having nominal compositions 100 Fe/3 Cu/0.2 K (Bukur et al., 1989a) and 100 Fe/0.3 Cu/0.8 K (Section III-2 of this report). Most of these observations can be explained utilizing results from characterization studies, and previous FT reaction studies on the effects of promoters, binders and bulk iron phases on catalyst activity and selectivity.

After the pretreatments with CO and syngas, the Hägg carbide is formed in addition to fine oxide/hydroxide particles (probably magnetite) which exhibit superparamagnetic behavior (Table III-3.3). The catalyst surface areas and pore volumes were also similar. During the subsequent FT synthesis, the catalyst activity and selectivity were also similar. This represents a strong correlation between the catalytic behavior and the structural properties of the catalyst after the pretreatment. A moderate decrease of catalyst activity with time may be attributed to partial conversion

of Hägg carbide to magnetite (Table III-3.4), and possible blocking of active sites by carbonaceous deposits on the surface of the catalyst (Dry, 1981; Krebs et al., 1979). In comparison with the precipitated iron catalysts without silica as a binder (100 Fe/3 Cu/0.2 K and 100 Fe/0.3 Cu/0.8 K) the activity of the Ruhrchemie catalyst was more stable during FT synthesis. The improvement in stability by incorporating silica into catalyst is in agreement with the results from our earlier studies on binder/support effect (Bukur et al; 1990b). On an unsupported catalyst the surface active sites are close to each other, which facilitates the crystallite size growth by sintering. Also, it is easier for carbonaceous deposits to grow and cover larger portion of the surface, both of which are resulting in faster catalyst deactivation. In contrast, the active sites are more isolated by silica binder on the Ruhrchemie catalyst. As a result the inactive carbon layer would cover a smaller number of active sites, and the growth of iron crystallites would be hindered during FT synthesis, and thus the catalyst deactivation would be slower. In addition, the incorporation of silica binder causes a decrease in surface basicity, which in turn lowers the carbon deposition rate and promotes the catalyst stability.

After H₂ reductions the initial catalyst activity during the conditioning period was lower than that of the CO pretreated catalyst (Figure III-4.1), which is consistent with the competition model of Niemantsverdriet and van der Kraan (1981). During FT synthesis with the H₂ reduced catalyst some of the active surface carbon is consumed to form bulk carbides, and thus the rate of FT synthesis is initially lower relative to a precarbided catalyst. In terms of bulk iron phases present after different pretreatments, these results could be interpreted as to imply that Hägg carbide is more active for FT synthesis than magnetite and/or metallic iron. During FT synthesis χ - carbide formed after CO and syngas pretreatments is gradually oxidized to magnetite, whereas magnetite and α - Fe phases formed after H₂ reductions are partially converted to iron carbides, and the working catalysts have similar bulk compositions regardless of the

pretreatment procedure employed (Section III-3 of this report). Differences in the catalyst activity during the steady state FT synthesis are fairly small (Figure III-4.2 and Table III-2), and may be attributed to differences in the catalyst surface areas (crystallite size) and the catalyst bulk and surface compositions.

Four reduction procedures with H_2 were employed by changing the flowrate of H_2 , temperature and/or duration of reduction. These procedures resulted in different degrees of reduction and different levels of stable catalyst activity. The Ruhrchemie catalyst is more difficult to reduce than a precipitated iron catalyst without silica. As XRD and MES results reveal after reduction with H_2 at $220^\circ C$, 150 cc/min for 1 h, the bulk phase of the Ruhrchemie catalyst was magnetite (Tables III-3.1 and III-3.3), and only after the reduction at $280^\circ C$ the catalyst was partially reduced to metallic iron. With unsupported 100 Fe/0.3 Cu/0.8 K catalyst, the metallic iron was already formed after reduction with H_2 at $220^\circ C$, and the complete reduction occurred at $250^\circ C$. The Ruhrchemie catalyst which was reduced to a lesser degree after reduction with H_2 at $220^\circ C$ (FA-0113) had higher activity during the subsequent FT synthesis than the one reduced to magnetite and metallic iron at $280^\circ C$ (FB-0183). This trend of activity with iron reducibility is contrary to that obtained on the 100 Fe/0.3 Cu/0.8 K catalyst. There it was found that the catalyst activity increases with the degree of reduction (section III-2). A possible explanation for these opposite trends is related to differences in surface areas after the reduction. After the reduction at $220^\circ C$, the BET surface area of the Ruhrchemie catalyst is about $180 \text{ m}^2/\text{g}$, which is significantly higher than that obtained after one hour reduction at $280^\circ C$, $136 \text{ m}^2/\text{g}$. Apparently, the difference in surface area (i.e., crystallite size, 5 vs. 8 nm) played a more important role in determining the catalyst activity than the degree of reduction, and the catalyst with larger surface area had about 10% higher activity during the FT synthesis. In the case of the 100 Fe/0.3 Cu/0.8K catalyst the surface areas after reductions at $250^\circ C$ and $280^\circ C$ were the

same, and the activity was higher on the catalyst which was completely reduced to α - Fe.

The Ruhrchemie catalyst was the least active after two H₂ reductions at 280°C (8 or 24 h in duration) using a low gas flow rate of 175 cc/min (STP), both during the conditioning period (Figure III-4.1) and the steady state FT synthesis (Figure III-4.2 and Table III-4.2). The apparent reaction rate constant in tests FB-1593 and FB-1733, was about 23% less than that obtained in the test FA-0113 (H₂ reduction at 220°C, 4000 cc/min for 1 h). Water vapor formed during reduction of metal oxides by hydrogen enhances sintering of metal particles (Coluccia et al., 1979). The use of higher reduction temperature favors faster reduction of the metal oxide and the water is released more rapidly. The use of low reductant flow rate increases the partial pressure of water, and both of these effects, the use of higher reduction temperature and low H₂ flowrate, would enhance sintering and thus decrease the catalyst activity. The average α - Fe particle size after H₂ reduction at 280°C was 10 nm (SA = 160 m²/g), whereas the average particle size after H₂ reduction at 220°C for 1 h was only 5 nm (SA = 180 m²/g). The use of high H₂ flowrate and low reduction temperature facilitates removal of water vapor and preserves the high surface area (Dry, 1981; Che and Bennett, 1989).

The above results show both similarities as well as differences with results obtained in studies with two precipitated iron having nominal compositions : 100 Fe/3 Cu/0.2 K (Bukur et al., 1989a) and 100 Fe/0.3 Cu/0.8 K (Section III-2 of this report). In the latter two studies the catalyst activity decreased markedly with increase in reduction temperature and/or duration of H₂ reduction, whereas in the present study decrease in activity with increase in reduction temperature was moderate, and the duration of reduction at 280°C (8 vs. 24 h) had no effect on the catalyst activity. The difference in sensitivity of the Ruhrchemie and the 100 Fe/3 Cu/0.2 K catalyst to reduction conditions may be explained in terms of sulfur migration and the extent of

surface coverage by sulfur after the reduction (Sault, 1991). According to Sault (1991) the sulfur (the origin of which are bulk sulfate impurities present in the metal nitrates used to prepare the catalyst) migration to the surface increases with both reduction duration and temperature, due to increase in the rate of sulfur diffusion with temperature. Sulfur coverage is greater on a low surface area catalyst ($SA = 10 \text{ m}^2/\text{g}$ for reduced 100 Fe/3 Cu/0.2 K catalyst) than on the high surface area Ruhrchemie catalyst. FT activity of the catalyst decreases in proportion to the sulfur coverage, due to catalyst poisoning. Thus, the difference in sensitivity of the two catalysts to reduction conditions is due to differences in their surface areas, i.e. different levels of sulfur poisoning.

The WGS activity was higher over the catalyst reduced with H_2 than with CO or syngas. This observation is in agreement with the results obtained in our earlier study with the 100 Fe/3 Cu/0.2 K catalyst (Bukur et al., 1989a). Higher WGS activity results in a higher effective H_2/CO surface ratio, which in turn promotes secondary hydrogenation and isomerization of 1-olefins. Consequently, the olefin content in the hydrocarbon product decreased and 2-olefin isomerization increased on the catalyst following reductions with H_2 , as shown in Figures III-4.6 and III-4.7. After all three H_2 reductions at 280°C (Runs FB-0183, FB-1593 and FB-1733) more gaseous hydrocarbons were produced than in tests following CO and syngas pretreatments (Figure III-4.3 and Table III-4.2). This is due to higher surface hydrogen concentration on H_2 reduced catalyst, which favors methanation and chain termination reactions. However, the catalyst reduced with H_2 at 220°C (FA-0113) produced less gaseous ($\text{C}_1\text{-C}_4$) and more C_{12+} hydrocarbons, than any other pretreatments employed. The reasons for this type of behavior are not clear at the present time.

III-4.3 Stirred Tank Slurry Reactor Tests

The results from slurry reactor test SA-0888 were described in detail elsewhere (Bukur et al 1989b, 1990c). Briefly, after pretreatment with CO at 280°C, 0.8 MPa, 1730 cc/min (3.0 NI/g-cat/h) for 16 h, the catalyst activity was stable during the first 340 h of testing at the baseline process conditions of 250°C, 1.48 MPa, 2.0 NI/g-cat/h and $H_2/CO = 0.67$, and the (H_2+CO) conversion was about 42.6 - 46.4 %. Following a period of process variable studies between 340 to 570 h on stream, the syngas conversion decreased to 36 %. Change in syngas conversion with time on stream at baseline conditions is shown in Figure III-4.8. The usage ratio was about 0.75 throughout the test. During 600 h of testing, the hydrocarbon selectivity shifted towards lower molecular weight products (Table III-4.3 and Figure III-4.9), the olefin content decreased, whereas 2-olefin selectivity increased with time on stream.

After reduction with H_2 at 220°C, 7,500 cc/min (15.0 NI/g-cat/h) for 1 h the catalyst was tested over a long period of time in run SB-1370. Variation of the (H_2+CO) conversion with time on stream is also plotted in Figure III-4.8. The initial conversion was low. It reached the steady state after about 60 h on stream (36-38%), and remained stable during the next 300 h of testing at the baseline process conditions. Between 360 and 620 h on stream, the catalyst was tested under various process conditions but it had not deactivated. The (H_2+CO) conversion at 620 and 670 h, after returning to the baseline conditions, was essentially the same, about 38-40 %, as that observed between 60 and 360 h on stream. The usage ratio at baseline conditions varied between 0.68 to 0.72 during the test. Hydrocarbon selectivity shifted towards lower molecular weight products with time-on-stream (Table III-4.3 and Figure III-4.9). For example, at 65 h on stream, methane and C_{12+} selectivities were 3.9 and 55.3 wt%, respectively. The fraction of high molecular weight hydrocarbons decreased with time, at 350 h C_{12+} selectivity decreased to 46 %, and further to 35 % at 662 h on

Figure III-4.8 Effect of pretreatment procedures on conversion and catalyst stability in slurry reactor tests.

Table III-4.3 Summary of Results for Pretreatment Effect Study with Ruhrchemie LP 33/81 Catalyst --
Slurry Reactor Tests

Test designation	SA-0888					SB-1370				
Time-on-stream, h	45	166	264	336	619	65	134	253	349	662
CO conversion, %	42.1	41.5	41.2	40.4	32.8	35.3	36.3	39.8	38.3	38.1
(H ₂ +CO) conversion, %	45.9	43.1	43.9	44.4	35.9	36.6	37.6	40.2	39.3	38.7
STY, mmol/g-cat/h	41.0	38.1	39.1	40.0	32.0	33.2	34.1	36.1	36.0	35.3
k, mmol/g-Fe/h/MPa ^a	187	167	173	181	135	133	138	149	152	142
(H ₂ /CO) usage ratio	0.79	0.74	0.77	0.83	0.83	0.72	0.72	0.68	0.72	0.69
(H ₂ /CO) exit ratio	0.58	0.62	0.59	0.55	0.59	0.63	0.62	0.65	0.68	0.64
$K_p = P_{CO_2} P_{H_2} / P_{CO} P_{H_2O}$	1.21	1.19	1.34	1.20	1.13	3.00	2.94	3.11	2.40	3.40
mmol CH ₄ /g-Fe/h	0.86	1.00	1.02	1.02	1.09	0.71	0.97	0.99	0.93	0.80
Hydrocarbon selectivity, wt%										
CH ₄	4.3	5.1	5.1	4.6	6.6	3.9	5.2	5.2	4.8	4.3
C ₂ -C ₄	17.8	20.8	22.3	21.3	27.3	15.3	16.0	15.9	16.2	21.6
C ₅ -C ₁₁	22.1	21.9	22.8	29.5	32.6	25.5	27.1	28.8	31.2	39.4
C ₁₂ +	55.8	52.2	49.8	44.6	33.5	55.3	51.7	50.1	45.8	34.7
Chain growth parameter, α_{1-10} ^b	0.76	0.73	0.73	0.75	0.71	0.78	0.76	0.73	0.74	0.75
Olefin content, wt%										
C ₂ -C ₄	79.7	78.4	77.9	74.9	74.2	76.7	76.6	74.5	74.8	72.5
C ₅ -C ₁₁	69.7	65.4	68.1	75.2	75.0	76.8	80.1	77.4	77.0	79.7

Process conditions: 250°C, 1.48 MPa (200 psig), 2.0 NI/g-cat/h, H₂/CO=0.67

^a: Apparent reaction rate constant for a first order reaction in hydrogen, based on measured usage ratio.

^b: Parameter estimated from products with carbon number in the range C₁-C₁₀.

Figure III-4.9 Effect of time on stream on hydrocarbon product distribution in slurry reactor tests.

stream. Methane selectivity increased with time and at 662 h, it was 4.3 %. Figures III-4.10 and III-4.11 illustrate the effect of time on stream on the olefin content and the 2-olefin selectivity, respectively. The olefin content decreased whereas the 2-olefin selectivity increased with time, which is consistent with trends observed in Run SA-0888 (CO activated catalyst).

III-4.4 Comparison between FBR and STSR Results

The catalyst was reduced under similar conditions with H_2 at 220°C in the fixed bed test FA-0113 and in the slurry phase test SB-1370. Also, similar pretreatment procedures were employed in the fixed bed test FB-1588 and slurry phase test SA-0888 using CO as reductant. During the subsequent FT synthesis, the catalyst exhibited stable activity in both fixed bed and slurry phase reactors, as demonstrated in Figures III-4.2 (FBR) and III-4.8 (STSR). However, the catalyst activity was significantly lower in the slurry reactor than in the fixed bed reactor following the H_2 reduction. In the fixed bed test FA-0113 the syngas conversion was about 72%. In the slurry phase test SB-1370 the catalyst activity gradually increased during the first 60 h on stream and steady state syngas conversion was about 40 %. The apparent first order rate constant was about 240 mmol/g-Fe/h/MPa in the fixed bed test FA-0113, whereas only 133-152 mmol/g-Fe/h/MPa (see Tables III-4.2 and III-4.3). It appears that the H_2 reduction was less effective in the slurry reactor than in the fixed bed, and the catalyst in the slurry had undergone further activation during the initial period of synthesis. Nonetheless its steady state activity was still much lower than in the fixed bed reactor. On the other hand, following the pretreatment with CO, the apparent first order rate constant obtained after 40 h under the process conditions was about 200 and 187 mmol/g-Fe/h/MPa in the FBR and STSR, respectively. Thus, the intrinsic catalyst activity was the same in both reactors.

Figure III-4.10 Effect of time on stream on olefin selectivity in test SB-1370.

Figure III-4.11 Variation of 2-olefin selectivity with time on stream in test SB-1370.

The effect of reactor type on hydrocarbon selectivity is shown in Figure III-4.12. Following CO activations, the hydrocarbon distributions were similar: 5.6 wt% (CH_4), 22.7% ($\text{C}_2\text{-C}_4$), 19.1% ($\text{C}_5\text{-C}_{11}$) and 52.2% (C_{12+}) in the fixed bed reactor, and 4.7 % (CH_4), 19.8% ($\text{C}_2\text{-C}_4$), 21.1% ($\text{C}_5\text{-C}_{11}$) and 54.2% (C_{12+}) in the slurry phase reactor. After H_2 reduction, selectivities to methane and $\text{C}_2\text{-C}_4$ hydrocarbons were similar in fixed bed and slurry reactors. However, $\text{C}_5\text{-C}_{11}$ selectivity was higher (29 vs. 21%), and C_{12+} selectivity was lower (50 vs. 55%) in the STSR than in the FBR.

The olefin content and 2-olefin selectivity changed with time on stream in the STSR test. In Figures III-4.13 and III-4.14, the initial selectivities, obtained in the first mass balance, were chosen to assess the effects of pretreatment and reactor type on olefin selectivities. Both the olefin content and the 2-olefin selectivity were similar in the fixed bed and slurry reactors after about 40 h at the process conditions following the CO pretreatment. In the case of H_2 reduction, the olefin content was lower and the olefin isomerization activity was markedly higher in the fixed bed (FA-0113) than in the slurry reactor (SB-1370). These differences in olefin selectivities are at least partly caused by differences in conversion levels, higher conversions favor secondary reactions. It is interesting to note that the initial olefin and 2 - olefin selectivities in the slurry reactor test SB - 1370 were similar to those obtained after the CO pretreatment. A possible explanation for this type of behavior is discussed below.

After the CO pretreatments, the catalyst intrinsic activity and selectivity was similar in fixed bed and slurry reactors, i.e. the catalyst performance was independent of the reactor type used, particularly during the initial period of synthesis following the pretreatment. An iron catalyst changes its structure during the FT synthesis (e.g., transformation of iron carbides to iron oxides), and these changes over long time periods could be different in a fixed bed reactor than in a slurry reactor environment.

Figure III-4.12 Comparison of hydrocarbon selectivities in fixed bed and slurry reactor tests.

Figure III-4.13 Comparison of olefin selectivities in fixed bed and slurry reactor tests.

Figure III-4.14 Comparison of 2-olefin selectivities in fixed bed and slurry reactor tests.

Thus, the long term catalyst activity and selectivity could become different in these two types of reactors, which was observed to some extent in our study (Bukur et al., 1990c).

Results after H₂ reductions show different type of behavior. Significant differences in catalyst activity and selectivity were observed between the fixed bed and slurry reactor tests, even during early periods of FT synthesis. Due to lack of catalyst characterization data of the reduced slurry catalyst, we could only speculate about possible reasons for the observed differences in the catalytic behavior. As already mentioned earlier, by employing low reduction temperature (220°C) and short duration (1 h), the Ruhrchemie catalyst was only reduced to Fe₃O₄ in the fixed bed reactor (Table III-3.1). It is likely that the extent of reduction was even lower in the slurry reactor. The existence of induction period following the reduction in the test SB - 1370 suggests that the catalyst was not properly activated. Instead, the catalyst activation took place under the synthesis conditions (i.e. activation with a syngas). These differences in pretreatment procedures, giving rise to different initial phases, may be the reason for the observed differences in catalyst activity and selectivity in the fixed bed and stirred tank reactor tests. In particular, the above hypothesis also provides an explanation for the observation that the olefin selectivities in the slurry test SB - 1370 were similar to those obtained after the CO pretreatments (Tests SA - 0880, and FB - 1588). It is known, from our studies with this and other precipitated iron catalysts, that olefin selectivities following CO and syngas pretreatments are similar.

III-4.5 Summary

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 catalyst reduced at 280°C for 24 hours. This is believed to be due to higher surface area (smaller crystallite size) of the catalyst reduced at low temperature, and differences in oxidation states of iron in the bulk and on the surface of the catalyst 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 H₂ at 220°C, even though its surface area after the pretreatment was significantly smaller than that of the H₂ reduced catalyst (99 vs. 179 m²/g). Hydrogenation activity of the syngas pretreated catalyst is slightly greater than that of the CO pretreated catalyst.

Two pretreatment procedures (H₂ 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 H₂ reduced catalyst increased by about 10% during the first 360 h on stream and then 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 H₂ 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.

III-4.6 References

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III-5 Pretreatment Effect Research - Reaction Studies with 100 Fe/5 Cu/4.2 K/16 SiO₂ Catalyst

This catalyst is one of the silicon oxide containing catalysts prepared in our laboratory which has shown desirable properties (activity, selectivity and stability) during a screening test in a fixed bed reactor. Three pretreatment procedures were used to study their effect on subsequent catalyst performance in a stirred tank slurry reactor. Test designations and pretreatment conditions are listed in Table III-5.1.

Table III-5.1 Pretreatment Conditions and Test Designations

Test (ID)	Temp. (°C)	Reductant	Duration (h)	Pressure (MPa)	Flowrate (cm ³ /min)
SB-2832	240	H ₂	2	0.8	7,500
SA-3172	280	H ₂ /CO=0.7	5.5	0.8	280
SB-3362	280	CO	8	0.8	750

SA, SB = Slurry phase reactor test

III-5.1 Experimental Procedure

Test SB-2832

The catalyst with particle size less than 270 mesh (53 μ m) was suspended in molten n-octacosane to form a 4.8 wt% slurry and then reduced with H₂ at 240°C, 0.8 MPa (150 psig) and flowrate 7,500 cc/min for 2 h. Following the reduction, the catalyst was tested at baseline process conditions of 260°C, 1.48 MPa (200 psig), 1.5 NI/g-cat/h (2.6 NI/g-Fe/h) and syngas feed H₂/CO = 0.67 during the first 263 h on stream.

The same baseline conditions were employed in all three tests reported in this section. Between 263 and 664 h, the catalyst was tested at 2.17 MPa (300 psig) and gas space velocities of 2.2 NI/g-cat/h (263 - 526 h) and 1.8 NI/g-cat/h (526 - 665 h). After testing at higher pressure, the catalyst was regenerated at 666 h with H₂ at 240°C, 1.48 MPa for 1 h, and the baseline conditions were re-established. The test was terminated voluntarily after 720 h on stream.

Test SA-3172

In this test an Ethylflo-164 oil, obtained from Ethyl Corporation, was used as the initial slurry medium. The Ethylflo-164 oil is a hydrogenated 1-decene homopolymer, with a dominant carbon number of C₃₀. Catalyst particles less than 270 mesh were loaded into the reactor, resulting in slurry concentration of about 6 wt%. The catalyst was activated using syngas (H₂/CO=0.68) at 280°C, 0.8 MPa, and 2 NI/g-Fe/h. During the pretreatment, the tail gas composition was continually analyzed by on-line gas chromatography. The pretreatment was stopped after 5.5 h when the two consecutive tail gas analyses showed no change in composition (Figure III-5.1). After the pretreatment, the catalyst was tested under the baseline conditions over a 105 h period. Between 106 and 197 h on stream, the reaction pressure and gas space velocity were increased to 2.17 MPa and 2.1 NI/g-cat/h, respectively. The baseline conditions were re-established at 198 h on stream. At 223 h the catalyst was regenerated with H₂ at 250°C, 1.48 MPa, 2,000 cc/min for 4 h. After that, the testing continued at the baseline conditions for additional 100 h. The test was terminated at 340 h on stream, and six mass balances were completed during the test.

Test SB-3362

The Ethylflo - 164 oil was used as the initial liquid medium, and the catalyst loading was about 5.5 wt%. The catalyst was pretreated with CO at 280°C, 0.8 MPa

Figure III-5.1 Tail gas composition change during the syngas pretreatment.

and 3.0 NI/g-cat/h (5.3 NI/g-Fe/h) for 8 h. During the preparation and pretreatment periods, a substantial amount of slurry medium was lost from the reactor as a result of operational accident and oil evaporation. The catalyst activity at the baseline process conditions was found to be very low (about 11 % syngas conversion) during the first 10-20 h of testing following the pretreatment. This was attributed to low slurry level inside the reactor, i.e. inefficient gas - catalyst contact in the slurry. The test was interrupted and additional Ethylflo oil was added under high purity nitrogen atmosphere into the reactor. The synthesis was then resumed at 39 h on stream under the baseline conditions. Between 235 and 406 h, the catalyst was tested at higher pressure and gas space velocity, 2.17 MPa and 2.2 NI/g-cat/h, respectively. The baseline conditions were then re-established, and the test continued for additional 70 h to check the catalyst activity after exposure to higher pressure. The test was terminated after 478 h on stream, during which period six mass balances were completed.

III-5.2 Results and Discussion

III-5.2.1 Catalyst Characterization Results

The elemental catalyst composition was determined by AA and/or ICP spectroscopy at our Laboratory, Sandia National Laboratory, DOE PETC and UOP Inc. Results are as follows (in parts per 100 parts of Fe): TAMU (5.6 Cu/6.3 K/18.5 SiO₂); Sandia (5 Cu/4.3 K/18 SiO₂); PETC (5.6 Cu/3.9 K/14.2 SiO₂); UOP (5.2 Cu/3.7 K/13.1 SiO₂). The results from different Laboratories are in a reasonable agreement with each other (except for high potassium content at TAMU), as well as with the intended catalyst composition.

The BET surface area and pore volume of a calcined sample (Air at 300°C for 5 h) were: 234 m²/g and 0.61 cm³/g, respectively. The pore size distribution was very broad with local maximum at about 2 nm.

After the reduction with H₂ at 240°C the catalyst had nearly amorphous structure (small crystallites). The magnetite (Fe₃O₄) and α - Fe₂O₃ were identified by XRD. During FT synthesis there is an increase in crystallinity (larger particles are formed) and the catalyst is partially carburized. At 665 h on stream the used catalyst sample consisted of Fe₃O₄ and iron carbide phases (Run SB-2832).

After the pretreatment with syngas (Run SA-3172) the following bulk iron phases were identified: magnetite, iron oxide and iron carbides. After 223 h on stream, in addition to these phases an iron carbonate (siderite) was also detected. After hydrogen regeneration at 223 h, the peaks associated with iron carbonate have disappeared (227 h, and 340 h on stream), whereas magnetite and iron carbides were present in these samples.

Magnetite and siderite were the only phases identified by XRD in the used catalyst sample at the end of Run SB-3362 (CO pretreatment) .

III-5.2.2 Reaction Results

Selected results obtained from all the mass balances, both at the baseline and higher pressure conditions, are summarized in Table III-5.2 for test SB-2832, Table III-5.3 for SA-3172 and Table III-5.4 for SB-3362, respectively.

Activity and Stability

The catalyst activity following the pretreatment is compared in Figures III-5.2 and III-5.3 for the three tests. Results from testing at the baseline conditions and at higher pressure are included. It can be seen that after H₂ reduction (SB-2832) the initial (H₂+CO) conversion was high (84 % at 17 h on stream). The syngas conversion gradually decreased with time to 77 % at 263 h, for a loss in conversion of about

Table III-5.2 Summary of Slurry Reactor Test Results for Pretreatment Effect Study with
100 Fe/5 Cu/4.2 K/16 SiO₂ Catalyst (Hydrogen Reduction)

Test designation	SB-2832					
Temperature, °C	260	260	260	260	260	260
Pressure, MPa	1.48	1.48	1.48	1.48	2.17	2.17
SV, NI/g-cat/h	1.50	1.50	1.50	1.50	2.20	2.20
Time-on-stream, h	41	92	139	210	308	355
CO conversion, %	87.5	86.4	85.5	83.1	78.0	77.9
(H ₂ +CO) conversion, %	81.1	80.3	79.5	78.7	74.6	74.1
STY, mmol/g-cat/h	54.1	54.2	53.3	53.1	73.0	73.2
k, mmol/g-Fe/h/MPa	268	265	260	277	254	244
(H ₂ /CO) usage ratio	0.58	0.58	0.58	0.59	0.59	0.58
(H ₂ /CO) exit ratio	1.59	1.46	1.40	1.12	0.93	0.95
$K_p = P_{CO_2} P_{H_2} / P_{CO} P_{H_2O}$	37.4	36.9	28.4	20.4	22.2	18.5
mmol CH ₄ /g-Fe/h	1.28	1.33	1.34	1.25	1.79	1.67
Hydrocarbon selectivity, wt%						
CH ₄	4.5	4.7	4.7	4.5	4.8	4.4
C ₂ -C ₄	15.2	15.2	15.3	16.6	17.1	17.1
C ₅ -C ₁₁	25.5	21.8	20.6	22.6	29.8	22.6
C ₁₂ +	54.8	58.3	59.4	56.3	48.3	55.9
Chain growth parameter, α_{1-10}^a	0.73	0.70	0.71	0.72	0.74	0.71
Olefin content, wt%						
C ₂ -C ₄	66.3	68.0	66.9	69.6	69.9	71.7
C ₅ -C ₁₁	69.8	72.0	73.6	74.5	72.8	73.7

H₂/CO=0.67 for all tests. ^a: Parameter estimated from products with carbon number in the range C₁-C₁₀.

Table III-5.2 (cont'd) Summary of Slurry Reactor Test Results for Pretreatment Effect Study with 100 Fe/5 Cu/4.2 K/16 SiO₂ Catalyst (Hydrogen Reduction)

Test designation	SB-2832				
Temperature, °C	260	260	260	260	260 ^b
Pressure, MPa	2.17	2.17	2.17	2.17	1.48
SV, Nl/g-cat/h	2.20	2.20	1.80	1.80	1.46
Time-on-stream, h	427	498	570	641	713
CO conversion, %	74.4	71.3	79.8	76.5	71.3
(H ₂ +CO) conversion, %	70.9	68.7	75.7	72.9	67.4
STY, mmol/g-cat/h	69.0	67.0	60.9	59.2	44.1
k, mmol/g-Fe/h/MPa	221	214	203	192	199
(H ₂ /CO) usage ratio	0.60	0.62	0.61	0.60	0.59
(H ₂ /CO) exit ratio	0.91	0.83	1.03	0.93	0.91
$K_p = P_{CO_2} P_{H_2} / P_{CO} P_{H_2O}$	18.4	15.4	20.6	20.6	24.6
mmol CH ₄ /g-Fe/h	1.59	1.52	1.43	1.55	1.02
Hydrocarbon selectivity, wt%					
CH ₄	4.4	4.3	4.7	5.3	4.5
C ₂ -C ₄	16.3	16.0	15.8	17.4	15.9
C ₅ -C ₁₁	23.1	22.5	21.3	24.7	23.6
C ₁₂ +	56.2	57.2	58.2	52.6	55.9
Chain growth parameter, α_{1-10} ^a	0.73	0.72	0.69	0.71	0.72
Olefin content, wt%					
C ₂ -C ₄	72.1	73.9	70.8	71.1	76.3
C ₅ -C ₁₁	73.1	73.2	72.9	73.3	75.9

H₂/CO=0.67 for all tests. ^a: Parameter estimated from products with carbon number in the range C₁-C₁₀.

^b: Following H₂ regeneration

Table III-5.3 Summary of Slurry Reactor Test Results for Pretreatment Effect Study with 100 Fe/5 Cu/4.2 K/16 SiO₂ Catalyst (Syngas Pretreatment)

Test designation	SA-3172					
	260	260	260	260	260	260 ^b
Temperature, °C	260	260	260	260	260	260 ^b
Pressure, MPa	1.48	1.48	2.17	2.17	1.48	1.48
SV, Nl/g-cat/h	1.44	1.44	2.10	2.10	1.44	1.48
Time-on-stream, h	49	95	152	177	215	272
CO conversion, %	89.4	80.9	80.6	79.8	79.1	76.9
(H ₂ +CO) conversion, %	85.6	77.9	78.9	78.6	77.1	75.3
STY, mmol/g-cat/h	55.2	50.1	73.0	72.9	49.0	50.3
k, mmol/g-Fe/h/MPa	372	326	340	345	316	295
(H ₂ /CO) usage ratio	0.61	0.62	0.63	0.64	0.62	0.63
(H ₂ /CO) exit ratio	1.29	0.93	0.82	0.77	0.83	0.78
$K_p = P_{CO_2} P_{H_2} / P_{CO} P_{H_2O}$	27.0	31.4	14.3	11.9	22.5	22.5
mmol CH ₄ /g-Fe/h	2.58	2.81	4.01	3.71	2.62	3.74
Hydrocarbon selectivity, wt%						
CH ₄	9.5	11.3	11.1	10.4	10.8	15.4
C ₂ -C ₄	17.0	19.4	18.8	17.6	18.3	21.3
C ₅ -C ₁₁	19.3	20.3	14.3	15.8	18.2	19.9
C ₁₂ +	54.2	49.0	55.8	56.2	52.7	43.4
Chain growth parameter, α_{1-10} ^a	0.59	0.61	0.58	0.60	0.60	0.58
Olefin content, wt%						
C ₂ -C ₄	53.5	55.8	59.1	60.8	61.8	55.5
C ₅ -C ₁₁	77.8	77.8	79.6	79.4	79.3	78.2

H₂/CO=0.67 for all tests. ^a: Parameter estimated from products with carbon number in the range C₁-C₁₀.

^b: Following H₂ regeneration.

Table III-5.4 Summary of Slurry Reactor Test Results for Pretreatment Effect Study with
100 Fe/5 Cu/4.2 K/16 SiO₂ Catalyst (CO Pretreatment)

Test designation	SB-3362					
Temperature, °C	260	260	260	260	260	260
Pressure, MPa	1.48	1.48	1.48	2.17	2.17	1.48
SV, NI/g-cat/h	1.50	1.50	1.50	2.20	2.20	1.50
Time-on-stream, h	95	144	193	265	384	432
CO conversion, %	77.5	76.1	78.1	69.4	67.6	72.9
(H ₂ +CO) conversion, %	74.6	72.9	74.0	67.7	66.1	69.9
STY, mmol/g-cat/h	50.1	49.0	50.0	67.2	65.1	47.3
k, mmol/g-Fe/h/MPa	246	244	247	221	221	225
(H ₂ /CO) usage ratio	0.60	0.60	0.58	0.63	0.63	0.59
(H ₂ /CO) exit ratio	0.88	0.89	0.97	0.76	0.74	0.84
$K_p = P_{CO_2} P_{H_2} / P_{CO} P_{H_2O}$	9.16	9.57	12.1	6.39	5.62	11.1
mmol CH ₄ /g-Fe/h	0.83	0.78	0.81	0.93	0.88	0.71
Hydrocarbon selectivity, wt%						
CH ₄	3.5	3.5	3.5	3.0	2.8	3.2
C ₂ -C ₄	16.6	15.6	15.6	14.6	14.2	13.6
C ₅ -C ₁₁	22.6	19.5	22.0	17.9	20.1	19.1
C ₁₂ +	57.3	61.4	58.9	64.5	62.9	64.1
Chain growth parameter, α_{1-10}^a	0.73	0.71	0.76	0.74	0.77	0.74
Olefin content, wt%						
C ₂ -C ₄	74.1	75.2	74.2	77.9	79.2	76.8
C ₅ -C ₁₁	80.5	80.3	79.2	80.3	80.3	80.5

H₂/CO=0.67 for all tests. ^a: Parameter estimated from products with carbon number in the range C₁-C₁₀.

0.68% per day. During testing at 2.17 MPa and 2.2 NI/g-cat/h (same absolute pressure to gas space velocity ratio, which results in the same contact time as at the baseline conditions), the syngas conversion continued to decrease gradually with time. For example, at 284 h and 480 h on stream, the syngas conversion was 74 and 69 %, respectively. Regeneration with H₂ at 666 h on stream could not recover the activity. After the regeneration, the (H₂+CO) conversion was only 68 % at the baseline conditions (not shown in Figure III-5.2).

In test SA-3172 (syngas pretreatment) the (H₂+CO) conversion was 84 - 87 % during the first 55 h on stream. At this time the Autoclave reactor head temperature was decreased from 260 to 210°C in an attempt to control the unusually high methane selectivity (about 9.5 wt%). Following this the syngas conversion decreased and stabilized at about 80 % (70 - 105 h on stream). After changing the reaction pressure and gas space velocity to 2.17 MPa and 2.1 NI/g-cat/h, respectively, the syngas conversion first increased to 83 % at 115 h, then gradually decreased and leveled to about 79 % at 194 h. Upon returning to the baseline conditions at 200 h on stream, the (H₂+CO) conversion stabilized at 78 %. The latter value is comparable to those obtained between 80 -100 h on stream. Regeneration with H₂ at 250°C, 1.48 MPa, 2000 cc/min for 4 h resulted in a temporary increase of conversion followed by a decline to 74% at 336 h on stream.

Catalyst activity immediately after CO pretreatment in test SB-3362 was low (not shown in Figure III-5.2) because of the loss of slurry liquid as stated earlier, and the reaction was temporarily interrupted. The catalyst activity increased quickly after a sufficient amount of liquid was added and synthesis gas flow resumed at 39 h as shown in Figure III-5.2. The (H₂+CO) conversion was fairly stable (71 - 74 %) between 70 and 230 h on stream. During testing at 2.17 MPa and 2.2 NI/g-cat/h (the same P/SV ratio as at the baseline conditions), the syngas conversion was lower, about 65 - 67 %. Upon returning to the baseline conditions (407-488 h) the (H₂+CO) conversion

Figure III-5.2 Effect of pretreatment conditions on conversion and catalyst stability (FT synthesis conditions: $T=260^\circ\text{C}$, $(\text{H}_2/\text{CO})=0.67$; open symbol: $P=1.48$ MPa, $\text{SV}=1.5$ NI/g-cat/h; closed symbol: $P=2.17$ MPa, $\text{SV}=2.2$ NI/g-cat/h).

increased to 70 %. The latter value is comparable to those obtained between 70 and 230 h on stream. The catalyst activity was fairly stable during the test after the initial upset, and the loss of conversion was only 0.24 % per day. However, the catalyst was not properly activated because of the loss of the liquid medium, and interruption of synthesis during the early part of the testing may have had a detrimental effect on catalyst activity.

The effect of pretreatment procedure on catalyst activity, measured by magnitude of the apparent first order reaction rate constant, is shown in Figure III-5.3. The syngas pretreated catalyst was the most active during FT synthesis, whereas activities of hydrogen and carbon monoxide pretreated catalysts were similar to each other.

Following the syngas pretreatment the apparent first order rate constant was 372 mmol/g-Fe/h/MPa, before decreasing the reactor head temperature. After lowering of the reactor head temperature to 210°C, the value of k decreased to 326 mmol/g-Fe/h/MPa at 95 h on stream, and then varied between 316 and 345 mmol/g-Fe/h/MPa up to 215 h on stream. This shows that the catalyst activity was stable, and there was no deactivation during testing under higher pressure. However, some deactivation was noted at 272 h on stream ($k = 295$ mmol/g-Fe/h/MPa).

Hydrogen reduced catalyst was rather stable during the first 210 h of testing at the baseline conditions. The apparent rate constant varied between 265 and 277 mmol/g-Fe/h/MPa during this time period, but it decreased significantly during testing at higher pressure (263-526 h). The rate constant decreased to 214 mmol/g-Fe/h/MPa at 498 h, and further to 192 mmol/g-Fe/h/MPa at 641 h on stream (not shown in Figure III-5.3). After the regeneration the rate constant increased slightly to 199 mmol/g-Fe/h/MPa at 713 h. Catalyst deactivation rate, during 641 h of testing, was about 1% per day. Here, the deactivation rate is expressed as a percent loss of initial k value (at 41 h on stream).

Figure III-5.3 Effect of pretreatment conditions on the apparent first order reaction rate constant (FT synthesis conditions: $T=260^{\circ}\text{C}$, $(\text{H}_2/\text{CO})=0.67$; open symbol: $P=1.48\text{ MPa}$, $\text{SV}=1.5\text{ NI/g-cat/h}$; closed symbol: $P=2.17\text{ MPa}$, $\text{SV}=2.2\text{ NI/g-cat/h}$).

The CO pretreated catalyst was very stable during the first 200 h at the baseline conditions, and the apparent reaction rate constant was about 245 mmol/g-Fe/h/MPa. Some deactivation occurred during testing at higher pressure, and k decreased to about 220 mmol/g-Fe/h/MPa during testing at 2.17 MPa (250 - 400 h). The rate constant was 225 mmol/g-Fe/h/MPa after returning to the baseline conditions (432 h). This corresponds to 8% loss in activity over 337 h of testing, or deactivation rate of 0.57% per day.

The reactor productivity increased in all three tests during testing at higher pressure (Tables III-5.2 to III-5.4). An increase in reaction pressure of 46.5% (from 1.48 to 2.17 MPa) accompanied by simultaneous equivalent increase in gas space velocity (from 1.5 to 2.2 NL/g-cat/h) resulted in increase of the space-time-yield (STY) ranging from 32% (H_2 reduced catalyst) to 47% (syngas pretreated catalyst). Obviously, these results provide a strong incentive for carrying FT synthesis at higher reaction pressures and gas space velocities. This, however, may result in faster catalyst deactivation and thus shorter catalyst lifetime.

The water-gas-shift (WGS) activity was high after H_2 reduction (SB-2832), and the usage ratio at baseline conditions was about 0.58-0.59 (Figure III-5.4a). Following syngas pretreatment (SA-3172) the usage ratio was 0.61-0.63 at the same conditions, which indicates that WGS activity was lower (higher usage ratio) in comparison with SB-2832. Due to differences in WGS activities the partial pressure of H_2 was significantly lower in run SA-3172 than in run SB-2832. The apparent rate constant was about 25 % higher after syngas pretreatment than after H_2 reduction, even though the total syngas conversion was approximately the same (~80 %) in these two tests. The usage ratio after CO pretreatment was about 0.58 - 0.60 at the baseline conditions. After increasing reaction pressure to 2.17 MPa, the usage ratio increased in all three tests, i.e. the WGS activity decreased. This may be attributed to catalyst deactivation (Runs SB-2832 and SB-3362) or higher FT activity (Run SA-3172).

Figure III-5.4 Effect of pretreatment conditions on: (a) (H₂/CO) usage ratio; (b) (H₂/CO) exit ratio (FT synthesis conditions: T=260°C, (H₂/CO)=0.67; open symbol: P=1.48 MPa, SV=1.5 NI/g-cat/h; closed symbol: P=2.17 MPa, SV=2.2 NI/g-cat/h).

Since the H_2/CO usage ratio was less than the feed ratio, the exit H_2/CO ratio was greater than the H_2/CO feed ratio. The exit ratio was high initially after H_2 and syngas pretreatments (1.3 - 1.6), but decreased in both tests to 0.8 - 0.9 as the conversion decreased with time. The values of the exit H_2/CO ratio were lower, between 0.7 and 1, in Run SB-3362 (CO pretreatment) as shown in Figure III-5.4b.

Selectivity

Hydrocarbon and Carbon Number Product Distributions

Hydrocarbon selectivities as a function of TOS for each of the pretreatment procedures are shown in Figure III-5.5. In these figures, cumulative values are shown for lumped product distributions of selected product groups: methane, C_1 - C_4 , and C_1 - C_{11} . Distances between numerical values for these groups show mass percentages of: methane, C_2 - C_4 (light gases), C_5 - C_{11} (gasoline) and C_{12+} (diesel and wax) hydrocarbon products. There were no significant changes in hydrocarbon product distributions during testing at the baseline conditions in all three tests. An increase in reaction pressure, from 1.48 to 2.17 MPa, either had no effect on hydrocarbon product distribution (SB-2832) or resulted in slight decrease of low molecular products (Runs SA-3172 and SB-3362) and the corresponding increase of C_{12+} products. The effect of pressure was the most pronounced in run SB-3362 (CO pretreatment), in which methane selectivity decreased from 3.5 to 2.9 wt% whereas C_{12+} increased from 59.5 to 63.7 %. In runs SB-2832 and SA-3172, the catalyst was also regenerated with H_2 during the test. In run SB-2832 hydrocarbon selectivity did not change after regeneration with H_2 at 240°C for 1 h (at 666 h on stream). However, hydrocarbon selectivity shifted significantly toward gaseous hydrocarbons in run SA-3172 after regeneration with H_2 at 250°C for 4 h (at 223 h on stream), as shown in Figure III-5.5b. Regeneration conditions were more severe in the latter case, which is probably the reason for the observed change in hydrocarbon selectivity.

Figure III-5.5 Effect of time-on-stream on hydrocarbon product distribution following different pretreatment procedures: (a) SB-2832; (b) SA-3172; (c) SB-3362 (FT synthesis conditions: $T=260^\circ\text{C}$, $(H_2/CO)=0.67$; open symbol: $P=1.48$ MPa, $SV=1.5$ NI/g-cat/h; closed symbol: $P=2.17$ MPa, $SV=2.2$ NI/g-cat/h).

The effect of pretreatment procedure on hydrocarbon selectivity is shown in Figure III-5.6. In this figure the average values from mass balances at the baseline conditions (up to 240 h on stream) are used for comparison. The catalyst had low methane and high C_{12+} selectivity after either CO or H_2 pretreatment. The average hydrocarbon product distribution at the baseline conditions after CO pretreatment was: $CH_4 = 3.5$ wt%, $(C_2-C_4) = 15.8$ %, $(C_5-C_{11}) = 21.2$ % and $C_{12+} = 59.5$ %; whereas after H_2 reduction it was: $CH_4 = 4.6$ wt%, $(C_2-C_4) = 15.5$ %, $(C_5-C_{11}) = 22.0$ % and $C_{12+} = 57.9$ %. Hydrocarbon selectivities were similar after these two pretreatment procedures. On the other hand, in run SA-3172, following syngas pretreatment, the catalyst produced significantly more methane and light gases. In this test the average hydrocarbon product distribution at the baseline conditions was: $CH_4 = 10.4$ wt%, $(C_2-C_4) = 18.2$ %, $(C_5-C_{11}) = 19.8$ % and $C_{12+} = 51.6$ %. This is completely unexpected, based on our previous studies with several precipitated iron catalysts. The syngas pretreated catalysts normally do not produce high yields of methane and gaseous hydrocarbons (e.g. see Bukur et al., 1989a, and Sections III-2 and III-4 of this report).

Typical carbon number distribution at the baseline process conditions, including the analyzed wax withdrawn from the slurry reactor, is presented in Figure III-5.7. Some positive deviations from the ASF distribution are noted in C_{11} to C_{20} carbon number range in two of the tests (SB-2832 and SA-3172). We are not certain whether this is due to the intrinsic catalytic selectivity or some experimental artifacts (e.g. loss of products and errors in analysis). The same trend was obtained in several other mass balances in each of these two tests. Experimental data were fitted with a three parameter model of Huff and Satterfield (1984). The model parameters were estimated by a nonlinear regression, and their numerical values are summarized in Table III-5.5 together with 95% confidence interval limits for these parameters.

Figure III-5.6 Effect of pretreatment conditions on hydrocarbon selectivity at the baseline conditions: (a) SB-2832; (b) SA-3172; (c) SB-3362.

Figure III-5.7 Carbon number product distribution at the baseline conditions: (a) SB-2832; (b) SA-3172; (c) SB-3362. (closed circles: included point; open circles: excluded point for parameter estimation).

Olefin Selectivity

The effects of time-on-stream and reaction pressure on olefin selectivity are illustrated in Figure III-5.8. In general, the olefin selectivity was fairly stable during testing at the baseline process conditions in all three tests. The olefin content exhibited a broad maximum in C₃ - C₇ carbon number range, which is typical for iron FT catalysts. This particular shape is due to high hydrogenation activity of ethylene, and high adsorptivity and long residence time of high molecular weight olefins (C₈₊). The olefin content was higher in all three tests during testing at higher pressure (2.17 MPa, SV = 2.2 NI/g-cat/h), which may be attributed to decrease in H₂/CO ratio with increase in pressure.

Table III-5.5 Chain Growth Probability Factors for Different Pretreatment Procedures^a

Test	TOS, h	α_1 (95% CI) ^b	α_2 (95% CI) ^b	β (95% CI) ^b
SB-2832	92	0.65 (0.63-0.66)	0.93 (0.92-0.94)	0.81 (0.80-0.83)
	355	0.68 (0.65-0.69)	0.93 (0.93-0.94)	0.82 (0.81-0.84)
SA-3172	95	0.59 (0.57-0.61)	0.92 (0.91-0.93)	0.93 (0.92-0.94)
	152	0.55 (0.52-0.58)	0.92 (0.91-0.93)	0.88 (0.86-0.90)
	272	0.58 (0.56-0.60)	0.93 (0.92-0.93)	0.93 (0.92-0.94)
SB-3362	95	0.70 (0.69-0.71)	0.93 (0.93-0.93)	0.89 (0.88-0.90)
	144	0.67 (0.66-0.68)	0.94 (0.94-0.94)	0.87 (0.86-0.88)
	265	0.65 (0.65-0.65)	0.93 (0.93-0.93)	0.77 (0.76-0.78)
	384	0.70 (0.69-0.71)	0.93 (0.93-0.93)	0.74 (0.73-0.75)

^a Parameters estimated from products with carbon number in the range C₁-C₄₅.

^b 95% confidence interval.

Figure III-5.8 Effects of time-on-stream and reaction pressure on olefin selectivity: (a) SB-2832; (b) SA-3172; (c) SB-3362.

Since variations in olefin content with time were small during testing under the baseline conditions the average values were used to examine the effect of pretreatment conditions on olefin selectivity (Figure III-5.9). In general, the olefin content was higher when the catalyst was activated with CO or syngas than with H₂, and such a trend is in agreement with results obtained in our studies with other iron FT catalysts. Olefin contents of C₂ - C₄ hydrocarbons were low following the syngas pretreatment, which is consistent with high methane selectivity during this test, but not with the data for C₅₊ hydrocarbons (Figure III-5.9).

2-Olefin Selectivity

Variations in 2-olefin selectivity, which is a measure of catalyst isomerization activity, with time are shown in Figure III-5.10 for all three STSR tests. During testing at the baseline process conditions the 2-olefin selectivity was fairly stable. Upon increasing reaction pressure and gas space velocity to 2.17 MPa and 2.2 NI/g-cat/h, respectively, the 2-olefin selectivity remained unchanged in run SA-3172 (syngas pretreatment), but decreased slightly in tests SB-2832 (H₂ reduction) and SB-3362 (CO pretreatment). This is consistent with observed trends in olefin selectivity, i.e. secondary hydrogenation and isomerization reactions are less pronounced at higher reaction pressure. Also, in run SB-2832 the 2-olefin selectivity decreased with time during testing at higher pressure (see data at 308 and 498 h on stream in Figure III-5.10a).

There were no significant differences in 2-olefin selectivities after different pretreatment procedures as shown in Figure III-5.11. The average values of 2-olefin selectivities during testing at the baseline conditions were used for this comparison. This catalyst has rather high olefin isomerization activity, especially for C₉₊ hydrocarbons.

Figure III-5.9 Effect of pretreatment conditions on olefin selectivity at the baseline conditions.

Figure III-5.10 Effect of time-on-stream and reaction pressure on 2-olefin selectivity: (a) SB-2832; (b) SA-3172; (c) SB-3362.

Figure III-5.11 Effect of pretreatment conditions on 2-olefin selectivity at the baseline conditions.

III-5.3 Summary

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 NI/g-cat/h to 2.17 MPa and 2.2 NI/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 (Hall et al., 1952; Anderson, 1956; Dry, 1981; Bukur and Brown, 1987). 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.

III-5.4 References

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IV. DEVELOPMENT OF IMPROVED IRON-SILICA CATALYSTS

Introduction

Supported catalyst systems with high support-to-metal ratios have not been overly effective in yielding good Fischer-Tropsch synthesis performance. In the slurry phase process, supported catalysts reduce the bulk concentration of metal and thus may hinder mass transfer of gas to liquid as solids loadings are increased to maintain metal concentrations. On the other hand, supported systems may actually increase the concentration of active metal sites by maintaining higher metal dispersions. The nature of the support is also important, since acidic sites on the support can render basic promoters like potassium ineffective, preventing interaction between promoter and metal. Previous work at the SASOL (Dry, 1981) in fixed bed reactors, examined the effects of promoters and supports on the performance of Ruhrchemie-type precipitated Fe catalysts. In one set of experiments, a series of Fe/Cu/K₂O precipitates were prepared using Cr₂O₃, MgO, Al₂O₃ or ZnO in place of the silica. None of these catalysts was as active as the standard SiO₂ containing material. An unsupported composition was also less active. Compositions containing both SiO₂ and a second support material also showed lower performance. Of all the supports, small amounts of added Al₂O₃ resulted in the lowest wax selectivity without excessive deactivation. This concept could be used to control selectivity to some extent.

A brief examination of precipitated iron catalysts containing silica or alumina as binder/support has been made in our laboratory at TAMU as a part of the DOE Contract DE-AC22-85PC80011 (Bukur et al., 1989b, 1990b). Six catalysts were employed in this study: an unsupported iron/copper/potassium catalyst (100 Fe/5 Cu/4.2 K in parts per weight), three silica-supported catalysts (100 Fe/5 Cu/4.2 K/xSiO₂, where x=8, 24 and 100), and two alumina-supported catalysts (100 Fe/5 Cu/4.2 K/xAl₂O₃, where x=8 and 24). The major findings from catalytic tests in fixed bed reactors are summarized below.

Addition of silica or alumina to the precipitated unsupported iron catalyst (100 Fe/5 Cu/4.2 K) influenced catalyst activity, stability, and selectivity during Fischer-Tropsch synthesis. Changes in catalyst performance became pronounced only at sufficiently high binder (support) concentrations and may be attributed to interactions between support and potassium and/or between metal and support.

The specific FTS activity decreased with increasing support content which may be ascribed to lower degree of iron reduction following the catalyst pretreatment with CO and to the reduction in the effective potassium content of the catalyst. However, the catalyst stability improved with addition of silica either because of stabilization of iron crystallites during synthesis or due to a decrease in the carbon deposition rate resulting from partial neutralization of potassium promoter by acidic sites on silica (i.e. reduction in surface basicity). It was also found that the WGS activity decreased with increasing silica content of the catalyst (catalysts with 24 and 100 g of SiO₂ per 100 g of Fe). This is attributed to reduction in surface basicity and decreased Fe/K contact due to the high catalyst surface area.

Product selectivities also changed markedly with increasing silica content of the catalyst, whereas no significant changes were observed with the two alumina-containing catalysts. The total olefin content and the fraction of branched hydrocarbons both decreased, whereas the fraction of internal olefins increased with an increase in the silica content of the catalyst. These observations reflect the expected trends arising from the reduction of surface basicity of the catalyst with increasing silica content and are in agreement with results obtained in previous studies with similar catalysts (Dry, 1981; Egiebor and Cooper, 1985)

Two of the three silica containing catalysts synthesized at TAMU (8 and 24 parts of SiO₂) and the Ruhrchemie catalyst (100 Fe/5 Cu/4.2 K/25 SiO₂) were also evaluated at a fixed set of process conditions over relatively long periods of time on stream (250-

480 hours) to determine their activity and selectivity maintenance, and the rate of deactivation (Bukur et al., 1989b).

The initial activity of the catalyst containing 8 parts of SiO_2 was much higher than that of the other two catalysts, but after 120 hours on stream it declined rapidly with time on stream. The catalyst containing 24 parts of SiO_2 was remarkably stable over 480 hours on stream. Its activity declined by 5.6% only over a 400 hour period and was about 20% higher than that of the commercial Ruhrchemie catalyst. The hydrocarbon product distributions obtained in the tests with the Ruhrchemie catalyst, and the catalyst containing 24 parts of SiO_2 were very similar with either $\text{H}_2/\text{CO}=1.0$ or $\text{H}_2/\text{CO}=0.67$ synthesis gas feed ratios. The catalyst containing 8 parts of SiO_2 produced less light hydrocarbons but its stability needs to be improved.

These promising results with silica containing catalysts warrant more detailed studies to develop catalysts suitable for commercial use. Further improvements can be achieved by judicious choice of silica content, which has significant effect on catalyst activity and stability, and promoter levels (particularly potassium) which have significant effect on product selectivity. Results from tests of baseline catalysts and catalysts synthesized at TAMU in stirred tank slurry reactors are described and discussed in the following sections of this report.

IV-1 Baseline Catalyst Testing

In order to evaluate advances achieved in catalyst synthesis, two baseline catalysts (Ruhrchemie and United Catalysts, Inc.) were tested in stirred tank reactors. In all tests a catalyst was crushed and sieved to either 270/325 mesh (44-53 μm in diameter) or less than 270 mesh size, prior to loading to a reactor. A pre-purified normal octacosane was used as the liquid (slurry) medium in tests of the Ruhrchemie catalyst, whereas Ethylflo 164 oil was used in tests of UCI catalysts. Two tests were conducted, during this contract, with the Ruhrchemie catalyst. In the test designated SB-0440, the catalyst was reduced with hydrogen externally, in a fixed bed reactor unit, and then transferred into the reactor in an inert gas atmosphere. A hot spot was detected during reduction with hydrogen in the fixed bed reactor (270°C instead of 220°C), which was quickly quenched by helium flow. During the test we have encountered several problems with product collection and handling, resulting in inaccurate mass and atomic balance closures. This test lasted 550 h, and the catalyst activity was stable throughout the test, however, product selectivities are not considered to be sufficiently accurate (Quarterly Technical Progress Report, January 1 - March 31, 1991). Results from this test will not be discussed here. In the second test, Run SB-1370, the catalyst was reduced in-situ with hydrogen. Results from this test, as well as from the test SA-0888 (CO pretreated catalyst) have been described and discussed in section III-4 of this report. The latter test (SA-0888) was completed during the course of our work on the previous DOE contract, and the complete results from this test were reported elsewhere (Bukur et al., 1989b; 1990c). Selected results from this test are also presented in this report for the sake of completeness.

IV-1.1 Testing of UCI Catalysts

Three tests were conducted with catalysts synthesized at United Catalysts, Inc. (UCI). These catalysts were potential candidates for use in a slurry bubble column

reactor Fischer-Tropsch demonstration run at LaPorte, Texas in August 1992. Their compositions and BET surface areas and pore volumes, as supplied by manufacturer, are listed in Table IV-1.1. There are significant differences in promoter concentrations and physical properties among different catalysts.

In all three tests the catalysts were pretreated using a procedure similar to those used in slurry bubble column reactor tests at Mobil (Kuo, 1983; 1985). Briefly, after loading of a catalyst and the initial slurry medium, the reactor was sealed and pressurized to 153 psig with nitrogen, and stirring was initiated at 1100 rpm. Then the slurry temperature was raised linearly to 280°C in 3 hours under nitrogen flow. When 280°C was reached, the nitrogen flow was replaced with synthesis gas (H_2/CO molar ratio of about 0.67) at a flow rate of 2 NI/g-Fe/h for 12 hours. Results from individual tests are described first, followed by comparison of performance of UCI catalysts, as well as between UCI catalysts and the Ruhrchemie catalyst.

IV-1.1.1 Run SA-3391 with UCI L-3950 Catalyst

After the pretreatment, the catalyst was initially tested at 265°C (actual temperature 270°C, see below), 290 psig (2.07 MPa), 3 NI/g-Fe/h and $H_2/CO = 0.7$. Changes in syngas conversion and methane selectivity with time-on-stream are shown in Figure IV-1.1. (H_2+CO) conversion increased gradually from 76% at 3 h to 80% at 24 h, and then remained stable during the next 80 h of testing. During the same time period methane selectivity increased markedly from 4% to 7%. At about 103 h, gas flow rate was decreased to give the gas space velocity of 2.4 NI/g-Fe/h in order to test the catalyst under the same process conditions as those employed at Universal Oil Products Inc. (UOP). Consequently (H_2+CO) conversion increased to 82-83% and remained stable during the next 60 h of testing. Since our values of syngas conversion (83%) and methane selectivity (~8%) were significantly higher than those obtained at UOP (70 and 4%, respectively) we suspected that there may be a problem with our

Table IV-1.1 Physico-Chemical Properties and Test Designations for UCI Catalysts.

RUN NUMBER	SA-3391	SA-1532	SA-2052
CATALYST DESIGNATION	L-3950	1207-175A	L-3950 (batch 3)
CATALYST COMPOSITION (wt.-%)			
K ₂ O	5.1	0.8	1.7
SiO ₂	8.3	2.5	4.9
CuO	2.6	1.1	5.0
Fe ₂ O ₃	69.6	86.9	76.6
LOI	14.8	9.5	11.8
CATALYST COMPOSITION			
Fe	100.0	100.0	100.0
Cu	4.3	1.4	7.5
K	8.7	1.1	2.6
SiO ₂	17.0	4.1	9.2
SURFACE AREA (m ² /g)	251	167	136
PORE VOLUME (cc/g)	0.50	0.18	0.30

Figure IV-1.1 (H₂+CO) conversion (a) and methane selectivity (b) as a function of time on stream for Run SA-3391.

instruments and/or apparatus. The ($\text{H}_2 + \text{CO}$) conversion decreased to 79%, and methane selectivity to 4.5%, when the temperature of the reactor head was lowered from 265 to 245°C at 170 h on stream. After this run, a blank test was performed which showed significant FT activity. After the blank test the reactor shaft was disassembled and residual catalyst was found in the space between the stirrer shaft and its housing. This residual catalyst was responsible for higher than expected syngas conversion and methane selectivity in Run SA-3391. By lowering the reactor head temperature, the reaction in the stirrer shaft housing was quenched.

At about 170 h on stream, a malfunctioning of the temperature readout device was detected, and at 196 h the reactor temperature was brought to its desired value of 265°C, and at 212 h the ($\text{H}_2 + \text{CO}$) conversion and methane selectivity decreased to 75% and 4%, respectively. During the remaining 100 h of testing, the conversion decreased slowly with time, reaching 71.5% at 310 h, whereas methane selectivity remained stable at about 4%. The latter values of syngas conversion and methane selectivity, are similar to those obtained at UOP.

Water-gas-shift activity was high and fairly stable throughout the test. The usage ratio varied between 0.56 and 0.61.

The information on hydrocarbon distribution obtained during six mass balances can be found in Table IV-1.2. The average hydrocarbon product distribution from the last two mass balances made at 265°C, 290 psig, 2.4 NI/g-Fe/h, $\text{H}_2/\text{CO} = 0.67\text{-}0.70$ was: $\text{CH}_4 = 4.4$; $(\text{C}_2 - \text{C}_4) = 16.5$; $(\text{C}_5\text{-C}_{11}) = 23.6$ and $\text{C}_{12+} = 55.5$ wt%. Olefin content increased, whereas 2-olefin content decreased slightly with time (Table IV-1.2).

A typical carbon number product distribution, for products collected at 297 h on stream, is shown in Figure IV-1.2. The data are well represented by a three parameter model of Huff and Satterfield (1984). Numerical values of parameters are shown in Figure IV-1.2. Results of analysis of the reactor wax withdrawn from the reactor at 297 h are shown in Figure IV-1.3 in the form of ASF plot. Products with carbon number greater

Table IV-1.2 Summary of Slurry Reactor Test Results for Run SA-3391.

Period	1	2	3	4	5	6
Date	12/08/91	12/10/91	12/12/91	12/14/91	12/16/91	12/19/91
Time on Stream (h)	43.0	91.0	139.0	187.0	235.0	297.0
Balance Duration (h)	7.0	6.0	6.0	6.0	6.0	10.0
Average Temperature (°C)	270.	270.	270.	270.	265.	265.
Pressure (MPa)	2.10	2.10	2.10	2.10	2.10	2.10
H ₂ /CO Feed Ratio	.698	.698	.698	.698	.698	.669
Space Velocity (NI/g-cat·h) ^a	1.71	1.71	1.37	1.37	1.37	1.37
Space Velocity (NI/g-Fe·h)	2.99	2.99	2.39	2.39	2.39	2.40
GHSV (h ⁻¹) ^b	101.	101.	74.2	74.2	74.2	67.5
CO Conversion (%)	85.5	85.9	87.3	84.6	79.2	73.9
H ₂ +CO Conversion (%)	79.9	81.1	82.8	79.3	74.4	71.7
H ₂ /CO Usage	.587	.604	.612	.592	.595	.620
STY (mols H ₂ +CO/g-cat·h) ^a	.061	.062	.051	.048	.045	.044
$P_{CO_2} \cdot P_{H_2} / P_{CO} \cdot P_{H_2O}$	21.4	22.5	21.6	22.3	18.8	13.8
Weight % of Outlet						
H ₂	1.37	1.23	1.11	1.36	1.56	1.45
H ₂ O	1.60	1.45	1.53	1.46	1.37	1.28
CO	14.1	13.6	12.0	14.8	19.9	25.0
CO ₂	61.9	62.9	62.7	62.1	57.9	53.2
Hydrocarbons	10.0	10.9	12.1	10.9	9.63	10.1
Oxygenates	.218	.294	.368	.368	.413	.409
Wax ^c	10.7	9.72	10.2	9.07	9.27	8.56
Yield (g/Nm ³ H ₂ + CO Converted)						
CH ₄	12.2	14.9	17.2	10.3	9.91	8.45
C ₂ -C ₄ Hydrocarbons	30.6	32.6	36.7	34.8	33.8	32.0
C ₅ -C ₁₁ Hydrocarbons	34.3	38.2	42.1	44.8	42.3	52.0
C ₁₂ + Hydrocarbons	119.	109.	114.	104.	110.	111.
Wax ^c	101.	92.1	95.9	87.9	95.8	93.5
Oxygenates	2.06	2.78	3.47	3.56	4.27	4.47
Total	198.	198.	214.	197.	200.	208.
1+2 Olefins/ <i>n</i> -Paraffin Ratio						
C ₂	1.41	1.14	.871	1.59	2.38	2.50
C ₃	6.13	5.61	5.19	6.19	6.11	6.22
C ₄	5.41	5.01	4.78	5.57	5.61	5.48
C ₆	2.91	2.85	2.57	3.44	3.70	3.29
C ₁₀	2.28	2.08	2.25	2.69	2.96	2.68

^a Based on unreduced catalyst^b Based on static slurry volume^c Unanalyzed wax withdrawn from reactor

Table IV-1.2 (cont'd) Summary of Slurry Reactor Test Results for Run SA-3391.

Period	1	2	3	4	5	6
Weight % of Hydrocarbons						
CH ₄	6.20	7.64	8.19	5.30	4.56	4.15
Ethane	2.05	2.51	3.02	2.18	1.57	1.38
Ethylene	2.71	2.68	2.45	3.23	3.49	3.21
Propane	.915	1.04	1.15	1.04	1.01	.898
Propylene	5.35	5.57	5.70	6.14	5.89	5.33
<i>n</i> -Butane	.722	.832	.902	.829	.819	.762
1+2 Butenes	3.77	4.02	4.16	4.46	4.43	4.03
C ₄ Isomers	.0614	.0689	.0716	.0825	.0897	.0857
<i>n</i> -Pentane	.621	.767	.846	.732	.728	.707
1+2 Pentenes	2.98	3.17	3.26	3.62	3.69	3.37
C ₅ Isomers	.642	.693	.792	.837	.845	2.35
<i>n</i> -Hexane	.603	.703	.790	.729	.677	.820
1+2 Hexenes	2.10	2.18	2.34	2.76	2.50	2.82
C ₆ Isomers	.793	.824	.880	1.06	.927	1.04
<i>n</i> -Heptane	.510	.625	.680	.666	.587	.636
1+2 Heptenes	1.72	1.93	1.95	2.38	2.26	2.34
C ₇ Isomers	.680	.667	.686	.770	.559	.744
<i>n</i> -Octane	.452	.536	.577	.544	.470	.547
1+2 Octenes	1.29	1.50	1.45	1.84	1.71	1.77
C ₈ Isomers	.527	.726	.442	.622	.386	.588
<i>n</i> -Nonane	.350	.436	.464	.443	.402	.475
1+2 Nonenes	.907	1.02	1.07	1.32	1.26	1.40
C ₉ Isomers	.214	.294	.304	.418	.348	.503
<i>n</i> -Decane	.379	.476	.442	.490	.433	.527
1+2 Decenes	.852	.978	.981	1.30	1.26	1.39
C ₁₀ Isomers	.293	.375	.380	.492	.510	.789
<i>n</i> -Undecane	.383	.410	.422	.475	.419	.495
1+2 Undecenes	.859	.937	.918	1.20	1.22	1.43
C ₁₁ Isomers	.324	.331	.341	.437	.470	.784
C ₂ -C ₄	15.6	16.7	17.5	18.0	17.3	15.7
C ₅ -C ₁₁	17.5	19.6	20.0	23.1	21.7	25.5
C ₁₂ +	60.7	56.1	54.3	53.6	56.5	54.6
Wax ^c	51.6	47.3	45.6	45.4	49.0	45.9

^c Unanalyzed wax withdrawn from reactor

Figure IV-1.2. Carbon number product distribution for Run SA-3391 (TOS=297 h).

Figure IV-1.3 Carbon number distribution of wax product for Run SA-3391 (TOS=297 h).

than C_{20} can be fitted well with a straight line, giving the chain growth parameter of 0.93. This value is very close to the one obtained from the three parameter model ($\alpha_2 = 0.94$).

IV-1.1.2 Run SA-1532 with UCI 1207-175A Catalyst

After the pretreatment, the catalyst was tested at 265°C, 290 psig (2.07 MPa), 2.4 NL/g-Fe/h and $H_2/CO = 0.7$. Changes in syngas conversion and methane selectivity with time-on-stream are shown in Figure IV-1.4. The catalyst activity was not stable, and it decreased continuously with time. The maximum syngas conversion was 49%, at about 40 h, and then it decreased gradually to 32% at the end of the test. WGS activity of the catalyst was high throughout the test, and the usage ratio varied between 0.57 and 0.65.

Methane (Figure IV-1.4) and hydrocarbon selectivities (Table IV-1.3) were fairly stable during 300 h of testing. For example, methane selectivity increased slightly from 2.2 wt% at 45 h, to 2.4% at 260 h, (C_2-C_4) varied between 9.9 and 11.5%, (C_5-C_{11}) decreased slightly from 18% to 15%, while C_{12+} increased from 69% to 72%. Olefin selectivity (total olefin content, and 2-olefin content) did not vary with time (Table IV-1.3).

A typical ASF plot for products collected at 164 h on stream is shown in Figure IV-1.5. The experimental data were fitted well with a three parameter model, except for methane. Its concentration is significantly lower than expected from the ASF distribution. Estimated values of parameters are also shown in Figure IV-1.5.

During testing of the same catalyst at the UOP the following results were obtained: ($H_2 + CO$) conversion decreased from 70 to 45% during 280 h of testing, the usage ratio varied between 0.57 and 0.60, and methane selectivity was about 2.8 mol%. Except for higher syngas conversion, but nevertheless declining with time on stream as

Figure IV-1.4 (H₂+CO) conversion (a) and methane selectivity (b) as a function of time on stream for Run SA-1532.

Table IV-1.3 Summary of Slurry Reactor Test Results for Run SA-1532.

Period	1	2	3	4	5
Time on Stream (h)	45.0	117.0	164.0	212.0	260.0
Balance Duration (h)	17.0	16.2	16.0	16.0	15.0
Average Temperature (°C)	265.	265.	265.	265.	265.
Pressure (MPa)	2.10	2.10	2.10	2.10	2.10
H ₂ /CO Feed Ratio	.733	.709	.709	.715	.715
Space Velocity (Nl/g-cat·h) ^a	1.42	1.43	1.43	1.47	1.47
Space Velocity (Nl/g-Fe·h)	2.34	2.35	2.35	2.42	2.42
GHSV (h ⁻¹) ^b	98.4	94.8	94.8	91.4	91.4
CO Conversion (%)	52.1	46.7	43.3	40.1	37.8
H ₂ +CO Conversion (%)	48.6	42.9	40.0	38.5	36.3
H ₂ /CO Usage	.616	.569	.578	.644	.649
STY (mols H ₂ +CO/g-cat·h) ^a	.031	.027	.026	.025	.024
$P_{CO_2} \cdot P_{H_2} / P_{CO} \cdot P_{H_2O}$	13.8	10.7	10.7	9.94	8.97
Weight % of Outlet					
H ₂	2.82	3.05	3.14	3.13	3.21
H ₂ O	.966	1.07	.978	.891	.937
CO	45.6	50.9	53.9	57.0	59.1
CO ₂	37.9	33.4	31.5	28.4	27.2
Hydrocarbons	5.09	4.21	4.05	3.81	3.28
Oxygenates	.344	.379	.385	.381	.343
Wax ^c	7.36	7.00	6.01	6.45	5.95
Yield (g/Nm ³ H ₂ + CO Converted)					
CH ₄	4.17	4.33	4.43	4.77	4.68
C ₂ -C ₄ Hydrocarbons	21.3	21.1	22.3	20.2	20.5
C ₅ -C ₁₁ Hydrocarbons	35.2	32.3	32.6	31.1	28.7
C ₁₂ + Hydrocarbons	133.	142.	134.	148.	141.
Wax ^c	115.	125.	115.	128.	126.
Oxygenates	5.37	6.77	7.41	7.59	7.25
Total	199.	207.	201.	212.	202.
1+2 Olefins/n-Paraffin Ratio					
C ₂	5.10	5.30	6.11	6.42	6.15
C ₃	5.83	5.10	5.92	7.80	5.30
C ₄	4.03	3.93	4.00	4.10	4.16
C ₈	2.92	2.82	3.30	3.41	3.12
C ₁₀	3.04	3.07	3.12	3.32	3.14

^a Based on unreduced catalyst^b Based on static slurry volume^c Unanalyzed wax withdrawn from reactor

Table IV-1.3 (cont'd) Summary of Slurry Reactor Test Results for Run SA-1532.

Period	1	2	3	4	5
Weight % of Hydrocarbons					
CH ₄	2.15	2.17	2.29	2.33	2.40
Ethane	.570	.531	.569	.477	.512
Ethylene	2.71	2.62	3.24	2.86	2.94
Propane	.637	.688	.633	.421	.654
Propylene	3.54	3.35	3.58	3.14	3.31
n-Butane	.651	.631	.660	.556	.570
1+2 Butenes	2.53	2.39	2.55	2.20	2.29
C ₄ Isomers	.322	.309	.307	.248	.261
n-Pentane	.537	.409	.415	.235	.338
1+2 Pentenes	2.36	2.21	2.36	1.99	2.08
C ₅ Isomers	.154	.148	.163	.154	.159
n-Hexane	.579	.556	.604	.504	.491
1+2 Hexenes	1.87	1.71	1.89	1.66	1.63
C ₆ Isomers	.885	.694	.757	.601	.583
n-Heptane	.543	.488	.499	.437	.416
1+2 Heptenes	1.64	1.43	1.51	1.37	1.32
C ₇ Isomers	.731	.516	.555	.572	.482
n-Octane	.555	.476	.419	.377	.411
1+2 Octenes	1.59	1.32	1.36	1.26	1.26
C ₈ Isomers	.535	.380	.407	.442	.322
n-Nonane	.517	.415	.435	.388	.448
1+2 Nonenes	1.47	1.34	1.38	1.31	1.31
C ₉ Isomers	.119	.185	.155	.165	.135
n-Decane	.453	.429	.441	.382	.364
1+2 Decenes	1.36	1.30	1.36	1.25	1.13
C ₁₀ Isomers	.240	.260	.246	.240	.242
n-Undecane	.407	.373	.377	.346	.292
1+2 Undecenes	1.26	1.22	1.25	1.21	.984
C ₁₁ Isomers	.339	.281	.313	.327	.321
C ₂ -C ₄	11.0	10.5	11.5	9.89	10.5
C ₅ -C ₁₁	18.2	16.1	16.9	15.2	14.7
C ₁₂ +	68.7	71.2	69.3	72.6	72.3
Wax ^c	59.1	62.4	59.8	62.9	64.5

^c Unanalyzed wax withdrawn from reactor

Figure IV-1.5. Carbon number product distribution for Run SA-1532 (TOS=164 h).

in the test at TAMU, the agreement between results obtained at tests conducted at TAMU and UOP is quite satisfactory.

IV-1.1.3 Run SA-2502 with UCI L-3905 (Batch 3) Catalyst

After the pretreatment, the catalyst was initially tested at 265°C, 290 psig (2.07 MPa), 2.4 NI/g-Fe/h and $H_2/CO = 0.7$. Changes in syngas conversion and methane selectivity with time-on-stream are shown in Figure IV-1.6. Both the syngas conversion and methane selectivity increased with time during the first 140 h of testing. The ($H_2 + CO$) conversion increased from 51% to 65%, whereas methane selectivity increased from 3.5% to 4.5 mol%. At 140 h the reactor head temperature was lowered from 265°C to 235°C, in order to suppress FTS activity in the stirrer shaft housing above the reactor head. After this, the syngas conversion remained fairly stable 65-66%, but the methane selectivity decreased back to 3.5% and remained stable during the next 140 h of testing. At about 280 h on stream, the reaction pressure was lowered to 200 psig (1.48 MPa) while the remaining process conditions were kept constant. After an initial decrease the syngas conversion stabilized at 54%, and the methane selectivity increased to 3.9%. At 355 h the reaction pressure and the gas space velocity were increased simultaneously to 400 psig (2.86 MPa) and 4.6 NI/g-Fe/h, respectively. This corresponds to the same contact (gas residence) time as that during testing at 200 psig and 2.4 NI/g-Fe/h. Following the change in process conditions there was an initial decrease in conversion to 47.5%, followed by gradual increase to 55% (360-400 h). This resulted in nearly doubling of the reactor STY from 0.031 mol ($H_2 + CO$)/g-cat/h at 334 h to 0.061 mol ($H_2 + CO$)/g-cat/h at 384 h (Table IV-1.4). Methane selectivity decreased to 2.9% during testing at 400 psig. At 401 h on stream the baseline conditions (265°C, 290 psig, 2.4 NI/g-Fe/h, $H_2/CO = 0.7$) were re-established and testing continued for another 40 h. The syngas conversion varied from 70 to 72% during this period, which is about 8% higher than during testing between 140 and 240 h on stream. Thus, the catalyst activity

Figure IV-1.6 (H_2+CO) conversion (a) and methane selectivity (b) as a function of time on stream for Run SA-2502.

Table IV-1.4 Summary of Slurry Reactor Test Results for Run SA-2052.

Period	1	2	3	4	5	6	7
Time on Stream (h)	29.0	120.0	168.0	264.0	334.0	384.0	431.0
Balance Duration (h)	16.0	15.0	14.0	12.0	12.5	11.5	13.0
Average Temperature (°C)	266.	265.	265.	265.	265.	265.	265.
Pressure (MPa)	2.10	2.10	2.10	2.10	1.48	2.86	2.10
H ₂ /CO Feed Ratio	.73	.73	.73	.73	.72	.72	.70
Space Velocity (NI/g-cat·h) ^a	1.25	1.25	1.25	1.32	1.27	2.45	1.29
Space Velocity (NI/g-Fe·h)	2.34	2.34	2.34	2.46	2.37	4.58	2.40
GHSV (h ⁻¹) ^b	90.	90.	90.	90.	87.	168.	88.
CO Conversion (%)	61.0	67.1	68.3	66.1	56.3	56.8	73.5
H ₂ +CO Conversion (%)	59.6	64.2	65.2	63.4	53.9	56.0	69.9
H ₂ /CO Usage	.69	.66	.66	.66	.64	.69	.62
STY (mols H ₂ +CO/g-cat·h) ^a	.033	.036	.037	.037	.031	.061	.040
$P_{CO_2} \cdot P_{H_2} / P_{CO} \cdot P_{H_2O}$	4.0	5.7	6.1	6.2	6.2	3.6	9.1
Weight % of Outlet							
H ₂	2.13	1.99	1.95	2.02	2.45	2.22	1.70
H ₂ O	3.47	2.94	2.82	2.66	2.17	3.26	2.20
CO	37.18	31.14	30.19	32.02	41.77	41.23	25.36
CO ₂	42.10	46.55	47.07	46.34	40.10	38.43	52.73
Hydrocarbons	9.23	10.02	9.23	10.04	7.37	8.21	9.79
Oxygenates	.58	.36	.50	.57	.35	.66	.57
Wax ^c	5.31	7.01	8.24	6.35	5.80	6.00	7.65
Yield (g/Nm ³ H ₂ + CO Converted)							
CH ₄	9.45	9.93	8.19	8.22	8.76	6.58	7.88
C ₂ -C ₄ Hydrocarbons	43.14	40.58	37.60	36.76	35.14	33.21	35.17
C ₅ -C ₁₁ Hydrocarbons	46.63	42.40	42.57	48.96	37.16	45.26	40.97
C ₁₂ + Hydrocarbons	85.34	108.89	114.68	103.40	105.00	108.91	107.51
Wax ^c	67.43	83.06	95.78	76.47	81.95	81.86	84.03
Oxygenates	7.42	4.23	5.78	6.88	4.88	8.98	6.27
Total	191.93	206.03	208.82	204.22	190.94	202.94	197.80
1+2 Olefins/n-Paraffin Ratio							
C ₂	2.00	1.53	1.57	1.59	1.57	3.22	1.51
C ₃	5.57	5.92	5.94	5.53	6.47	5.69	5.99
C ₄	4.90	5.12	5.08	4.96	5.29	4.49	5.00
C ₈	3.27	3.00	3.43	3.52	3.63	3.75	3.20
C ₁₀	2.67	2.38	2.75	2.80	2.93	3.35	2.62

^a Based on unreacted catalyst

^b Based on static slurry volume

^c Unanalyzed wax withdrawn from reactor

Table IV-1.4 (cont'd) Summary of Slurry Reactor Test Results for Run SA-2052.

Period	1	2	3	4	5	6	7
Weight % of Hydrocarbons							
CH ₄	5.12	4.92	4.03	4.17	4.71	3.39	4.12
Ethane	2.33	2.21	2.02	2.04	2.07	1.11	2.12
Ethylene	4.36	3.15	2.96	3.02	3.02	3.33	2.98
Propane	1.48	1.24	1.13	1.22	1.09	1.09	1.11
Propylene	7.90	7.02	6.40	6.43	6.70	5.93	6.34
n-Butane	1.16	.99	.93	.94	.90	.97	.91
1+2 Butenes	5.49	4.91	4.57	4.49	4.61	4.19	4.42
C ₄ Isomers	.65	.58	.50	.50	.48	.50	.48
n-Pentane	.99	.87	.80	.81	.75	.84	.80
1+2 Pentenes	4.70	4.14	3.84	3.83	3.96	3.72	3.80
C ₅ Isomers	1.19	1.05	.95	.96	.85	.98	.99
n-Hexane	.72	.59	.54	.61	.52	.58	.56
1+2 Hexenes	3.05	2.44	2.23	2.33	2.29	2.40	2.31
C ₆ Isomers	.94	.81	.64	.72	.83	.83	.77
n-Heptane	.60	.49	.44	.51	.43	.53	.44
1+2 Heptenes	2.21	1.70	1.71	1.89	1.81	1.98	1.68
C ₇ Isomers	.90	.69	.63	.62	.69	.78	.65
n-Octane	.51	.42	.44	.52	.37	.47	.40
1+2 Octenes	1.64	1.23	1.48	1.81	1.33	1.72	1.25
C ₈ Isomers	.75	.47	.50	.61	.41	.70	.47
n-Nonane	.51	.45	.45	.62	.37	.46	.45
1+2 Nonenes	1.48	1.15	1.43	1.89	1.20	1.64	1.31
C ₉ Isomers	.40	.30	.43	.53	.34	.45	.39
n-Decane	.49	.50	.46	.69	.39	.46	.55
1+2 Decenes	1.29	1.17	1.23	1.89	1.13	1.52	1.43
C ₁₀ Isomers	.66	.41	.50	.69	.37	.66	.57
n-Undecane	.51	.50	.48	.74	.40	.46	.56
1+2 Undecenes	1.18	1.17	1.21	1.89	1.06	1.52	1.39
C ₁₁ Isomers	.54	.46	.58	.63	.48	.66	.60
C ₂ -C ₄	23.38	20.11	18.52	18.63	18.88	17.12	18.36
C ₅ -C ₁₁	25.26	21.01	20.97	24.81	19.97	23.34	21.39
C ₁₂ +	46.24	53.96	56.48	52.40	56.43	56.15	56.13
Wax ^d	36.54	41.16	47.17	38.75	44.05	42.20	43.87

^d Unanalyzed wax withdrawn from reactor

increased slightly with time, and there was no deactivation after the testing at 400 psig. WGS activity increased with time as evidenced by decrease in the usage ratio from 0.69 at 29 h to 0.62 at 431 h on stream. Methane selectivity was about 3.5%, which is the same as that between 140 and 240 h on stream. Selected results from seven mass balances are summarized in Table IV-1.4. Hydrocarbon product distribution at the baseline conditions was stable after the reactor head temperature was decreased to 235°C (Mass balances 3,4 and 7). Olefin selectivity (total olefin content, and 2-olefin content) did not vary with time, during testing at the baseline conditions. The olefin content was slightly higher, whereas 2-olefin content was slightly lower at 400 psig relative to 200 psig (Table IV-1.4).

A typical ASF plot for products collected at 168 h on stream is shown in Figure IV-1.7. The experimental data were fitted well with a three parameter model. Estimated values of parameters are also shown in Figure IV-1.7.

This catalyst was also tested in a STSR at UOP Laboratories in Des Plaines, Illinois. During the first 120 h of testing at the baseline conditions the syngas conversion was very erratic and varied between 50 and 70%, whereas methane selectivity was about 3.5 mol%. These values are in good agreement with our results, confirming good reproducibility of data between these two Laboratories.

IV-1.2 Comparison of Baseline Catalysts

UCI catalysts were tested at a common set of process conditions (baseline conditions) which facilitates comparison of their activities and selectivities. Here, we are excluding results which were affected either by side reactions in the stirrer shaft housing (Runs SA-3391 and SA-2052) or by higher reaction temperature due to malfunctioning of the temperature readout (Run SA-3391, the first 200 h on stream).

Variation of syngas conversion with time for all three tests with UCI catalysts is shown in Figure IV-1.8a. During the first 300 h of testing the ($H_2 + CO$) conversion was

Figure IV-1.7 Carbon number product distribution for Run SA-2502 (TOS=168 h).

Figure IV-1.8 Effect of time on stream on (H₂+CO) conversion (a) and methane selectivity (b) for UCI catalysts.

the highest in test SA-3391, whereas the lowest syngas conversion was obtained in test SA-1532. Activities of these three catalysts are compared in Figure IV-1.9, in terms of values of apparent first order reaction rate constant evaluated at 260°C. The latter value was calculated from data at different temperatures by using the activation energy of 90 kJ/mol, which is a typical value for iron FT catalysts (Zimmerman and Bukur, 1990). These results show that the catalyst in Run SA-3391 was the most active, whereas the catalyst in Run SA-1532 was the least active. Also, both catalysts deactivated with time, whereas in Run SA-2052 the catalyst activity increased slightly with time. These data indicate that activity increases with the increasing silica and potassium contents of the catalyst (see Table IV-1.1). The most active catalyst (Run SA-3391) had the highest total surface area, but the activity in the other two tests does not correlate with the total surface area of the catalyst (Table IV-1.1). The apparent rate constants from two tests of the Ruhrchemie catalyst (Runs SA-0888 and SB-1370) are also shown in Figure IV-1.9 for comparison. Activity of the Ruhrchemie catalyst is markedly higher than that of the UCI catalysts, regardless of the pretreatment procedure employed (CO activation in test SA-0888, and H₂ reduction in SB-1370).

Values of the (H₂/CO) usage ratio and partial pressure quotient, K_p , provide information on relative rates of water-gas-shift reaction (lower usage ratios or higher values of K_p correspond to higher WGS activity). Catalyst used in Run SA-3391 had the highest WGS activity (UR = 0.56 - 0.62, K_p = 14 - 22), whereas the catalyst used in Run SA-2052 had the lowest WGS activity (UR = 0.61 - 0.70, K_p = 3.6 - 9). The WGS activity of the Ruhrchemie catalyst during testing at 1.48 MPa, 265°C, 3.8 NI/g-Fe/h, H₂/CO = 0.67 was similar to that of the UCI catalysts (UR = 0.66, K_p = 4.4 - 11).

Variations of methane and hydrocarbon selectivities with time, for all three UCI catalysts, are shown in Figures IV-1.8b and IV-1.10, respectively. Catalyst with low silica and potassium contents, used in Run SA-1532, had the lowest methane and gaseous hydrocarbons selectivities. It favored the production of high molecular weight

Figure IV-1.9 Apparent first order reaction rate constant of Ruhrchemie and UCI catalysts as a function of time on stream.

Figure IV-1.10 Comparison of hydrocarbon product distribution of UCI catalysts.

hydrocarbons (> 69 wt% of C₁₂₊ hydrocarbons), and its selectivity was fairly stable with time on stream. The other two catalysts, used in Runs SA-3391 and SA-2052, had similar selectivities. Methane selectivity was about 3.8 - 4 mol% (4.1 - 4.4 wt%), and C₁₂₊ selectivity varied between 52 and 56 wt%. The Ruhrchemie catalyst was tested under a different set of baseline process conditions (1.48 MPa, 250°C, 3.8 NI/g-Fe/h, H₂/CO = 0.67) than the UCI catalysts. Average values of hydrocarbon selectivities obtained during the initial 360 h of testing at the baseline conditions are shown in Table IV-1.5. As can be seen the hydrocarbon selectivities in two tests of the Ruhrchemie catalyst were similar to those obtained in Runs SA-3391 and SA-2052. Results from testing of the Ruhrchemie catalyst at 265°C are also shown in this Table. In both tests there was a significant shift toward lower molecular weight hydrocarbons. Methane selectivity increased to : 6.0 wt% (SB-1370) and 7.0 wt% (SA-0888), whereas C₁₂₊ selectivity decreased to: 42.9 wt% (SB-1370) and 23.0 wt% (SA-0888). This shift toward low molecular weight products is not entirely due to higher reaction temperature, but also due to aging of the catalyst (See Section III-4 of this report) since data at 265°C were obtained at 570 - 590 h on stream.

Olefin hydrogenation activities of the UCI catalysts are compared in Figure IV-1.11. Olefin selectivities of the two catalysts used in Runs SA-3391 and SA-2052 were nearly the same, and followed the usual trend of declining selectivity with carbon number and relatively low ethylene selectivity (60 wt%). Low silica catalyst, used in Run SA-1532, had very high ethylene selectivity (85%) and higher olefin content in high molecular weight hydrocarbons (C₁₁₊ products) than the other two catalysts. Low hydrogenation activity of this catalyst is consistent with its low methane selectivity.

Comparison of olefin isomerization activity of the three catalysts at 164 - 187 h on stream is made in Figure IV-1.12. The 2-olefin selectivity of all three catalysts was rather low. Catalysts used in Runs SA-3391 and SA-2052 had similar 2-olefin selectivities, and the olefin isomerization activity increased with carbon number (C₉₊ products). The low

Table IV-1.5 Comparison of Slurry Reactor Test Results with UCI and Ruhrchemie Catalysts.

Run ID	SA-3391	SA-1532	SA-2052	SA-0888	SB-1370
Catalyst	UCI L-3950 (1309-37-1)	UCI 1207-175A	UCI L-3950 (batch 3)	Ruhrchemie	Ruhrchemie
Reduction Conditions	H ₂ /CO=0.7, 12 h 280°C	H ₂ /CO=0.7, 12 h 280°C	H ₂ /CO=0.7, 12 h 280°C	CO, 16 h 280°C	H ₂ , 1 h 220°C
TOS (h)	227-322	35-301	140-276, 401-444	0-343	0-360
%CO Conv.	73-80	35-52	68-75	40-43	34-39
%(H ₂ +CO) Conv.	71-75	33-49	65-72	43-46	38-41
Hydrocarbon Selectivities (wt-%):					
CH ₄	4.4	2.3	4.1	4.7	4.5
C ₂ -C ₄	16.5	10.7	18.5	20.6	15.5
C ₅ -C ₁₁	23.6	16.2	22.4	23.2	27.7
C ₁₂ +	55.5	70.8	55.0	51.5	52.3

Test conditions for UCI Catalysts: 265°C, 2.10 MPa, 2.4 NI/g-Fe/h, feed H₂/CO=0.7

Test conditions for Ruhrchemie Catalyst: 250°C, 1.48 MPa, 3.8 NI/g-Fe/h, feed H₂/CO=0.67

Figure IV-1.11 Comparison of olefin selectivities of UCI catalysts (time on stream 164 - 187 h).

Figure IV-1.12 Comparison of 2-olefin selectivities of UCI catalysts (time on stream 164 - 187 h).

silica catalyst (SA-1532) had the lowest 2-olefin content , and the 2-olefin selectivity of C₁₀₊ olefins was fairly constant (~10%).

Olefin selectivities (total olefin content and 2-olefin content) of the Ruhrchemie catalyst during the first 150 h on stream were similar to those of the UCI catalysts used in Runs SA-3391 and SA-2052 (see Figures III-4.13 and 14, and Figures IV-1.11 and 12).

IV-1.3 Summary

Four catalysts prepared by two catalyst manufacturers (UCI 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, K₂O and SiO₂ were used as promoters. The amounts of promoters (in parts per weight per 100 parts of iron) in these four catalysts were as follows: SiO₂ = 4.1-25; K = 1.1-8.7 and Cu = 1.4 - 7.5. Total BET surface area varied between 136 and 290 m²/g, and increased with the amount of silica, with the exception of two UCI catalysts having 4.1 and 9.2 g of SiO₂ per 100 g of Fe (see Table IV-1.1).

The Ruhrchemie and two of the UCI's catalysts (SA-3391 and SA-2052) had low deactivation rates, whereas the UCI catalyst with low silica content (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 surface area, except for the UCI catalysts with 4.1 and 9.2 parts of SiO₂.

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 (C₂ - C₄) 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.

V-1.4 References

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IV-2 Testing of Iron/Silica Catalysts Synthesized at TAMU

Eight catalysts containing potassium and copper as promoters and silicon oxide as a binder were evaluated in a stirred tank slurry reactor (STSR). In all tests a calcined catalyst was crushed and sieved to either 270/325 mesh size (44 - 53 μm) or less than 270 mesh size, prior to loading to a reactor. A pre-purified normal octacosane was used as the liquid (slurry) medium (about 400 cm^3 of static volume) in all tests. The initial amount of catalyst used in different tests was between 7 and 31 g, resulting in slurry concentrations of 2.5 to 11 wt% (typically, 3-5.5%). Test designations and physico-chemical properties of catalysts are summarized in Table IV-2.1.

In general, the elemental chemical composition of all catalysts, determined by atomic absorption, is in good agreement with the intended (nominal) catalyst composition. The potassium content of catalysts used in runs SB-0261, SB-0921, SB-1421 and SB-2141 was higher than the nominal one. The agreement between results of analysis performed at TAMU, and other laboratories (UOP, PETC and Sandia National Laboratory) is satisfactory. Our analysis tends to overestimate the potassium content of a catalyst.

The surface areas of all calcined catalysts were about the same (220 - 260 m^2/g), regardless of their silica contents. Also, the pore volumes of seven of the eight catalysts were between 0.6 and 0.7 cm^3/g . The catalyst with nominal composition 100 Fe/ 5 Cu/ 4.2 K/ 8 SiO_2 (Run SB-1910) had markedly lower pore volume (0.38 cm^3) than the other catalysts. One of the two catalysts with the same nominal composition, i.e. 100 Fe/ 5 Cu/ 4.2 K/ 16 SiO_2 , was prepared in 1988 (Run SB-2270), and the other one in 1990 (Run SB-2832) by different researchers. Similarity in chemical composition and physical properties of these two catalysts is indicative of good reproducibility of the catalyst preparation procedure.

Table IV-2.1 Physico-Chemical Properties and Test Designation for Iron/Silica Catalysts.

Run ID	SA-1371	SB-0931	SB-1910	SB-0261	SB-2270	SB-2832	SB-1931	SB-3101
Nominal Catalyst Composition (Fe/Cu/K/SiO ₂)	100/3/3/8	100/3/4/8	100/5/4.2/8	100/3/4/16	100/5/4.2/16	100/5/4.2/16	100/5/6/24	100/5/8/24
Actual Catalyst Composition (Fe/Cu/K/SiO ₂)	100/3.3/4.5/12	100/3.1/4.7/9.6	100/4.6/4.6/9	100/3/6.7/15.5 100/3.1/5.9/15.5 ^c	100/5.1/5/18.5 100/5/4.3/18 ^b	100/5.6/6.3/18.5 100/5.6/3.9/14.2 ^a 100/5.1/3.7/13.1 ^c	100/5.1/8.1/26 100/5.5/6.6/24 ^a	100/5.1/10.2/28
BET Surface Area (m ² /g)	225	225*	250	245	257	234	222	222**
Pore Volume (cm ³ /g)	0.59	0.59	0.38	0.65	0.70	0.61	0.68	0.68

*: Catalysts 100 Fe/3 Cu/x K/8 SiO₂ (x = 3 or 4) have the same precursor

**:: Catalysts 100 Fe/5 Cu/y K/24 SiO₂ (y = 6 or 8) have the same precursor

Measurements conducted at: (a) Pittsburgh Energy Technology Center

(b) Sandia National Laboratory

(c) Universol Oil Products, Inc.

Catalyst compositions are in mass basis.

On the basis of results obtained in the two most successful studies of FT synthesis in bubble column slurry reactors (Kölbel and Ralek, 1980; Kuo, 1985), the PETC had established guidelines for desired activity, selectivity and stability of the iron FT catalysts. These guidelines (target performance) were given in the DOE's Request for Proposal (No. DE-PR22-90PC90021) entitled "Technology Development for Iron Fischer-Tropsch Catalysts", and are reproduced in Table IV-2.2.

Results from individual tests (grouped according to their silicon oxide content) are described first followed by summary of results, including comparisons of the catalysts performance with the target performance and with other iron FT catalysts.

IV-2.1 Run SA-1371 with 100 Fe/3 Cu/3 K/8 SiO₂ Catalyst

The catalyst was tested at 260°C, 1.48 MPa (200 psig), 1.7 NI/g-cat/h and H₂/CO = 0.67 during the first 50 h. After withdrawal of a slurry sample the gas space velocity was increased to 1.87 NI/g-cat/h. There were no major operational problem encountered during the test. The run was terminated after 360 h on stream. Results from five mass balances made during the test are summarized in Table IV-2.3, whereas major events are listed in Table IV-2.4.

Catalyst Activity and Stability

The catalyst deactivated continuously with time on stream. The (H₂+CO) conversion decreased from 82% initially to 52% at 360 h, while the VC decreased from 54% to 32% during the same time period (Figure IV-2.1). WGS activity of the catalyst was high, and the usage ratio varied between 0.54 – 0.58.

Wax and Catalyst Withdrawals/Inventories

Wax was withdrawn through a porous sintered metal filter with nominal pore size of 0.5 µm. The filter was placed horizontally at a height corresponding to the static slurry volume of 400 cc. Initial pressure drop across the filter was 15 psi but it

Table IV-2.2 Catalyst Target Performance

ACTIVITY

(H ₂ +CO) conversion, %	88
CO conversion, %	90
Nm ³ (H ₂ +CO) reacted/(kg-Fe·h)	2.6
STY (kg C ₃ ⁺ /m ³ reactor/day)	900

HYDROCARBON SELECTIVITY

(g HC/Nm ³ (H ₂ +CO) reacted)	≥178
(g C ₃ ⁺ /Nm ³ (H ₂ +CO) reacted)	≥166
(C ₁ +C ₂), wt%	6.7-8.0

PROCESS CONDITIONS

(H₂/CO) feed ratio = 0.6-1.0

Pressure (bar) = 1-20

Temperature (°C) = 230-300

Space velocity = 2-4 (Nm³/kg-Fe·h)

DEACTIVATION RATE: ≤ 1% per day during 30 days of continuous testing.

Table IV-2.3 Summary of Slurry Reactor Test Results for Run SA-1371.

Period	1	2	3	4	5
Time on Stream (h)	41.0	103.0	158.0	233.5	305.0
Balance Duration (h)	6.0	12.0	7.5	6.5	6.2
Average Temperature (°C)	260.	260.	260.	260.	260.
Pressure (MPa)	1.48	1.48	1.48	1.48	1.48
H ₂ /CO Feed Ratio	.684	.684	.709	.704	.692
Space Velocity (NI/g-cat·h) ^a	1.69	1.87	1.87	1.87	1.87
Space Velocity (NI/g-Fe·h)	2.94	3.25	3.25	3.25	3.25
GHSV (h ⁻¹) ^b	44.0	45.3	45.3	45.3	45.3
CO Conversion (%)	87.2	83.4	80.5	71.6	62.0
H ₂ +CO Conversion (%)	82.2	77.0	74.5	66.4	57.9
H ₂ /CO Usage	.586	.554	.582	.580	.580
STY (mols H ₂ +CO/g-cat·h) ^a	.062	.062	.062	.055	.048
$P_{CO_2} \cdot P_{H_2} / P_{CO} \cdot P_{H_2O}$	31.2	53.2	53.8	34.7	62.5
Weight % of Outlet					
H ₂	1.20	1.51	1.64	2.00	2.27
H ₂ O	1.12	.638	.558	.624	.263
CO	12.3	15.7	18.5	27.4	36.0
CO ₂	63.1	62.1	59.4	52.1	46.0
Hydrocarbons	13.3	12.3	12.3	12.2	11.2
Oxygenates	.965	.923	1.17	1.10	1.00
Wax ^c	8.12	6.81	6.43	4.56	3.29
Yield (g/Nm ³ H ₂ + CO Converted)					
CH ₄	9.18	10.9	11.1	11.9	12.4
C ₂ -C ₄ Hydrocarbons	36.3	39.1	37.9	37.8	40.8
C ₅ -C ₁₁ Hydrocarbons	64.0	58.7	60.2	66.1	70.0
C ₁₂ + Hydrocarbons	90.8	86.1	85.5	76.1	71.2
Wax ^c	76.1	69.3	66.7	52.3	44.2
Oxygenates	9.05	9.39	12.1	12.6	13.5
Total	209.	204.	207.	205.	208.
1+2 Olefins/n-Paraffin Ratio					
C ₂	1.16	1.62	2.04	2.54	3.16
C ₃	5.35	4.70	5.15	4.23	4.19
C ₄	4.48	4.10	3.74	3.40	3.22
C ₆	2.63	2.69	2.52	2.51	2.28
C ₁₀	2.19	2.41	2.61	2.40	2.46

^a Based on unreduced catalyst^b Based on static slurry volume^c Unanalyzed wax withdrawn from reactor

Table IV-2.3 (cont'd) Summary of Slurry Reactor Test Results for Run SA-1371.

Period	1	2	3	4	5
Weight % of Hydrocarbons					
CH ₄	4.58	5.58	5.68	6.20	6.38
Ethane	2.16	2.17	1.80	1.56	1.48
Ethylene	2.33	3.27	3.43	3.70	4.38
Propane	1.20	1.45	1.32	1.53	1.63
Propylene	6.12	6.51	6.48	6.17	6.53
n-Butane	1.09	1.22	1.27	1.42	1.51
1+2 Butenes	4.70	4.84	4.58	4.66	4.70
C ₄ Isomers	.542	.615	.595	.644	.732
n-Pentane	1.33	1.54	1.81	1.57	1.86
1+2 Pentenes	4.70	4.93	4.97	4.93	4.92
C ₅ Isomers	.978	.973	1.00	1.03	.928
n-Hexane	1.03	1.05	1.18	1.39	1.45
1+2 Hexenes	3.34	3.18	3.26	3.68	3.34
C ₆ Isomers	.878	1.02	1.07	1.47	1.64
n-Heptane	.939	.881	.957	1.14	1.37
1+2 Heptenes	2.52	2.22	2.37	2.70	2.84
C ₇ Isomers	.718	1.32	.784	1.17	1.36
n-Octane	.946	.785	.921	1.01	1.17
1+2 Octenes	2.44	2.07	2.28	2.49	2.62
C ₈ Isomers	.570	.616	.769	.848	1.22
n-Nonane	1.10	.769	.757	.975	.879
1+2 Nonenes	2.54	2.00	2.09	2.22	2.19
C ₉ Isomers	.416	.425	.524	.366	.544
n-Decane	1.08	.828	.716	.946	.967
1+2 Decenes	2.33	1.97	1.84	2.24	2.35
C ₁₀ Isomers	.636	.518	.564	.649	.830
n-Undecane	.928	.733	.654	.885	.807
1+2 Undecenes	1.88	1.72	1.69	2.16	2.05
C ₁₁ Isomers	.645	.588	.704	.610	.710
C ₂ -C ₄	18.1	20.1	19.5	19.7	21.0
C ₅ -C ₁₁	31.9	30.1	30.9	34.5	36.0
C ₁₂ +	45.3	44.2	43.9	39.7	36.6
Wax ^c	38.0	35.6	34.2	27.3	22.8

^c Unanalyzed wax withdrawn from reactor

Table IV-2.4 Major Events in Run SA-1371.

TOS(h)	Event
	Slurry loading: 300 g n-octacosane, 11.0 g (particle size < 270 mesh) catalyst
	Catalyst pretreatment: H ₂ at 240°C
	Slurry sample withdrawal: 19.3 g wax; 0.7 g catalyst
	Wax withdrawal through filter: 13.6 g
0	Initiate synthesis gas flow
2	Achieved process conditions: 260°C, 1.48 MPa, 1.7 NI/g-cat/h, H ₂ /CO = 0.67
50	Slurry sample withdrawal: 18.4 g wax, 0.6 g catalyst
359	Two slurry sample withdrawals: 41.5 g wax, 1.5 g catalysts
360	End of run: 237 g wax, 7.3 g catalyst recovered from reactor
	Wax/catalyst removed during the run: 250 g wax, 2.1 g catalyst
	Catalyst recovery: 92%; Wax recovery: 90%

Figure IV-2.1 (H₂+CO) conversion (solid symbols) and volumetric contraction (open symbols) as a function of time on stream for Run SA-1371.

reached equilibrium very quickly. Filtration had to be repeated many times in order to withdraw excess wax. No significant amount of catalyst was removed with the withdrawn wax (based on color of the wax). The wax production rate decreased from 1.1 to 0.5 g/h as catalyst deactivated with time on stream.

At the end of the test, 7.3 g of catalyst was recovered from the reactor (determined by burning slurry samples in a crucible). Another estimated 2.8 g was removed from the reactor during the test with three slurry samples for catalyst characterization (Table IV-2.4). The catalyst recovery was about 92% based on the amount of catalyst charged into the reactor, whereas the wax recovery was about 90%.

Catalyst Characterization by XRD and/or MES

After the reduction with hydrogen at 240°C for 2 h and prior to FT synthesis, magnetite was the only phase detected by XRD analysis. After 50 h of synthesis, there has been no change in the catalyst composition. A sample withdrawn at 359 h from the reactor in an inert atmosphere, and the one at the end of the run, after exposure to the air prior to catalyst/wax separation had similar XRD patterns, and in addition to magnetite the peaks characteristic to iron carbides were observed. Thus the catalyst was only partially carburized after 360 hours of FT synthesis.

Hydrocarbon and Carbon Number Product Distributions

Hydrocarbon product distribution shifted gradually toward lower molecular weight products with time on stream. For example, methane selectivity increased from 4.6% in balance 1 (TOS = 42 h) to 6.4% in balance 5 (TOS = 305 h), (C₂–C₄) varied between 18 - 21, (C₅–C₁₁) increased from 32 to 36, while C₁₂+ decreased from 45 to 37 wt %, respectively (Table IV-2.3).

A typical ASF plot for products collected in mass balance 3 (TOS = 158 h) is shown in Figure IV-2.2. The existence of double alpha phenomenon is evident from this plot, and experimental data are fitted well with the three parameter model.

Figure IV-2.2 Carbon number product distribution for Run SA-1371 (TOS=158 h).

IV-2.2 Run SB-0931 with 100 Fe/3 Cu/4 K/8 SiO₂ Catalyst

Slurry reactor run SB-0931 was conducted to evaluate performance of a precipitated iron catalyst with nominal composition 100 Fe/3 Cu/4 K/8 SiO₂. Reaction pressure and syngas feed composition were held constant throughout the test at 1.48 MPa (200 psig) and H₂/CO = 0.66 – 0.69, respectively. On the basis of process conditions employed the run can be divided into three periods: 0 – 350 h (T = 260°C, SV = 1.25 – 1.5 NI/g-cat/h); 350 – 460 h (T = 265°C, SV = 1.25 NI/g-cat/h); and 460 – 560 h (T = 260°C, SV = 1.5 – 2.1 NI/g-cat/h). The test was terminated voluntarily after 570 h on stream. Results from nine mass balances made during the test are summarized in Table IV-2.5, whereas major events are listed in Table IV-2.6.

Catalyst Activity and Stability

The catalyst deactivated slowly with time during the first 230 h of testing at 260°C, 200 psig, 1.5 NI/g-cat/h and H₂/CO = 0.66. During this period the (H₂+CO) conversion varied between 80 and 88% (Figure IV-2.3), whereas the gas volumetric contraction (VC) was between 52 and 60% (Figure IV-2.4). The rate of catalyst deactivation was much higher during the next 30 h, and the (H₂+CO) conversion and VC decreased to 76% and 50%, respectively. At this point the gas flow rate was decreased (SV = 1.25 NI/g-cat/h) in order to increase the (H₂+CO) conversion, and these conditions were maintained over the next 90 h (TOS = 260 – 350 h). During this period, the catalyst continued to deactivate with time (see Figures IV-2.3 and 2.4), and at 356 h the reaction temperature was increased to 265°C. Both the (H₂+CO) conversion and VC, increased initially and then started to decline with time. For example, the (H₂+CO) conversion decreased from 79.3% at 360 h to 71.8% at 458 h on stream, whereas the VC decreased from 53.2 to 45.8% during the same period of time.

At 460 h on stream the baseline conditions were reestablished (260°C, 250 cc/min), however, the gas space has velocity increased to about 1.6 NI/g-cat/h due to

Table IV-2.5 Summary of Slurry Reactor Test Results for Run SB-0931.

Period	1	2	3	4	5
Time on Stream (h)	49.0	109.0	171.0	244.0	329.0
Balance Duration (h)	12.0	10.0	13.0	8.5	8.0
Average Temperature (°C)	260.	260.	260.	260.	260.
Pressure (MPa)	1.48	1.48	1.48	1.48	1.48
H ₂ /CO Feed Ratio	.661	.661	.661	.661	.661
Space Velocity (NI/g-cat·h) ^a	1.49	1.49	1.51	1.53	1.25
Space Velocity (NI/g-Fe·h)	2.44	2.44	2.48	2.52	2.06
GHSV (h ⁻¹) ^b	34.9	34.9	34.9	34.9	27.9
CO Conversion (%)	92.6	89.1	88.9	81.0	79.8
H ₂ +CO Conversion (%)	86.3	84.3	83.5	75.3	73.6
H ₂ /CO Usage	.547	.572	.559	.543	.533
STY (mols H ₂ +CO/g-cat·h) ^a	.057	.054	.054	.048	.041
$P_{CO_2} \cdot P_{H_2} / P_{CO} \cdot P_{H_2O}$	49.8	42.6	41.8	39.1	73.6
Weight % of Outlet					
H ₂	1.06	1.04	1.13	1.52	1.63
H ₂ O	1.17	.871	.955	.737	.387
CO	7.02	10.5	10.6	18.1	19.4
CO ₂	68.3	65.4	65.9	60.5	59.5
Hydrocarbons	9.38	9.78	9.69	8.89	6.84
Oxygenates	.772	.510	.426	.422	.328
Wax ^c	12.3	11.9	11.3	9.87	11.9
Yield (g/Nm ³ H ₂ + CO Converted)					
CH ₄	4.86	5.34	5.53	5.97	6.78
C ₂ -C ₄ Hydrocarbons	21.1	22.6	22.6	24.5	24.5
C ₅ -C ₁₁ Hydrocarbons	43.1	40.3	31.4	33.2	32.8
C ₁₂ + Hydrocarbons	130.	134.	138.	132.	136.
Wax ^c	113.	111.	106.	103.	127.
Oxygenates	7.08	4.76	4.02	4.41	3.50
Total	206.	207.	202.	200.	204.
1+2 Olefins/ <i>n</i> -Paraffin Ratio					
C ₂	2.15	2.26	2.26	3.05	3.17
C ₃	6.85	7.07	7.05	6.54	6.42
C ₄	5.68	6.27	6.28	5.62	5.47
C ₈	4.27	3.66	3.72	4.17	3.98
C ₁₀	8.80	2.51	3.20	3.66	3.07

^a Based on unreduced catalyst^b Based on static slurry volume^c Unanalyzed wax withdrawn from reactor

Table IV-2.5 (cont'd) Summary of Slurry Reactor Test Results for Run SB-0931.

Period	6	7	8	9
Time on Stream (h)	397.0	446.0	545.0	554.0
Balance Duration (h)	9.0	12.0	6.0	10.0
Average Temperature (°C)	265.	265.	260.	260.
Pressure (MPa)	1.48	1.48	1.48	1.48
H ₂ /CO Feed Ratio	.695	.695	.695	.667
Space Velocity (Nl/g-cat·h) ^a	1.26	1.30	2.05	1.44
Space Velocity (Nl/g-Fe·h)	2.08	2.14	3.38	2.37
GHSV (h ⁻¹) ^b	27.9	27.9	34.9	24.4
CO Conversion (%)	81.6	79.0	66.6	76.5
H ₂ +CO Conversion (%)	75.2	71.7	60.3	71.1
H ₂ /CO Usage	.561	.538	.533	.549
STY (mols H ₂ +CO/g-cat·h) ^a	.042	.037	.039	.046
$P_{CO_2} \cdot P_{H_2} / P_{CO} \cdot P_{H_2O}$	136.	84.2	53.8	59.6
Weight % of Outlet				
H ₂	1.64	1.86	2.33	1.71
H ₂ O	.233	.366	.384	.409
CO	17.7	20.1	31.8	22.6
CO ₂	60.0	58.4	49.6	56.7
Hydrocarbons	10.0	10.9	9.91	10.4
Oxygenates	.198	.154	.160	.191
Wax ^c	10.2	8.19	5.75	7.94
Yield (g/Nm ³ H ₂ + CO Converted)				
CH ₄	7.22	7.73	7.51	7.80
C ₂ -C ₄ Hydrocarbons	24.5	25.5	24.8	24.3
C ₅ -C ₁₁ Hydrocarbons	35.2	36.8	35.5	34.6
C ₁₂ + Hydrocarbons	140.	136.	133.	135.
Wax ^c	105.	88.2	73.8	87.1
Oxygenates	2.02	1.66	2.05	2.09
Total	209.	208.	203.	203.
1+2 Olefins/n-Paraffin Ratio				
C ₂	3.76	3.90	4.75	4.05
C ₃	6.25	6.18	6.09	6.26
C ₄	5.62	5.50	5.16	5.40
C ₈	3.82	4.37	4.05	5.15
C ₁₀	3.04	4.99	4.44	4.30

^a Based on unreduced catalyst^b Based on static slurry volume^c Unanalyzed wax withdrawn from reactor

Table IV-2.5 (cont'd) Summary of Slurry Reactor Test Results for Run SB-0931.

Period	1	2	3	4	5
Weight % of Hydrocarbons					
CH ₄	2.45	2.65	2.80	3.05	3.38
Ethane	.948	1.05	1.07	.942	.899
Ethylene	1.90	2.21	2.26	2.68	2.66
Propane	.533	.553	.564	.649	.645
Propylene	3.48	3.73	3.80	4.05	3.96
<i>n</i> -Butane	.533	.480	.489	.599	.598
1+2 Butenes	2.92	2.91	2.96	3.24	3.16
C ₄ Isomers	.321	.276	.281	.324	.318
<i>n</i> -Pentane	.111	.436	.448	.587	.579
1+2 Pentenes	.665	2.54	2.61	3.06	2.92
C ₅ Isomers	.215	.592	.627	.711	.557
<i>n</i> -Hexane	.389	.356	.549	.421	.499
1+2 Hexenes	1.72	1.39	1.74	1.65	1.70
C ₆ Isomers	.739	.639	.939	.818	.644
<i>n</i> -Heptane	.338	.325	.305	.221	.299
1+2 Heptenes	1.38	1.29	1.20	.938	2.31
C ₇ Isomers	.421	.717	.932	.324	.415
<i>n</i> -Octane	.330	.476	.251	.224	.327
1+2 Octenes	1.39	1.71	.917	.919	1.28
C ₈ Isomers	.516	.725	.285	.213	.356
<i>n</i> -Nonane	.582	.558	.283	.382	.569
1+2 Nonenes	1.00	1.81	1.07	1.44	.923
C ₉ Isomers	.216	.316	.191	.147	.0849
<i>n</i> -Decane	.177	.644	.340	.460	.298
1+2 Decenes	1.53	1.59	1.07	1.66	.902
C ₁₀ Isomers	2.69	.543	.253	.174	.164
<i>n</i> -Undecane	.272	.640	.422	.553	.305
1+2 Undecenes	1.77	1.63	1.15	1.78	.927
C ₁₁ Isomers	5.24	1.02	.318	.278	.311
C ₂ -C ₄	10.6	11.2	11.4	12.5	12.2
C ₅ -C ₁₁	21.7	19.9	15.9	17.0	16.4
C ₁₂ +	65.2	66.2	69.9	67.5	68.0
Wax ^c	56.7	54.8	53.8	52.6	63.6

^c Unanalyzed wax withdrawn from reactor

Table IV-2.5 (cont'd) Summary of Slurry Reactor Test Results for Run SB-0931.

Period	6	7	8	9
Weight % of Hydrocarbons				
CH ₄	3.49	3.75	3.74	3.87
Ethane	.733	.749	.634	.718
Ethylene	2.57	2.72	2.81	2.72
Propane	.664	.707	.722	.689
Propylene	3.96	4.17	4.19	4.12
n-Butane	.597	.630	.658	.608
1+2 Butenes	3.24	3.34	3.28	3.17
C ₄ Isomers	.0911	.0793	.0738	.0674
n-Pentane	.626	.675	.713	.631
1+2 Pentenes	2.48	2.61	2.46	2.36
C ₅ Isomers	1.39	.639	.553	.559
n-Hexane	.481	.595	.465	.440
1+2 Hexenes	1.64	1.98	1.56	1.48
C ₆ Isomers	.616	.775	.408	.617
n-Heptane	.242	.401	.333	.253
1+2 Heptenes	.981	1.57	1.17	.962
C ₇ Isomers	.400	.551	.467	.386
n-Octane	.229	.369	.337	.248
1+2 Octenes	.859	1.58	1.34	1.25
C ₈ Isomers	.226	.414	.299	.170
n-Nonane	.364	.349	.377	.442
1+2 Nonenes	1.21	1.55	1.59	1.76
C ₉ Isomers	.112	.0764	.0707	.0709
n-Decane	.560	.301	.482	.490
1+2 Decenes	1.68	1.48	2.11	2.08
C ₁₀ Isomers	.269	.0934	.156	.156
n-Undecane	.632	.330	.520	.521
1+2 Undecenes	1.53	1.44	2.16	2.16
C ₁₁ Isomers	.494	.0690	.113	.115
C ₂ -C ₄	11.9	12.4	12.4	12.1
C ₅ -C ₁₁	17.0	17.9	17.7	17.2
C ₁₂ +	67.6	66.0	66.2	66.9
Wax ^c	50.6	42.8	36.7	43.3

^c Unanalyzed wax withdrawn from reactor

Table IV-2.6 Major Events in Run SB-0931.

TOS(h)	Event
	Slurry loading: 301 g n-octacosane, 10.4 g (270 – 325 mesh) catalyst Catalyst pretreatment: H ₂ at 220°C Slurry sample removal: 8.9 g wax; 0.3 g catalyst Wax withdrawal through a filter: 42.4 g
1	Achieved initial process conditions: 260°C, 1.48 MPa, 250 cc/min, H ₂ /CO=0.66
49 – 252	Mass balances 1 – 4 at above conditions
262	Change gas flow rate to 200 cc/min
61 – 328	10 wax withdrawals (244 g of wax; 0.41 g catalyst)
329 – 337	Mass balance 5
352	Change reaction temperature to 265°C
374 – 495	9 wax withdrawals (128 g wax; 0.87 g catalyst)
397 – 458	Mass balances 6 and 7 at 265°C, 1.48 MPa, 200 cc/min , H ₂ /CO = 0.69
459	Change reaction temperature to 260°C and gas flow rate to 250 cc/min
497 – 500	Reactor overflow with accumulated wax; wax withdrawal through a dipleg to an external settler (106 g wax; 1.4 g catalyst)
519	Catalyst regeneration with H ₂ at 220 – 245°C
545 – 551	Mass balance 8 at 260°C, 1.48 MPa 250 cc/min, H ₂ /CO = 0.69
551	Change gas flow rate to 175 cc/min
554 – 564	Mass balance 9 at 260°C, 1.48 MPa, 175 cc/min, H ₂ /CO = 0.69
565	Two slurry sample removals: 23.8 g wax; 0.32 g catalyst
570	End of run: 378.3 g wax; 6 g catalyst Catalyst recovery: 89.4%; Wax recovery: 89%

Figure IV-2.3 Volumetric contraction versus time on stream for Run SB-0931.

Figure IV-2.4 (H₂+CO) conversion versus time on stream for Run SB-0931.

losses of catalysts during wax withdrawals as discussed in the following section. As shown in Figures IV-2.3 and 2.4, a significant decrease in (H₂+CO) conversion and VC occurred at about 500 h, which may be attributed in part to the removal of the catalyst from the system following slurry withdrawal at 497 h through a dipleg. About 1.4 g of the catalyst was removed from the reactor, which resulted in increase of the gas space velocity to about 2.05 (NI/g-cat/h). At 519 h, the catalyst was regenerated with H₂ at about 230°C for 2 h, and this resulted in marked increase in catalyst activity. At 550 h the gas flow rate was decreased in order to obtain the baseline gas space velocity of 1.5 NI/g-cat/h. The (H₂+CO) conversion at 560 h was about 70%. The loss of conversion over 560 h of testing was about 39% (i.e. ~1.7% per day).

The water-gas-shift (WGS) activity was high throughout the test. The usage ratio varied between 0.54 and 0.60, with an average value of 0.56.

Wax and Catalyst Inventories/Withdrawals

During the first 500 h on stream the excess wax produced was withdrawn through a 2 µm porous metal filter placed horizontally at a height corresponding to a static slurry volume of 410 cm³. The first two withdrawals (after the reduction – 42 g, and after the first mass balance at 65 h – 84 g) were successful. However, the subsequent wax withdrawals were not complete and as a result the wax continued to accumulate in the reactor. At about 490 h on stream, the amount of wax accumulated in the reactor was large enough to cause overflow, and shortly after that the excess wax (106 g) was withdrawn through a dipleg to an external settler. The wax withdrawn through the internal filter, as well as the wax from the external settler contained some catalyst. The amounts of catalyst in the wax withdrawn from the reactor, and in the slurry at the end of the run were determined by burning slurry (wax) samples in a crucible (see Table IV-2.6). The catalyst recovery was about 89%, based on the amount of catalyst charged into the reactor. Gas space velocities reported in Table IV-2.5 were adjusted to reflect partial removal of the catalyst throughout the test.

Due to incomplete wax withdrawals during the test, total mass, and atomic closures for carbon and hydrogen were low, however the oxygen atomic closures were within $100 \pm 3\%$ in all mass balances. Wax production rates in different mass balances were estimated to get good atomic closures. After adjustments in the wax production rates, total and atomic closures were all within $100 \pm 3\%$. Hydrocarbon selectivities reported in Table IV-2.5 are based on estimated wax production rates. The estimated wax production rates were decreasing with time on stream and ranged from 0.75 to 1.3 g/h. Average (experimental) wax production rate for the entire test was 1.1 g/h.

Catalyst Characterization by XRD and/or MES

A slurry sample withdrawn from the reactor after hydrogen reduction at 220°C for 2 h contained a small amount of catalyst which was insufficient for XRD analysis. A sample withdrawn at 564 h from the reactor was analyzed by MES and found to contain: Superparamagnetic oxide/oxyhydroxide - 30%; magnetite - 20%; and ϵ' -carbide - 50%. The following phases were detected by XRD in a sample from the end of the run slurry (570 h) : magnetite, iron carbide(s) and iron carbonate. The catalyst was only partially carburized after 570 hours of FT synthesis.

Hydrocarbon and Carbon Number Product Distributions

During the first period of testing (0 – 350 h) at 260°C, methane and light gas selectivities increased with time on stream. Methane selectivity varied between 2.5 and 3.4%, whereas (C₂–C₄) selectivity varied between 10.6 and 12.5%. (C₁+C₂) selectivity was lower than 7% during this period. During testing at 265°C (350 – 460 h on stream) methane selectivity increased to 3.5% – 3.8%, whereas (C₁+C₂) selectivity was between 6.7 and 7.2%. After the catalyst regeneration, methane and (C₁+C₂) selectivities were about 3.8 and 7.3%, respectively.

Figure IV-2.5 Carbon number product distribution for Run SB-0931 (TOS=329 h).

Carbon number product distribution is shown in Figure IV-2.5 (Mass balance 5, TOS = 329 h). The existence of "double alpha" phenomenon is evident from this plot. Chain growth probabilities are $\alpha_1 = 0.79$ and $\alpha_2 = 0.94$.

Concluding Remarks

Overall this run has been successful. Initial catalyst activity, selectivity, and deactivation rate were within the DOE targets. Catalyst deactivation rate increased with time on stream, however hydrocarbon selectivity remained within the target throughout the test. Regeneration procedure employed at the end of this test (H_2 at 220 – 240°C for 2 h) did not result in complete recovery of catalyst activity, and alternative procedures should be explored.

IV-2.3 Run SB-1910 with 100 Fe/5 Cu/4.2 K/8 SiO₂ Catalyst

This was the first slurry reactor test of one of the most active catalysts synthesized in our laboratory during the DOE Contract No. DE-AC22-85PC80011. This catalyst was evaluated in a fixed bed reactor (Runs FA-63-0418 and FA-63-1308), and results from these tests were reported previously (Bukur et al., 1989b). In both of these tests the catalyst was very active, and had excellent hydrocarbon selectivity (low methane yield and high yield of C_{12} + hydrocarbons) but its deactivation rate was higher than the target rate of 1% per day.

The catalyst was tested initially (first 160 h) at 250°C, 200 psig (1.48 MPa), 2NI/g-cat/h using the synthesis gas with H_2 to CO molar ratio of about 0.7 (0.65-0.75). Two mass balances were made during this time period, but the (H_2 +CO) conversion and volumetric gas contraction (VC) were monitored more frequently. After the second mass balance, the reaction temperature was increased to 258°C (160-270 h) in order to achieve higher (H_2 +CO) conversion (mass balances 3 and 4). At 273 h on stream the gas flow rate was decreased to give the gas space velocity of 1.5 (NI/g-cat/h) based on the initial amount of catalyst charged to the reactor. These operating

conditions were maintained over next 94 h, and two additional mass balances were made (balances 5 and 6). At 365 h on stream the baseline conditions were established again to check the catalyst activity (365-397h). The run was terminated voluntarily after 400 h on stream. Results from all six mass balances are summarized in Table IV-2.7.

Catalyst Activity and Stability

The catalyst activity was very stable between 30 and 100 h on stream, as shown in Figures IV-2.6 (contraction vs. TOS) and IV-2.7 (conversion vs. TOS). During this time period the volumetric contraction (VC) was between 36 and 38%, whereas the (H_2+CO) conversion varied between 53.6 and 56.4%. After slurry withdrawal through a dipleg tube at about 110 h, the VC and (H_2+CO) values decreased by about 10%, but remained fairly stable during the next fifty hours (TOS = 110-160 h). This decrease may be attributed in part to loss of catalyst with wax removed from the system (1.7 catalyst, or about 6% of the total amount of the catalyst left in the reactor after the reduction and slurry sample withdrawal for catalyst characterization - Table IV-2.8).

At about 162 h on stream, the temperature was increased to 258°C, and during the next 44 hours (162-206 h on stream) the volumetric contraction and the (H_2+CO) conversion declined slightly with time (Figures IV-2.6 and IV-2.7). During the mass balance period 3 (201-207 h) the volumetric contraction varied between 41 and 43%, whereas after withdrawal of about 154 g of wax and 1.4 g of catalyst from the reactor the contraction decreased to 37.1% (Figure IV-2.6). Further drop in activity occurred at about 230 h on stream, VC = 32.6%, after a temporary stoppage (~2h) of syngas flow due to plugging of the reactor inlet line. The contraction continued to decrease slowly with time (TOS = 230-258 h), but another sharp decline occurred after the slurry withdrawal from the reactor (134 g of wax, and 1.5 g of catalyst) at about 270 h on stream (VC = 25.4%). At this time the feed flow rate was changed to 750 (cc/min), corresponding to the gas space velocity of 1.5 (NI/g-cat/h) based on the initial amount

Table IV-2.7 Summary of Slurry Reactor Test Results for Run SB-1910.

Period	1	2	3	4	5	6
Date	07/12/90	07/14/90	07/18/90	07/20/90	07/23/90	07/24/90
Time on Stream (h)	55.0	102.5	201.0	247.0	316.5	346.5
Balance Duration (h)	6.0	6.0	6.0	6.0	6.0	6.0
Average Temperature (°C)	250.	250.	258.	258.	258.	258.
Pressure (MPa)	1.48	1.48	1.48	1.48	1.48	1.48
H ₂ /CO Feed Ratio	.754	.639	.752	.754	.786	.821
Space Velocity (NI/g-cat·h) ^a	2.03	2.14	2.26	2.38	1.90	2.00
Space Velocity (NI/g-Fc·h)	3.30	3.47	3.67	3.87	3.08	3.25
GHSV (h ⁻¹) ^b	140.	140.	118.	118.	88.6	88.6
CO Conversion (%)	59.2	59.6	66.0	48.3	54.6	46.7
H ₂ +CO Conversion (%)	54.1	56.1	62.2	45.6	51.1	43.4
H ₂ /CO Usage	.602	.545	.650	.658	.671	.692
STY (mols H ₂ +CO/g-cat·h) ^a	.049	.054	.063	.048	.043	.039
P _{CO₂} · P _{H₂} / P _{CO} · P _{H₂O}	21.2	30.6	34.1	31.0	36.6	33.9
Weight % of Outlet						
H ₂	2.74	2.16	2.20	2.98	2.86	3.40
H ₂ O	.780	.467	.554	.383	.395	.367
CO	39.1	38.6	32.1	49.1	43.0	50.5
CO ₂	41.4	44.8	48.6	34.4	38.1	32.5
Hydrocarbons	8.04	7.36	9.35	8.13	10.6	9.49
Oxygenates	.937	.823	1.19	.933	1.26	1.00
Wax ^c	7.06	5.74	6.07	4.07	3.71	2.81
Yield (g/Nm ³ H ₂ + CO Converted)						
CH ₄	6.43	6.16	6.30	7.68	6.85	7.67
C ₂ -C ₄ Hydrocarbons	27.4	24.6	25.4	27.5	26.7	26.7
C ₅ -C ₁₁ Hydrocarbons	44.2	48.4	42.2	48.4	59.0	59.5
C ₁₂ + Hydrocarbons	130.	107.	113.	117.	114.	112.
Wax ^c	97.1	81.7	73.7	67.0	53.7	47.0
Oxygenates	12.9	11.7	14.5	15.4	18.2	16.7
Total	221.	198.	202.	216.	225.	222.
1+2 Olefins/n-Paraffin Ratio						
C ₂	4.28	3.92	3.79	4.89	4.30	4.44
C ₃	4.34	4.23	4.49	4.39	4.28	4.19
C ₄	3.42	3.39	3.31	3.50	3.48	3.26
C ₈	1.57	1.37	1.57	1.65	1.83	1.46
C ₁₀	1.74	1.39	1.01	2.11	1.99	1.92

^a Based on unreduced catalyst^b Based on static slurry volume^c Unanalyzed wax withdrawn from reactor

Table IV-2.7 (cont'd) Summary of Slurry Reactor Test Results for Run SB-1910.

Period	1	2	3	4	5	6
Weight % of Hydrocarbons						
CH ₄	3.10	3.30	3.36	3.83	3.32	3.73
Ethane	.707	.724	.771	.635	.680	.666
Ethylene	2.82	2.65	2.73	2.90	2.73	2.76
Propane	.952	.997	.968	1.00	.961	.984
Propylene	3.95	4.03	4.15	4.20	3.93	3.93
<i>n</i> -Butane	1.03	1.04	1.09	1.04	.980	1.03
1+2 Butenes	3.38	3.40	3.50	3.50	3.29	3.23
C ₄ Isomers	.349	.354	.355	.417	.367	.374
<i>n</i> -Pentane	1.10	1.09	1.02	1.09	1.01	1.07
1+2 Pentenes	3.12	3.10	3.12	3.18	2.90	2.88
C ₅ Isomers	.550	.555	.952	1.10	.763	1.07
<i>n</i> -Hexane	.599	.609	.673	.673	.731	1.02
1+2 Hexenes	2.98	1.82	1.98	1.95	1.85	1.88
C ₆ Isomers	1.06	.661	.740	.762	.982	.742
<i>n</i> -Heptane	.587	.716	.703	.701	.900	.932
1+2 Heptenes	1.67	.967	1.02	1.24	1.85	1.19
C ₇ Isomers	.693	.487	.593	.519	.558	.502
<i>n</i> -Octane	.751	.820	.620	.780	1.27	1.36
1+2 Octenes	1.16	1.10	.958	1.26	2.27	1.95
C ₈ Isomers	.178	.132	.566	.0732	.886	.164
<i>n</i> -Nonane	.615	1.13	.946	.888	1.49	1.68
1+2 Nonenes	1.03	1.35	.969	1.65	2.75	2.82
C ₉ Isomers	.197	.305	.248	.0781	.155	.140
<i>n</i> -Decane	.779	1.53	1.19	.923	1.38	1.67
1+2 Decenes	1.34	2.09	1.18	1.92	2.71	3.17
C ₁₀ Isomers	.423	2.34	1.85	2.57	.185	.261
<i>n</i> -Undecane	.899	.955	1.13	.744	.906	1.25
1+2 Undecenes	1.25	1.72	1.22	1.86	2.70	3.00
C ₁₁ Isomers	.307	2.49	.853	.162	.312	.218
C ₂ -C ₄	13.2	13.2	13.6	13.7	12.9	13.0
C ₅ -C ₁₁	21.3	26.0	22.5	24.1	28.6	29.0
C ₁₂ +	62.4	57.5	60.5	58.4	55.2	54.3
Wax ^c	46.7	43.8	39.3	33.4	26.0	22.9

^c Unanalyzed wax withdrawn from reactor

Figure IV-2.6 Volumetric contraction versus time on stream for Run SB-1910 (weight indicate amount of wax withdrawn).

Figure IV-2.7 (H₂+CO) conversion versus time on stream for Run SB-1910.

of catalyst charged to the reactor. During the next fifty hours (TOS = 272-322 h) the volumetric contraction and the (H₂+CO) conversion were fairly stable, i.e. VC = 33.4-37% and (H₂+CO) = 49.7-51.9%. After the slurry withdrawal (122 g of wax, and 1.2 g of catalyst) at 324 h, a marked decrease in activity was observed again. The volumetric contraction was 29.1% at 328 h on stream, and is remained fairly stable during the next 24 hours. After another slurry withdrawal at 354-364 h, the contraction decreased to 26.5%. At this point the reaction temperature was decreased to 250°C, whereas the syngas flow rate was increased to 1000 cc/min (baseline conditions), and these conditions were maintained during the next 30 h. During this period the volumetric contraction varied between 20 and 21.7%, and the (H₂+CO) conversion between 29.2 and 31%.

Wax and Catalyst Inventories

Two methods of wax (slurry) withdrawal were employed during this run, i.e. wax withdrawal through a 10 µm vertical cylindrical element and slurry withdrawal to an external settler via a dipleg tube followed by wax removal and return of concentrated slurry to the reactor. Results from all wax (slurry) withdrawals are summarized in Table IV-2.8.

At the end of the reduction period 65 g of wax was removed from the reactor through the filter. The withdrawn wax was clear in appearance, and contained trace amounts of solids only. At 62 h on stream about 17.5 g of wax was withdrawn through the filter. This wax had a black color, and it was suspected that the filter element had developed a crack. At this point it was decided to change the method of wax withdrawal, and slurry withdrawal through a dipleg tube was employed throughout the remainder of the test. At the end of the run the filter element was inspected and no cracks were found. This means that the catalyst particles had disintegrated to size smaller than 10 µm during the first 60 h of synthesis (The catalyst particles charged to the reactor were between 43 and 53 µm; 270/325 mesh particles).

Table IV-2.8 Wax and Solids Inventory for Run SB-1910.

TOS (h)	Description
	Slurry loading: 330 g wax, 30 g catalyst
	Wax filtration following reduction: 65 g wax
	Slurry withdrawal for catalyst characterization: 6.05 g (5.55 g of wax, 0.5 g of catalyst)
62	Wax filtration: 16.1 g wax, 1.46 g catalyst
110	Wax removal: 137.5 g wax, 1.48 g catalyst
210	Wax removal: 154.0 g wax, 1.34 g catalyst
254	Wax removal: 134.8 g wax, 1.50 g catalyst
324	Wax removal: 122.2 g wax, 1.20 g catalyst
354	Wax removal: 125.3 g wax, 1.52 g catalyst
387	End of run: Slurry withdrawal for catalyst characterization: 10 g (9.35 g of wax, 0.65 g of catalyst)
	Slurry from the reactor: 299.5 g wax, 14.8 g catalyst
	Recoveries: 113% for wax; 77.3% for catalyst
	Catalyst pretreatment: H ₂ at 220°C

The wax transferred from the settling vessel was of black color. The amount of catalyst in the wax was determined by filtration, and subsequent burning of the solids material retained on the filter. As can be seen from results in Table IV-2.8, the catalyst content in the wax was about 1%. Therefore, the amount of catalyst remaining in the reactor was decreasing with each slurry withdrawal. The gas space velocities reported in Table IV-2.7 are based on the estimated amount of catalyst in the reactor.

At the end of the run, the catalyst content in the slurry was determined by the above procedure. The overall wax and catalyst recoveries were: 113 and 77.3%, respectively. (% Recovery = (Amount out)/(Amount in) x 100).

Catalyst Characterization by XRD and/or MES

The iron phases determined by MES analysis after hydrogen reduction at 220°C for 1 h were: 77% α - FeOOH (iron oxyhydroxide), and 23% magnetite. A sample withdrawn at 397 h on stream from the reactor was analyzed by MES and found to contain: Superparamagnetic oxides/oxyhydroxides - 17%; magnetite - 55%; and ϵ' -carbide - 28%. The catalyst was only partially carburized after 390 hours of FT synthesis.

Hydrocarbon Product Distribution

Hydrocarbon selectivities were similar in all six mass balances, even though the process conditions were not constant throughout the test ($T = 250$ - 258°C , $SV = 1.9$ - 2.4 NI/g-cat/h, $(\text{H}_2/\text{CO}) = 0.64$ - 0.82). Methane selectivity varied between 3.1 and 3.8%, and selectivity of light hydrocarbons (C_2 - C_4) varied between 12.9 and 13.7%. Fraction of C_{12}^+ hydrocarbons decreased slightly with time on stream (TOS), whereas fraction of hydrocarbons in the gasoline range (C_5 - C_{11}) increased with time (Table IV-2.7).

Overall the performance of this catalyst was very good. It is evident that loss of catalyst from the reactor had contributed to decrease in $(\text{H}_2 + \text{CO})$ conversion with time

on stream. The hydrocarbon selectivity of the catalyst was within the DOE target, i.e. $(C_1+C_2) \leq 8$ wt%.

IV-2.4 Run SB-0261 with 100 Fe/3 Cu/4 K/16 SiO₂ Catalyst

This test was conducted to evaluate performance of a silica containing precipitated iron catalyst with nominal composition 100 Fe/3 Cu/4 K/16 SiO₂. During the first 168 h, and between 236 and 549 h on stream, the catalyst was tested at 260°C, 1.48 MPa (200 psig), 1.4 NI/g-cat/h and H₂/CO = 0.68 – 0.70 (mass balances 1-3, 5-8). After the third mass balance, the reaction temperature was increased to 263°C (168 – 236 h) while keeping the remaining conditions constant (mass balance 4). Between 549 and 622 h, the catalyst was tested at a lower gas space velocity of 1 NI/g-cat/h (260°C, 200 psig), whereas during the last 100 h (TOS = 622 – 722 h) the process conditions were: 260°C, 2.17 MPa (300 psig), 1.4 NI/g-cat/h and H₂/CO = 0.64. The test was terminated voluntarily after 725 h on stream. Results from eleven mass balances made during the test are summarized in Table IV-2.9, whereas major events are listed in Table IV-2.10.

Catalyst Activity and Stability

The catalyst was very stable and active during the first 120 h on stream, as shown in Figure IV-2.8. The (H₂+CO) conversion and volumetric gas contraction (VC) varied between 80-83%, and 53-54%, respectively. The conversion and VC were decreasing between 120 and 165 h, and at 168 h the reaction temperature was increased to 263°C in attempt to increase the catalyst activity. After initial increase in activity, the catalyst continued to deactivate with time. At 170 h the (H₂+CO) conversion was 80%, whereas at 220 h the conversion was 75%. At about 240 h, the baseline conditions were reestablished (T=260°C), and the (H₂+CO) conversion was only 68.5%. This value is significantly lower in comparison to conversions obtained during the first 170 h of testing (76 – 83%). However, after this the catalyst activity

Table IV-2.9 Summary of Slurry Reactor Test Results for Run SB-0261.

Period	1	2	3	4	5	6
Date	01/29/91	01/31/91	02/02/91	02/05/91	02/08/91	02/11/91
Time on Stream (h)	44.0	92.0	140.0	214.0	286.0	356.0
Balance Duration (h)	6.0	6.0	6.0	6.0	6.0	6.0
Average Temperature (°C)	260.	260.	260.	263.	260.	260.
Pressure (MPa)	1.48	1.48	1.48	1.48	1.48	1.48
H ₂ /CO Feed Ratio	.701	.701	.704	.704	.704	.676
Space Velocity (Nl/g-cat·h) ^a	1.39	1.39	1.39	1.39	1.40	1.40
Space Velocity (Nl/g-Fe·h)	2.39	2.39	2.39	2.39	2.41	2.41
GHSV (h ⁻¹) ^b	65.1	65.1	65.1	65.1	62.8	62.8
CO Conversion (%)	88.2	87.4	85.5	82.0	73.0	72.4
H ₂ +CO Conversion (%)	81.6	81.4	77.7	74.8	67.3	67.4
H ₂ /CO Usage	.574	.584	.547	.554	.572	.561
STY (mols H ₂ +CO/g-cat·h) ^a	.050	.050	.048	.046	.042	.042
P _{CO₂} · P _{H₂} / P _{CO} · P _{H₂O}	39.8	24.1	31.8	37.8	16.7	20.7
Weight % of Outlet						
H ₂	1.34	1.30	1.63	1.72	1.99	1.87
H ₂ O	1.10	1.64	1.32	.909	1.38	1.03
CO	11.3	12.0	13.9	17.3	26.0	26.5
CO ₂	65.1	64.0	63.1	60.8	53.1	53.0
Hydrocarbons	9.20	9.87	10.8	11.0	9.38	8.44
Oxygenates	.229	.274	.218	.149	.245	.174
Wax ^c	11.7	10.9	8.96	8.16	7.89	8.98
Yield (g/Nm ³ H ₂ + CO Converted)						
CH ₄	4.47	5.40	5.37	5.56	4.63	4.35
C ₂ -C ₄ Hydrocarbons	20.4	24.1	24.5	25.4	20.7	19.6
C ₅ -C ₁₁ Hydrocarbons	29.2	27.5	28.8	30.4	27.4	26.1
C ₁₂ + Hydrocarbons	143.	139.	136.	135.	143.	151.
Wax ^c	110.	103.	88.1	83.6	89.3	103.
Oxygenates	2.16	2.59	2.14	1.53	2.78	2.00
Total	199.	199.	197.	198.	198.	203.
1+2 Olefins/n-Paraffin Ratio						
C ₂	2.02	1.62	1.75	2.11	3.24	4.26
C ₃	7.50	7.29	7.11	7.23	7.00	7.07
C ₄	6.77	6.84	6.78	6.70	6.48	6.19
C ₅	3.80	3.99	3.99	4.13	4.42	4.28
C ₁₂	1.21	2.17	2.80	2.42	3.74	3.65

^a Based on unreduced catalyst^b Based on static slurry volume^c Unanalyzed wax withdrawn from reactor

Table IV-2.9 (cont'd) Summary of Slurry Reactor Test Results for Run SB-0261.

Period	7	8	9	10	11
Date	02/14/91	02/18/91	02/21/91	02/25/91	02/26/91
Time on Stream (h)	428.0	523.0	505.0	602.0	716.0
Balance Duration (h)	6.0	6.0	7.0	6.0	6.0
Average Temperature (°C)	260.	260.	260.	260.	260.
Pressure (MPa)	1.48	1.48	1.48	2.17	2.17
H ₂ /CO Feed Ratio	.678	.678	.684	.684	.637
Space Velocity (Nl/g-cat·h) ^a	1.40	1.29	.980	1.44	1.44
Space Velocity (Nl/g-Fe·h)	2.41	2.22	1.69	2.48	2.48
GHSV (h ⁻¹) ^b	62.8	53.0	36.7	53.9	53.9
CO Conversion (%)	71.2	72.6	80.9	70.1	65.0
H ₂ +CO Conversion (%)	66.6	67.9	75.7	67.1	62.8
H ₂ /CO Usage	.568	.570	.574	.613	.580
STY (mols H ₂ +CO/g-cat·h) ^a	.042	.039	.033	.043	.040
$P_{CO_2} \cdot P_{H_2} / P_{CO} \cdot P_{H_2O}$	18.6	26.4	37.2	13.7	10.8
Weight % of Outlet					
H ₂	1.90	1.81	1.50	1.74	1.79
H ₂ O	1.08	.798	.743	1.26	1.30
CO	27.7	26.0	18.2	28.5	33.6
CO ₂	51.4	53.4	58.8	49.4	46.2
Hydrocarbons	8.27	7.25	9.22	7.56	7.51
Oxygenates	.160	.150	.165	.436	.360
Wax ^c	9.43	10.5	11.4	11.1	9.23
Yield (g/Nm ³ H ₂ + CO Converted)					
CH ₄	4.25	4.41	4.38	3.56	3.48
C ₂ -C ₄ Hydrocarbons	19.1	19.2	18.8	17.2	18.1
C ₅ -C ₁₁ Hydrocarbons	25.2	32.1	26.7	28.2	29.8
C ₁₂ + Hydrocarbons	157.	150.	162.	167.	160.
Wax ^c	109.	122.	117.	128.	117.
Oxygenates	1.85	1.74	1.70	5.06	4.56
Total	207.	207.	214.	221.	216.
1+2 Olefins/n-Paraffin Ratio					
C ₂	4.45	3.44	2.64	3.54	4.49
C ₃	7.22	7.11	7.26	6.35	6.39
C ₄	6.23	6.22	6.45	5.16	5.40
C ₈	4.16	4.30	4.19	4.34	4.00
C ₁₀	3.00	3.33	4.24	3.91	4.32

^a Based on unreduced catalyst^b Based on static slurry volume^c Unanalyzed wax withdrawn from reactor

Table IV-2.9 (cont'd) Summary of Slurry Reactor Test Results for Run SB-0261.

Period	1	2	3	4	5	6
Weight % of Hydrocarbons						
CH ₄	2.27	2.75	2.76	2.83	2.37	2.17
Ethane	1.01	1.36	1.33	1.22	.746	.619
Ethylene	1.90	2.05	2.18	2.40	2.25	2.46
Propane	.497	.614	.644	.648	.544	.465
Propylene	3.56	4.28	4.37	4.47	3.63	3.14
n-Butane	.421	.517	.532	.550	.463	.404
1+2 Butenes	2.75	3.41	3.48	3.56	2.90	2.41
C ₄ Isomers	.251	.0533	.0584	.0624	.0693	.246
n-Pentane	.397	.304	.316	.329	.260	.251
1+2 Pentenes	2.39	2.66	2.76	2.80	2.32	2.05
C ₅ Isomers	.479	.664	.814	.788	.693	.998
n-Hexane	.352	.379	.403	.433	.369	.318
1+2 Hexenes	1.69	1.82	1.76	1.92	1.62	1.40
C ₆ Isomers	.501	.573	.584	.696	.554	.470
n-Heptane	.279	.296	.308	.356	.298	.240
1+2 Heptenes	1.35	1.37	1.32	1.54	1.29	1.08
C ₇ Isomers	.370	.404	.806	.508	.424	.352
n-Octane	.309	.282	.268	.328	.266	.256
1+2 Octenes	1.15	1.11	1.05	1.33	1.15	1.08
C ₈ Isomers	.261	.224	.284	.338	.271	.267
n-Nonane	.472	.236	.251	.258	.240	.208
1+2 Nonenes	.927	.854	.933	.939	1.02	.917
C ₉ Isomers	.0913	.0525	.0551	.0523	.0404	.0586
n-Decane	.759	.394	.314	.342	.294	.270
1+2 Decenes	.908	.844	.867	.816	1.08	.971
C ₁₀ Isomers	.0927	.0675	.0642	.0693	.0638	.0944
n-Undecane	.935	.503	.451	.627	.426	.438
1+2 Undecenes	.971	.880	1.05	.926	1.29	1.17
C ₁₁ Isomers	.134	.0928	.0948	.0956	.0717	.132
C ₂ -C ₄	10.4	12.3	12.6	12.9	10.6	9.74
C ₅ -C ₁₁	14.8	14.0	14.8	15.5	14.0	13.0
C ₁₂ +	72.5	71.0	69.9	68.8	73.0	75.1
Wax ^c	56.0	52.5	45.2	42.6	45.7	51.5

^c Unanalyzed wax withdrawn from reactor

Table IV-2.9 (cont'd) Summary of Slurry Reactor Test Results for Run SB-0261.

Period	7	8	9	10	11
Weight % of Hydrocarbons					
CH ₄	2.07	2.15	2.06	1.65	1.64
Ethane	.561	.648	.761	.435	.418
Ethylene	2.33	2.08	1.88	1.44	1.75
Propane	.440	.460	.427	.470	.482
Propylene	3.03	3.12	2.96	2.85	2.94
n-Butane	.382	.395	.363	.421	.437
1+2 Butenes	2.30	2.37	2.26	2.10	2.28
C ₄ Isomers	.237	.241	.222	.244	.258
n-Pentane	.242	.355	.335	.389	.429
1+2 Pentenes	1.95	1.94	1.97	1.95	2.08
C ₅ Isomers	1.15	.405	.345	.359	.389
n-Hexane	.315	.372	.327	.319	.366
1+2 Hexenes	1.32	1.66	1.39	1.27	1.44
C ₆ Isomers	.500	.461	.394	.438	.467
n-Heptane	.255	.301	.252	.270	.313
1+2 Heptenes	1.10	1.16	1.05	1.05	1.14
C ₇ Isomers	.372	.377	.303	.362	.403
n-Octane	.211	.287	.217	.247	.274
1+2 Octenes	.864	1.21	.893	1.05	1.08
C ₈ Isomers	.362	.410	.304	.316	.377
n-Nonane	.192	.342	.194	.205	.222
1+2 Nonenes	.768	1.22	.870	.974	1.10
C ₉ Isomers	.0591	.391	.309	.241	.282
n-Decane	.272	.405	.241	.274	.277
1+2 Decenes	.802	1.33	1.01	1.06	1.18
C ₁₀ Isomers	.0891	.426	.367	.230	.266
n-Undecane	.430	.544	.354	.377	.359
1+2 Undecenes	.919	1.49	1.18	1.29	1.23
C ₁₁ Isomers	.114	.553	.291	.387	.394
C ₂ -C ₄	9.28	9.32	8.87	7.95	8.56
C ₅ -C ₁₁	12.3	15.6	12.6	13.1	14.0
C ₁₂ +	76.4	72.9	76.5	77.3	75.8
Wax ^c	53.3	59.2	55.3	59.4	55.1

^c Unanalyzed wax withdrawn from reactor

Table IV-2.10 Major Events in Run SB-0261.

TOS (h)	Event
	Slurry loading: 298 g n-octacosane, 20.2 g catalyst (325-270 mesh)
	Catalyst pretreatment: H ₂ at 240°C
	Slurry sample withdrawal: 3 g wax, 0.2 g catalyst
	Wax withdrawal through filter: 43 g of wax
0	Initiate synthesis gas flow
2	Plug in inlet line – break in synthesis gas supply
6	Achieved initial process conditions: T=260°C, P=1.48 MPa, SV=1.4 NI/g-cat/h, (H ₂ /CO)=0.70
168	Temperature change from 260 to 263°C
220	Slurry sample withdrawal: 9 g wax, 0.7 g catalyst
236	Temperature change from 263 to 260°C
435	Slurry sample withdrawal: 22 g wax, 1.6 g catalyst
477	Wax removal through a dipleg: 183 g wax, 1.6 g catalyst
529	Space velocity change from 1.4 to 1.1 NI/g-cat/h
622	Pressure change from 1.48 to 2.17 MPa and space velocity from 1.1 to 1.4 NI/g-cat/h
721	Slurry sample withdrawal: 23 g wax, 0.7 g catalyst
722	End of run: 414 g wax, 13.1 g catalyst recovered from reactor
	Wax catalyst removed during the run: 1391 g of wax, 3.9 g of catalyst
	Catalyst recovery: 85%; wax recovery: 164%

Figure IV-2.8 (H₂+CO) conversion (solid symbols) and volumetric contraction (open symbols) as a function of time on stream for Run SB-0261.

remained stable during the next 300 h of testing. Between 240 and 530 h on stream, the (H₂+CO) conversion fluctuated between 65 and 68%. At about 550 h, the gas flow rate was decreased (SV = 1 NI/g-cat/h) in order to achieve higher conversion. During the next 70 h on stream (550 – 620 h) the catalyst was stable, and the (H₂+CO) conversion was between 75 and 76%. After that both the reaction pressure and the gas space velocity were increased to 2.17 MPa and 1.4 NI/g-cat/h, respectively, and the testing continued at these conditions for additional 100 h. The catalyst deactivation was observed during this period. The (H₂+CO) conversion decreased from 70.7% at 643 h, to 62.7% at 722 h.

WGS activity of the catalyst was high and stable throughout the entire test. The usage ratio varied between 0.53 and 0.62, with an average value of 0.57.

Wax and Catalyst Inventories/Withdrawals

Wax was withdrawn through a cylindrical porous filter element with nominal pore size of 0.5 µm. The filter was placed horizontally at a height corresponding to a static slurry volume of 410 cc. Wax withdrawal rate decreased with time on stream. During the first 100 h, withdrawals were made at initial pressure drop (across the filter) of 15 psi, and the rate of wax withdrawal decreased from 60 g/h to 15 g/h. The latter rate of withdrawal was maintained during the next 100 h on stream by increasing gradually the pressure drop to 80 psi. During the period of 200 – 700 h, the initial pressure drop was maintained at 80 – 100 psi, but the rate of withdrawal decreased with time from 15 g/h to 5 g/h. One successful slurry withdrawal (183 g of slurry) to an external settling vessel was made at about 480 h, but this method had to be abandoned due to plugging of valves between the reactor and the settler.

The average wax production rate for the entire test was 1.90 g/h, whereas the range of wax production rates during the test was 0.7 – 3.1 g/h. At the end of the run 13.1 g of catalyst was recovered from the reactor (calculated from concentration of catalyst in the slurry, which was determined by burning slurry sample in a crucible),

and another 4.8 g was removed from the reactor during the test (with slurry samples for catalyst characterization and with wax removed from the external settler). The catalyst recovery was about 89%, based on the amount of catalyst charged into the reactor. At the end of the run 413 g of the wax was found in the reactor, whereas the initial amount (after the slurry sample withdrawal following catalyst reduction) was 252 g (see Table IV-2.10). This indicates that wax withdrawals throughout the test were not complete, and that 161 g of wax had accumulated in the reactor.

Catalyst Characterization by XRD and/or MES

A slurry sample withdrawn from the reactor after hydrogen reduction at 240°C for 2 h contained a small amount of catalyst which was insufficient for XRD analysis. The following phases were detected by XRD in a sample withdrawn from the reactor at 220 h : magnetite, iron carbide(s) and iron carbonate. The same phases were identified in samples withdrawn from the reactor at 435 and 722 h on stream. It is presumed that carbon dioxide formed by water gas shift reaction may be responsible for the formation of FeCO_3 (siderite). The MES analysis of the above samples indicates the presence of superparamagnetic oxides/oxyhydroxides, magnetite and siderite in varying proportions. The amount of superparamagnetic phase was found to decrease with time, from 64% at 220 h to 19% at 722 h, whereas the amount of siderite was found to increase from 13 to 64% during the same period of time.

Hydrocarbon and Carbon Number Product Distributions

Selectivities of low molecular weight products (CH_4 , $\text{C}_2\text{-C}_4$, $\text{C}_5\text{-C}_{11}$) passed through a local maximum at about 200 h on stream (mass balance 4), whereas selectivity C_{12}^+ products passed through a local minimum (Table IV-2.9). For example, methane selectivity increased from 2.3% in balance 1 (TOS = 44) to 2.8% in balances 2-4, and then decreased to 2.1 – 2.4% between 220 and 620 h on stream. During testing at 300 psig, methane selectivity was even lower ~1.6% (620-720 h). Selectivity of gaseous hydrocarbons was low throughout the entire test, ($\text{C}_2\text{-C}_4$) = 8-

Figure IV-2.9 Carbon number product distribution for Run SB-0261 (TOS=92 h).

15%, whereas selectivity of C_{12}^+ products was high (69-77%). Selectivity of (C_1+C_2) products was always within the DOE target (less than 8 %).

A typical carbon number distribution obtained at baseline conditions (TOS = 92 h), including the analyzed wax products collected in a high pressure trap is shown in Figure IV-2.9. Experimental data were fitted with a three parameter model of Huff and Satterfield. Some positive deviations from the ASF distribution are noted in C_{11} - C_{17} carbon number range. We do not know whether this is due to the intrinsic catalyst selectivity or some experimental artifacts (e.g. loss of products and errors in the analysis).

Overall this run has been very successful. After initial drop in activity (first 220 h on stream), the activity remained very stable until the catalyst was exposed to higher reaction pressure (300 psig during the last 100 h on stream; 620–720 h). Hydrocarbon selectivity was within the DOE target throughout the entire test.

IV-2.5 Run SB-2270 with 100 Fe/5 Cu/4.2 K/16 SiO₂ Catalyst

The catalyst was tested initially (first 230 h) at 260°C, 200 psig (1.48 MPa), 1.4 NI/g-cat/h using the synthesis gas with H₂ to CO molar feed ratio of 0.69, and three mass balances were made during this time period. Following this the reaction pressure and the gas space velocity were changed to 300 psig (2.17 MPa) and 2.3 (NI/g-cat/h), respectively. At 300 h on stream the catalyst was regenerated in-situ with H₂ at 220°C, and 200 psig for 2 hours. Two mass balances were made at these process conditions, one before and the other one after the regeneration with H₂. The test was terminated voluntarily after 400 h on stream. Results from all five mass balances are summarized in Table IV-2.11.

Catalyst Activity and Stability

The catalyst activity, expressed in terms of volumetric contraction and (H₂+CO) conversion, declined slowly with time during the first 180 h on stream, as shown in

Table IV-2.11 Summary of Slurry Reactor Test Results for Run SB-2270.

Period	1	2	3	4	5
Date	08/16/90	08/18/90	08/21/90	08/26/90	08/28/90
Time on Stream (h)	45.0	93.5	162.0	284.5	332.0
Balance Duration (h)	14.0	20.0	20.0	11.5	14.0
Average Temperature (°C)	260.	260.	260.	260.	260.
Pressure (MPa)	1.48	1.48	1.48	2.17	2.17
H ₂ /CO Feed Ratio	.689	.689	.689	.689	.661
Space Velocity (Nl/g-cat·h) ^a	1.37	1.37	1.37	2.30	2.14
Space Velocity (Nl/g-Fe·h)	2.40	2.40	2.40	4.04	3.75
GHSV (h ⁻¹) ^b	33.7	33.7	33.7	56.6	52.6
CO Conversion (%)	68.7	67.2	64.9	35.2	46.5
H ₂ +CO Conversion (%)	65.7	64.2	61.7	34.5	44.2
H ₂ /CO Usage	.613	.612	.604	.656	.578
STY (mols H ₂ +CO/g-cat·h) ^a	.040	.039	.038	.035	.042
$P_{CO_2} \cdot P_{H_2} / P_{CO} \cdot P_{H_2O}$	19.0	20.9	22.5	6.80	9.22
Weight % of Outlet					
H ₂	1.85	1.92	2.05	3.11	2.73
H ₂ O	.904	.786	.706	1.08	1.10
CO	30.0	31.5	33.6	61.2	51.6
CO ₂	49.1	47.3	45.8	25.4	33.7
Hydrocarbons	6.97	8.22	10.0	6.64	6.76
Oxygenates	.587	.447	.521	.296	.356
Wax ^c	10.5	9.80	7.32	2.23	3.76
Yield (g/Nm ³ H ₂ + CO Converted)					
CH ₄	6.71	8.65	9.78	9.16	8.24
C ₂ -C ₄ Hydrocarbons	25.9	32.5	39.9	39.1	37.2
C ₅ -C ₁₁ Hydrocarbons	25.7	35.5	40.6	38.1	34.5
C ₁₂ + Hydrocarbons	146.	139.	127.	115.	105.
Wax ^c	123.	118.	91.7	50.6	66.2
Oxygenates	6.88	5.36	6.53	6.70	6.26
Total	212.	221.	224.	208.	192.
1+2 Olefins/n-Paraffin Ratio					
C ₂	1.27	1.37	.846	1.38	1.55
C ₃	4.99	4.74	4.85	4.49	4.32
C ₄	4.34	4.25	4.29	4.03	3.83
C ₈	2.28	2.19	2.40	2.42	2.87
C ₁₀	1.48	2.01	1.99	2.60	2.95

^a Based on unreduced catalyst

^b Based on static slurry volume

^c Unanalyzed wax withdrawn from reactor

Table IV-2.11 (cont'd) Summary of Slurry Reactor Test Results for Run SB-2270.

Period	1	2	3	4	5
Weight % of Hydrocarbons					
CH ₄	3.28	4.00	4.50	4.55	4.44
Ethane	1.57	2.04	2.65	2.03	2.29
Ethylene	1.85	2.60	2.10	2.62	3.33
Propane	.854	1.03	1.32	1.53	1.62
Propylene	4.07	4.65	6.13	6.55	6.67
n-Butane	.784	.870	1.12	1.25	1.20
1+2 Butenes	3.29	3.57	4.63	4.88	4.45
C ₄ Isomers	.251	.290	.409	.582	.481
n-Pentane	.748	.791	1.00	1.07	.815
1+2 Pentenes	2.88	3.07	3.83	3.86	2.90
C ₅ Isomers	.374	.424	.604	.831	.714
n-Hexane	.414	.456	.453	.655	.684
1+2 Hexenes	1.25	1.97	1.59	2.04	2.20
C ₆ Isomers	.422	.520	.605	.976	1.08
n-Heptane	.270	.354	.496	.492	.537
1+2 Heptenes	.792	1.20	1.24	1.28	1.48
C ₇ Isomers	.210	.303	.362	.927	.969
n-Octane	.211	.451	.547	.480	.487
1+2 Octenes	.473	.971	1.29	1.14	1.37
C ₈ Isomers	.132	.393	.273	.157	.153
n-Nonane	.447	.689	.653	.620	.685
1+2 Nonenes	.749	1.14	1.42	1.24	1.41
C ₉ Isomers	.0342	.0786	.151	.101	.125
n-Decane	.626	.605	.639	.355	.339
1+2 Decenes	.916	1.20	1.25	.912	.985
C ₁₀ Isomers	.156	.111	.169	.119	.154
n-Undecane	.477	.554	.686	.499	.363
1+2 Undecenes	.682	1.000	1.21	.989	.988
C ₁₁ Isomers	.278	.130	.192	.224	.199
C ₂ -C ₄	12.7	15.0	18.4	19.5	20.1
C ₅ -C ₁₁	12.5	16.4	18.7	19.0	18.6
C ₁₂ +	71.5	64.5	58.5	57.0	56.9
Wax ^c	60.1	54.4	42.2	25.2	35.7

^c Unanalyzed wax withdrawn from reactor

Figures IV-2.10 and IV-2.11. After the wax withdrawal at 184 h, the volumetric contraction decreased markedly from 41% to 31%, whereas the (H₂+CO) conversion decreased from about 64% to 45%. During the next 40 hours, the volumetric contraction remained fairly stable (29-31%). Although, the reasons for this sharp drop in activity are not known, we suspect that it might have been caused by removal of the catalyst particles from the slurry. After withdrawal of approximately 280 cm³ of wax, a significant portion of the catalyst remained above the slurry level (e.g. deposited on the reactor wall or on the internal filter element), and it appears that this catalyst is not as active as the one in the slurry.

At about 230 h on stream the reaction pressure and the gas space velocity were increased to 300 psig (2.17 MPa) and 2.3 (NI/g-cat/h); respectively. During the next 60 hours, the activity remained fairly constant (VC=21-23%; (H₂+CO) = 33-34%). At 250 h on stream an attempt was made to increase the activity, by adding 65 g of wax to raise the liquid level in the slurry reactor. However, this did not result in increased catalyst activity.

At about 300 h on stream the catalyst was regenerated in-situ with H₂ at 220°C and 200 psig for two hours. After regeneration, the catalyst activity increased markedly. At 311 h on stream the values of volumetric contraction and (H₂+CO) conversion were: 33.8 and 47.6%, respectively. However, the activity declined with time and at 400 h the volumetric contraction was only 23.5%.

The WGS activity was rather high throughout the entire test, e.g. the H₂/CO usage ratio varied between 0.6 and 0.7, whereas the approach to equilibrium was between 0.1 and 0.3 (see Table IV-2.11).

Wax and Catalyst Inventories

The reactor was charged initially with 10 g of catalyst and 289 g of purified n-octacosane. We have deliberately chosen to add only a small amount of catalyst for this test, in order to minimize the need for wax withdrawals throughout the run. Wax

Figure IV-2.10 Volumetric contraction versus time on stream for Run SB-2270
 (weights indicate amount of wax withdrawn (-) or added (+)).

Figure IV-2.11 (H₂+CO) conversion versus time on stream for Run SB-2270.

withdrawals result in disturbance of the system and may have adverse effect on the rate of catalyst deactivation (Bukur et al., 1989b). Only three wax withdrawals were made through a 2 μm cylindrical filter element placed vertically in the reactor. Results from all withdrawals are summarized in Table IV-2.12.

There were no operational problems during wax withdrawals, and the collected wax was clear in appearance. At the end of the run 8.9 g of catalyst was recovered in the reactor, after separation from wax by filtration and burning in the air to convert the used catalyst into Fe_2O_3 . It is estimated that about 0.3 g of catalyst was removed from the reactor with the slurry sample withdrawn at the end of reduction. The catalyst recovery was 92.6%, whereas the wax recovery was 78%.

Catalyst Characterization by XRD and/or MES

A slurry sample withdrawn from the reactor after hydrogen reduction at 220°C for 2 h contained a small amount of catalyst which was insufficient for XRD analysis. MES analysis of the sample revealed the presence of superparamagnetic oxide/oxyhydroxide phases. No other samples were withdrawn from the reactor during or after the test.

Hydrocarbon and Carbon Number Product Distributions

Hydrocarbon selectivities were similar in balances 2-5, and the average values for methane and product group lumps by carbon numbers were: (CH_4) = 4.2; ($\text{C}_2\text{-C}_4$) = 17.7; ($\text{C}_5\text{-C}_{11}$) = 17.7, and (C_{12}^+) = 60.4 wt%.

During the first mass balance the fraction of high molecular weight products was markedly higher, and the methane yield was markedly lower in comparison to selectivities obtained in balances 2 to 5 (see Table IV-2.11).

A typical carbon number distribution of products collected at 162 h on stream is shown in Figure IV-2.12. Experimental data were fitted reasonably well with a three parameter model of Huff and Satterfield.

Table IV-2.12 Wax and Solids Inventory for Run SB-2270.

TOS	Description
	Slurry loading: 289 g wax, 10.0 g catalyst
	Wax filtration following reduction: 70.8 g
	Slurry withdrawal for catalyst characterization: 10 g (9.7 g of wax, 0.3 g of catalyst)
184	Wax filtration: 194 g
249	Wax addition: 65 g
372	Wax filtration: 137 g
400	End of run: 170 g of wax and 9 g of catalyst were recovered from the reactor. Wax recovery: 78%; Catalyst recovery: 92.6%

Figure IV-2.12 Carbon number product distribution for Run SB-2270 (TOS=162 h).

IV-2.6 Run SB-2832 with 100 Fe/5 Cu/4.2 K/16 SiO₂ Catalyst

The catalyst used in this test was synthesized in our laboratory during the current contract, whereas the catalyst used in Run SB-2270 was synthesized prior to the current contract in 1988. Physical properties of the two catalysts are similar as noted in section IV-2 of this report (Table IV-2.1). Catalyst from the same preparation batch as that used in Run SB-2832 was used in two other slurry reactor tests (Runs SA-3162 and SB-2932). Results from these tests were described in section III-5 of this report (Pretreatment Effect Research).

The catalyst was reduced with hydrogen at 0.8 MPa (100 psig), 240°C for 2 hours. After the reduction, the catalyst was tested at baseline conditions of 1.48 MPa (200 psig), 260°C, 1.5 NI/g-cat/h (2.6 NI/g-Fe/h) during the first 263 h on stream using syngas with H₂/CO=0.7. Between 263 and 526 h on stream the catalyst was tested at 2.17 MPa (300 psig) and gas space velocity (SV) of 2.2 NI/g-cat/h (3.9 NI/g-Fe/h), which corresponds to the same pressure to SV ratio as at the baseline conditions. At 527 h on stream the gas space velocity was reduced to 1.8 NI/g-cat/h while other process conditions remained constant (2.17 MPa, 260°C, H₂/CO=0.7). The catalyst was regenerated at 664 h with hydrogen at 240°C, 1.48 MPa for 2h, and then the baseline conditions were reestablished. The test was terminated voluntarily after 720 h on stream. Results from eleven mass balances made during the tests are summarized in Table IV-2.13, while major events are listed in Table IV-2.14.

Catalyst Activity and Stability

The catalyst activity was high and it deactivated only moderately during this test. The initial (H₂+CO) conversion at baseline conditions was 84% at 17 h, then it gradually decreased to 77 % at 263 h. Volumetric gas contraction (VC) also decreased from 56 to 52 % during the same time period (Figure IV-2.13). The usage ratio during this period was about 0.58. When the pressure and SV were increased at 263 h, the syngas conversion decreased to 74 % at 284 h and further to 69 % at 480 h

Table IV-2.13 Summary of Slurry Reactor Test Results for Run SB-2832.

Period	1	2	3	4	5	6
Time on Stream (h)	41.0	92.0	139.0	210.0	308.0	355.0
Balance Duration (h)	7.5	6.0	6.5	6.0	6.0	6.0
Average Temperature (°C)	260.	260.	260.	260.	260.	260.
Pressure (MPa)	1.48	1.48	1.48	1.48	2.17	2.17
H ₂ /CO Feed Ratio	.706	.704	.704	.681	.667	.667
Space Velocity (NI/g-cat·h) ^a	1.50	1.50	1.50	1.50	2.20	2.20
Space Velocity (NI/g-Fe·h)	2.63	2.63	2.63	2.63	3.86	3.86
GHSV (h ⁻¹) ^b	37.0	37.0	37.0	37.0	54.2	54.2
CO Conversion (%)	87.5	86.4	85.5	83.1	78.0	77.9
H ₂ +CO Conversion (%)	81.1	80.3	79.5	78.7	74.6	74.1
H ₂ /CO Usage	.581	.584	.585	.591	.594	.585
STY (mols H ₂ +CO/g-cat·h) ^a	.054	.054	.053	.053	.073	.073
$P_{CO_2} \cdot P_{H_2} / P_{CO} \cdot P_{H_2O}$	37.4	36.9	28.4	20.4	22.2	18.5
Weight % of Outlet						
H ₂	1.36	1.37	1.40	1.30	1.41	1.46
H ₂ O	1.09	.999	1.23	1.33	.959	1.17
CO	11.9	13.0	13.9	16.1	21.1	21.3
CO ₂	62.8	61.7	60.7	59.2	56.1	55.4
Hydrocarbons	13.0	13.1	12.8	14.1	16.2	12.0
Oxygenates	.253	.226	.174	.230	.336	.604
Wax ^c	9.60	9.57	9.72	7.68	3.86	8.13
Yield (g/Nm ³ H ₂ + CO Converted)						
CH ₄	9.60	10.1	10.3	9.73	10.0	9.36
C ₂ -C ₄ Hydrocarbons	32.6	32.9	33.3	35.8	35.9	36.2
C ₅ -C ₁₁ Hydrocarbons	54.8	47.1	44.9	48.7	62.4	47.7
C ₁₂ + Hydrocarbons	118.	126.	129.	121.	101.	118.
Wax ^c	91.0	91.3	93.7	75.9	40.3	85.5
Oxygenates	2.40	2.16	1.68	2.27	3.50	6.35
Total	217.	219.	219.	218.	213.	218.
1+2 Olefins/n-Paraffin Ratio						
C ₂	.593	.794	.690	.885	1.05	1.27
C ₃	4.70	4.84	4.74	4.93	4.81	4.70
C ₄	4.05	4.25	4.28	4.60	3.90	3.99
C ₅	1.77	2.09	2.20	2.28	2.37	2.50
C ₁₀	1.50	1.47	1.64	1.80	1.95	2.18

^a Based on unreduced catalyst^b Based on static slurry volume^c Unanalyzed wax withdrawn from reactor

Table IV-2.13 (cont'd) Summary of Slurry Reactor Test Results for Run SB-2832.

Period	7	8	9	10	11
Time on Stream (h)	427.0	498.0	570.0	641.0	713.0
Balance Duration (h)	6.0	6.0	6.0	6.0	6.0
Average Temperature (°C)	260.	260.	260.	260.	260.
Pressure (MPa)	2.17	2.17	2.17	2.17	1.48
H ₂ /CO Feed Ratio	.681	.681	.695	.681	.681
Space Velocity (Nl/g-cat·h) ^a	2.20	2.20	1.80	1.80	1.46
Space Velocity (Nl/g-Fe·h)	3.86	3.86	3.16	3.16	2.56
GHSV (h ⁻¹) ^b	54.2	54.2	44.4	44.4	29.2
CO Conversion (%)	74.4	71.3	79.8	76.5	71.3
H ₂ +CO Conversion (%)	70.9	68.7	75.7	72.9	67.4
H ₂ /CO Usage	.602	.619	.609	.603	.589
STY (mols H ₂ +CO/g-cat·h) ^a	.069	.067	.061	.059	.044
$P_{CO_2} \cdot P_{H_2} / P_{CO} \cdot P_{H_2O}$	18.4	15.4	20.6	20.6	24.6
Weight % of Outlet					
H ₂	1.61	1.65	1.45	1.52	1.80
H ₂ O	1.06	1.11	1.17	1.01	.781
CO	24.6	27.4	19.5	22.6	27.4
CO ₂	52.5	50.3	56.8	54.7	51.5
Hydrocarbons	12.4	12.8	12.1	12.9	13.1
Oxygenates	.636	.748	.816	.701	.279
Wax ^c	7.07	5.96	8.28	6.48	5.12
Yield (g/Nm ³ H ₂ + CO Converted)					
CH ₄	9.36	9.21	9.59	10.8	9.52
C ₂ -C ₄ Hydrocarbons	34.6	34.0	32.4	35.8	33.4
C ₅ -C ₁₁ Hydrocarbons	49.2	47.9	43.9	51.0	49.5
C ₁₂ + Hydrocarbons	120.	122.	120.	108.	117.
Wax ^c	77.1	67.5	83.8	68.8	59.1
Oxygenates	6.94	8.47	8.25	7.44	3.22
Total	220.	221.	214.	214.	213.
1+2 Olefins/n-Paraffin Ratio					
C ₂	1.36	1.76	1.14	1.16	1.89
C ₃	4.60	4.65	4.69	4.73	5.59
C ₄	3.84	3.84	3.96	3.97	4.58
C ₅	2.46	2.42	2.28	2.43	2.71
C ₁₀	2.13	2.22	2.09	2.20	2.50

^a Based on unreduced catalyst^b Based on static slurry volume^c Unanalyzed wax withdrawn from reactor

Table IV-2.13 (cont'd) Summary of Slurry Reactor Test Results for Run SB-2832.

Period	1	2	3	4	5	6
Weight % of Hydrocarbons						
CH ₄	4.47	4.67	4.74	4.51	4.78	4.43
Ethane	2.33	2.26	2.38	2.32	2.33	2.10
Ethylene	1.29	1.68	1.53	1.92	2.27	2.49
Propane	1.14	1.08	1.13	1.18	1.24	1.25
Propylene	5.09	5.00	5.11	5.55	5.68	5.59
n-Butane	.990	.923	.918	.948	1.06	1.06
1+2 Butenes	3.87	3.79	3.79	4.21	4.91	4.09
C ₄ Isomers	.476	.461	.463	.486	.550	.562
n-Pentane	1.10	.920	.897	.927	1.04	1.01
1+2 Pentenes	3.68	3.41	3.43	3.72	3.65	3.48
C ₅ Isomers	.464	.445	.446	.465	.561	.518
n-Hexane	.950	.850	.844	.891	1.10	.926
1+2 Hexenes	2.75	2.59	2.65	3.04	3.32	2.71
C ₆ Isomers	.829	.867	.895	.962	1.15	.950
n-Heptane	1.03	.787	.754	.799	1.10	.821
1+2 Heptenes	2.03	1.98	2.03	2.10	2.68	2.02
C ₇ Isomers	.594	.563	.609	.705	.937	.686
n-Octane	1.04	.779	.669	.715	1.04	.701
1+2 Octenes	1.82	1.60	1.45	1.60	2.41	1.72
C ₈ Isomers	.661	.439	.445	.653	.784	.456
n-Nonane	.853	.687	.529	.617	.813	.548
1+2 Nonenes	1.56	1.24	1.02	1.23	1.78	1.28
C ₉ Isomers	.308	.124	.135	.187	.416	.229
n-Decane	1.02	.775	.622	.663	1.000	.605
1+2 Decenes	1.52	1.12	1.00	1.18	1.92	1.30
C ₁₀ Isomers	.368	.165	.154	.184	.532	.339
n-Undecane	1.12	.991	.765	.700	1.07	.634
1+2 Undecenes	1.45	1.25	1.11	1.07	1.92	1.26
C ₁₁ Isomers	.409	.178	.170	.157	.599	.375
C ₂ -C ₄	15.2	15.2	15.3	16.6	17.1	17.1
C ₅ -C ₁₁	25.5	21.8	20.6	22.6	29.8	22.6
C ₁₂ +	54.8	58.4	59.3	56.3	48.3	55.9
Wax ^c	42.4	42.2	43.1	35.2	19.2	40.4

^c Unanalyzed wax withdrawn from reactor

Table IV-2.13 (cont'd) Summary of Slurry Reactor Test Results for Run SB-2832.

Period	7	8	9	10	11
Weight % of Hydrocarbons					
CH ₄	4.40	4.33	4.66	5.25	4.54
Ethane	1.92	1.78	1.99	2.16	1.64
Ethylene	2.44	2.93	2.11	2.33	2.90
Propane	1.21	1.11	1.16	1.28	.980
Propylene	5.32	4.94	5.20	5.77	5.22
n-Butane	1.03	.987	.982	1.08	.862
1+2 Butenes	3.81	3.66	3.75	4.15	3.81
C ₄ Isomers	.539	.557	.558	.609	.532
n-Pentane	.967	.983	.923	1.02	.834
1+2 Pentenes	3.28	3.26	3.13	3.53	3.31
C ₅ Isomers	.496	.484	.443	.504	.380
n-Hexane	.902	.817	.746	.909	.709
1+2 Hexenes	2.58	2.34	2.22	2.68	2.54
C ₆ Isomers	1.15	.936	.732	.925	.843
n-Heptane	.841	.700	.719	.898	.697
1+2 Heptenes	1.98	1.66	1.68	2.04	1.87
C ₇ Isomers	.673	.581	.437	.600	.693
n-Octane	.696	.615	.635	.768	.699
1+2 Octenes	1.68	1.47	1.42	1.84	1.86
C ₈ Isomers	.450	.423	.387	.521	.462
n-Nonane	.593	.607	.627	.672	.650
1+2 Nonenes	1.35	1.41	1.35	1.57	1.73
C ₉ Isomers	.325	.462	.301	.282	.319
n-Decane	.703	.722	.737	.759	.692
1+2 Decenes	1.48	1.58	1.52	1.65	1.70
C ₁₀ Isomers	.360	.491	.441	.440	.461
n-Undecane	.759	.796	.816	.823	.779
1+2 Undecenes	1.50	1.65	1.62	1.71	1.87
C ₁₁ Isomers	.352	.502	.429	.593	.532
C ₂ -C ₄	16.3	16.0	15.8	17.4	15.9
C ₅ -C ₁₁	23.1	22.5	21.3	24.7	23.6
C ₁₂ +	56.2	57.2	58.3	52.6	55.9
Wax ^c	36.2	31.7	40.7	33.4	28.2

^c Unanalyzed wax withdrawn from reactor

Table IV-2.14 Major Events in Run SB-2832.

TOS (h)	Event
	Slurry loading: 300 g n-octacosane, 11.5 g catalyst (particle size <270 mesh)
	Catalyst pretreatment: H ₂ , 240°C, 0.78 MPa, for 2 h
	Slurry sample withdrawal after the pretreatment: 24 g wax, 0.9 g catalyst
	Wax withdrawal through filter: 49 g of wax
0	Initiate synthesis gas flow
2	Achieve initial process conditions: T=260°C, P=1.48 MPa, SV=1.5 NI/g-cat/h, (H ₂ /CO)=0.68
263	Pressure change from 1.48 to 2.17 MPa and space velocity from 1.5 to 2.2 NI/g-cat/h
526	Space velocity change from 2.2 to 1.8 NI/g-cat/h
665	Slurry sample withdrawal: 26 g wax, 1.1 g catalyst
666	Regeneration of catalyst: H ₂ at 240°C for 1 h
667	Slurry sample withdrawal: 20 g wax, 0.9 g catalyst
669	Change to initial baseline process conditions: T=260°C, P=1.48 MPa, SV=1.5 NI/g-cat/h, (H ₂ +CO)=0.68
720	End of run: 207 g wax, 8.1 g catalyst recovered from reactor
	Wax and catalyst removal during the run: 754 g wax, 2 g catalyst
	Catalyst recovery: 95%; Wax recovery: 91%

Figure IV-2.13 (H₂+CO) conversion (solid symbols) and volumetric contraction (open symbols) as a function of time on stream for Run SB-2832.

on stream, while the usage ratio varied between 0.58 and 0.61. At 527 h, the space velocity was lowered to 1.8 NI/g-cat/h in attempt to increase the catalyst activity. After initial increase in activity, the catalyst continued to deactivate slowly with time. The syngas conversion was about 77 % at 531 h, but became 74 % at 647 h. Regeneration with hydrogen at 664 h could not recover the catalyst activity. The syngas conversion was 68 % after the regeneration, in comparison with 77 % at 263 h under the same baseline conditions, indicating loss in catalyst activity.

Wax and Catalyst Withdrawal/Inventory

About 11.5 g of the catalyst (less than 270 mesh) was loaded initially and suspended in n-octacosane to give a 3.7 weight % catalyst slurry. During the test, wax was withdrawn periodically (approximately every 50 h) through a porous sintered metal filter with nominal pore size of 0.5 micron. The filter was placed horizontally at a height corresponding to a static slurry volume of 430 cc. A pressure drop of 15 psig across the filter was employed during the withdrawal. The rate of wax withdrawal decreased with time, varying from 85 g/h to 24 g/h.

One slurry sample was withdrawn after the reduction for catalyst characterization. Additional two slurry samples were taken, one just before and another one after the regeneration, at 665 and 667 h, respectively.

At the end of the run, about 206 g of wax was recovered from the autoclave reactor, while the initial amount (after the slurry sample and wax withdrawal following the pretreatment) was estimated to be 228 g (wax recovery of 90%). About 8.1 g of catalyst was recovered from the reactor at the end of the test, whereas approximately 2.9 g was removed with the slurry samples during the test (catalyst recovery of 88%).

Catalyst Characterization by XRD and/or MES

A catalyst sample withdrawn from the reactor after hydrogen reduction at 240°C for 2 h exhibited broad peaks (small crystallites), which were assigned to magnetite (Fe_3O_4) and/or maghemite (Fe_2O_3). A sample withdrawn at 665 h from the reactor

contained mostly iron carbides, and some magnetite. After the regeneration with hydrogen at 240°C for 1 h, the peaks associated with magnetite had increased, whereas those associated with iron carbides have decreased. It is suggested that water formed during the reduction process may be responsible for partial reoxidation of the catalyst. On introduction of syngas after the catalyst regeneration, the amount of carbide(s) seemed to have increased (a sample withdrawn from the reactor at 720 h).

Hydrocarbon and Carbon Number Product Distributions

Hydrocarbon selectivity was fairly stable during the entire test at various process conditions although the catalyst deactivated slowly with time. For example, during the first 260 h under the baseline conditions, the average methane selectivity was 4.5 wt%, (C₂-C₄) =15.5 %, (C₅-C₁₁) =22 %, and C₁₂+ = 58 %. At 300 psig and 2.2 NI/g-cat/h, the average values of methane, C₂-C₄, C₅-C₁₁ and C₁₂+ selectivities were 4.4, 16.6, 23.1 and 57.0 wt%, respectively. Between 527 and 664h at 300 psig and 1.8 NI/g-cat/h, methane selectivity increased from 4.5 to 5.2 wt%, while C₁₂+ decreased from 58 to 52 wt%. After the catalyst regeneration and return to baseline conditions, the hydrocarbon selectivities were: 4.5 (methane), 16 (C₂-C₄), 23.5 (C₅-C₁₁) and 56 wt% of C₁₂+. These values are very similar to those obtained during the first 260 h of testing.

A typical carbon number distribution obtained at baseline conditions, including the analyzed wax products collected in a high pressure trap is shown in Figure IV-2.14. Experimental data were fitted with a three parameter model of Huff and Satterfield. Some positive deviations from the ASF distribution are noted in C₁₁-C₁₇ carbon number range. We do not know whether this is due to the intrinsic catalyst selectivity or some experimental artifacts (e.g. loss of products and errors in the analysis).

In summary, this test was quite successful. Syngas conversion was 78-84 %, and (C₁+C₂) selectivity 8.1 wt% during the first 200 h of testing. The catalyst

Figure IV-2.14 Carbon number product distribution for Run SB-2832 (TOS=139 h).

deactivated slowly at a rate of about 0.4 % (syngas conversion) per day during 27 days of continuous testing.

IV-2.7 Run SB-1931 with 100 Fe/5 Cu/6 K/24 SiO₂ Catalyst

Slurry reactor run SB-1931 was conducted to evaluate performance of a precipitated iron catalyst with nominal composition 100 Fe/5 Cu/6 K/24 SiO₂. Reaction pressure and syngas composition were maintained constant throughout the test at 1.48 MPa (200 psig) and (H₂/CO) = 0.66 – 0.69, respectively. Reaction temperature during the first 520 h of testing was maintained at 260°C, and then was increased to 265°C during the next 170 h. Gas space velocity varied between 2.2 NI/g-cat/h and 1.2 (NI/g-cat/h). The test was terminated voluntarily after 692 h on stream. Results from eleven mass balances made during the test are summarized in Table IV-2.15, whereas major events are listed in Table IV-2.16. There were three operational upsets at 15, 80 and 229 h on stream (see Table IV-2.16), which caused temporary disruptions in synthesis gas supply. However, we have not observed any adverse effects on the catalyst performance following these upsets.

Catalyst Activity and Stability

During the first 62 h of testing at 260°C, 1.48 MPa, H₂/CO = 0.66 and space velocity of 2.2 NI/g-cat/h (H₂+CO) conversion increased gradually and stabilized at about 74% (Figure IV-2.15). Following this, the gas space velocity was decreased to 1.8 NI/g-cat/h in attempt to increase conversion. At 76 h on stream the (H₂+CO) conversion was 77.6%, but then decreased to about 75% following the upset between 80 and 92 hours on stream (no syngas flow due to a plug in lines downstream of the reactor). At 138 h on stream gas space velocity was decreased to 1.6 NI/g-cat/h and then maintained at this value during next 236 h (TOS = 138 – 374 h). During this period of time the (H₂+CO) conversion was very stable and its value fluctuated between 75 and 78% (balances 3 to 6). Between 375 and 520 h on stream, gas space

Table IV-2.15 Summary of Slurry Reactor Test Results for Run SB-1931.

Period	1	2	3	4	5	6
Date	04/04/91	04/07/91	04/09/91	04/11/91	04/14/91	04/17/91
Time on Stream (h)	42.0	98.0	162.0	208.0	280.0	351.0
Balance Duration (h)	7.0	6.0	6.0	6.0	6.0	6.0
Average Temperature (°C)	260.	260.	260.	260.	260.	260.
Pressure (MPa)	1.48	1.48	1.48	1.48	1.48	1.48
H ₂ /CO Feed Ratio	.689	.689	.689	.689	.689	.661
Space Velocity (NI/g-cat·h) ^a	2.15	1.83	1.61	1.61	1.61	1.61
Space Velocity (NI/g-Fe·h)	4.03	3.43	3.02	3.02	3.02	3.02
GHSV (h ⁻¹) ^b	33.5	28.5	25.1	25.1	25.1	25.1
CO Conversion (%)	78.2	78.4	81.2	81.4	81.6	80.8
H ₂ +CO Conversion (%)	74.0	75.1	77.2	77.3	77.3	77.3
H ₂ /CO Usage	.597	.618	.606	.605	.601	.588
STY (mols H ₂ +CO/g-cat·h) ^a	.071	.061	.055	.056	.056	.056
$P_{CO_2} \cdot P_{H_2} / P_{CO} \cdot P_{H_2O}$	23.5	9.85	11.6	10.6	16.1	15.1
Weight % of Outlet						
H ₂	1.53	1.40	1.36	1.35	1.35	1.28
H ₂ O	.995	2.15	2.12	2.33	1.63	1.51
CO	20.8	20.6	18.1	17.7	17.4	18.3
CO ₂	56.1	54.5	57.3	57.0	59.3	57.4
Hydrocarbons	9.97	8.56	11.0	11.6	12.5	11.7
Oxygenates	.243	.354	.377	.455	.358	.330
Wax ^c	10.3	12.5	9.79	9.52	7.44	9.41
Yield (g/Nm ³ H ₂ + CO Converted)						
CH ₄	5.22	6.01	5.89	5.95	6.57	6.28
C ₂ -C ₄ Hydrocarbons	23.1	22.1	22.8	22.9	25.5	24.0
C ₅ -C ₁₁ Hydrocarbons	38.1	28.7	31.9	28.7	33.4	30.9
C ₁₂ + Hydrocarbons	146.	160.	147.	155.	136.	154.
Wax ^c	108.	129.	98.0	95.8	75.5	95.9
Oxygenates	2.53	3.65	3.77	4.58	3.63	3.37
Total	215.	221.	212.	218.	206.	219.
1+2 Olefins/ <i>n</i> -Paraffin Ratio						
C ₂	1.77	2.08	1.60	1.81	1.40	1.49
C ₃	5.72	5.94	6.99	7.95	6.82	6.96
C ₄	5.09	5.30	5.84	5.82	5.91	6.24
C ₅	2.80	3.28	3.34	3.76	3.70	3.58
C ₁₀	1.22	2.73	2.68	3.00	3.02	3.02

^a Based on unreduced catalyst^b Based on static slurry volume^c Unanalyzed wax withdrawn from reactor

Table IV-2.15 (cont'd) Summary of Slurry Reactor Test Results for Run SB-1931.

Period	7	8	9	10	11
Date	04/20/91	04/23/91	04/26/91	04/29/91	05/01/91
Time on Stream (h)	423.0	496.0	566.0	639.0	686.0
Balance Duration (h)	6.0	6.0	6.0	6.0	6.0
Average Temperature (°C)	260.	260.	265.	265.	265.
Pressure (MPa)	1.48	1.48	1.48	1.48	1.48
H ₂ /CO Feed Ratio	.661	.684	.689	.683	.689
Space Velocity (NI/g-cat·h) ^a	1.20	1.20	1.20	1.20	1.20
Space Velocity (NI/g-Fe·h)	2.25	2.25	2.25	2.25	2.25
GHSV (h ⁻¹) ^b	18.7	18.7	18.7	18.7	18.7
CO Conversion (%)	84.8	83.3	84.7	81.6	79.7
H ₂ +CO Conversion (%)	81.2	79.5	80.7	78.7	75.7
H ₂ /CO Usage	.592	.608	.610	.630	.604
STY (mols H ₂ +CO/g-cat·h) ^a	.043	.043	.043	.042	.041
$P_{CO_2} \cdot P_{H_2} / P_{CO} \cdot P_{H_2O}$	14.6	20.1	31.2	29.7	26.8
Weight % of Outlet					
H ₂	1.10	1.22	1.19	1.20	1.42
H ₂ O	1.77	1.30	.894	.768	.890
CO	14.7	16.0	14.7	17.5	19.3
CO ₂	60.5	60.0	60.6	58.7	56.9
Hydrocarbons	15.0	15.2	15.9	16.6	17.3
Oxygenates	.338	.321	.279	.322	.354
Wax ^c	6.54	5.89	6.43	4.95	3.83
Yield (g/Nm ³ H ₂ + CO Converted)					
CH ₄	6.72	7.56	8.99	9.89	10.6
C ₂ -C ₄ Hydrocarbons	26.5	30.1	33.7	37.3	38.6
C ₅ -C ₁₁ Hydrocarbons	36.2	40.3	42.4	47.5	51.5
C ₁₂ + Hydrocarbons	138.	128.	129.	118.	117.
Wax ^c	62.8	57.3	61.6	49.0	39.4
Oxygenates	3.25	3.13	2.67	3.19	3.65
Total	210.	209.	217.	216.	221.
1+2 Olefins/ <i>n</i> -Paraffin Ratio					
C ₂	1.33	1.33	.774	.792	.815
C ₃	6.63	6.41	6.04	5.91	5.77
C ₄	5.85	5.68	5.51	5.77	5.27
C ₈	3.08	3.07	2.64	2.56	2.54
C ₁₀	2.67	2.51	2.17	1.96	2.02

^a Based on unreduced catalyst

^b Based on static slurry volume

^c Unanalyzed wax withdrawn from reactor

Table IV-2.15 (cont'd) Summary of Slurry Reactor Test Results for Run SB-1931.

Period	1	2	3	4	5	6
Weight % of Hydrocarbons						
CH ₄	2.46	2.77	2.83	2.79	3.26	2.92
Ethane	1.10	.997	1.26	1.23	1.53	1.30
Ethylene	1.82	1.93	1.88	2.07	1.99	1.81
Propane	.677	.608	.569	.483	.675	.583
Propylene	3.70	3.45	3.79	3.66	4.39	3.87
n-Butane	.560	.481	.474	.451	.546	.472
1+2 Butenes	2.75	2.46	2.68	2.54	3.11	2.84
C ₄ Isomers	.286	.283	.309	.303	.365	.253
n-Pentane	.539	.433	.421	.394	.473	.423
1+2 Pentenes	2.51	2.14	2.42	2.27	2.73	2.47
C ₅ Isomers	.282	.390	.394	.379	.509	.397
n-Hexane	.480	.381	.387	.352	.407	.366
1+2 Hexenes	1.81	1.48	1.73	1.63	1.90	1.74
C ₆ Isomers	.550	.504	.543	.504	.580	.533
n-Heptane	.412	.316	.367	.317	.399	.360
1+2 Heptenes	1.33	1.16	1.33	1.22	1.53	1.41
C ₇ Isomers	.392	.384	.415	.348	.400	.396
n-Octane	.391	.342	.385	.286	.415	.336
1+2 Octenes	1.08	1.10	1.26	1.06	1.51	1.18
C ₈ Isomers	.405	.346	.393	.283	.362	.283
n-Nonane	.619	.323	.369	.273	.355	.277
1+2 Nonenes	.909	.974	1.11	.907	1.29	.930
C ₉ Isomers	.405	.121	.196	.107	.160	.118
n-Decane	.759	.344	.415	.325	.382	.329
1+2 Decenes	.910	.925	1.09	.961	1.14	.979
C ₁₀ Isomers	1.49	.145	.235	.130	.161	.125
n-Undecane	.492	.347	.462	.439	.449	.427
1+2 Undecenes	.830	.909	1.17	1.12	1.19	1.09
C ₁₁ Isomers	1.36	.170	.250	.166	.211	.154
C ₂ -C ₄	10.9	10.2	11.0	10.7	12.6	11.1
C ₅ -C ₁₁	18.0	13.2	15.3	13.5	16.5	14.3
C ₁₂ +	68.7	73.8	70.9	73.0	67.6	71.6
Wax ^c	50.9	59.3	47.1	45.0	37.4	44.5

^c Unanalyzed wax withdrawn from reactor

Table IV-2.15 (cont'd) Summary of Slurry Reactor Test Results for Run SB-1931.

Period	7	8	9	10	11
Weight % of Hydrocarbons					
CH ₄	3.25	3.67	4.19	4.64	4.86
Ethane	1.71	1.99	2.50	2.76	2.80
Ethylene	2.12	2.47	1.81	2.04	2.13
Propane	.680	.794	.936	1.05	1.08
Propylene	4.30	4.86	5.39	5.94	5.94
n-Butane	.544	.630	.729	.825	.863
1+2 Butenes	3.08	3.46	3.87	4.60	4.39
C ₄ Isomers	.383	.433	.492	.288	.550
n-Pentane	.502	.553	.659	.712	.766
1+2 Pentenes	2.64	2.92	3.39	3.60	3.69
C ₅ Isomers	.523	.660	.752	1.54	.785
n-Hexane	.495	.553	.537	.620	.678
1+2 Hexenes	1.77	2.31	2.26	2.50	2.65
C ₆ Isomers	.548	.633	.666	.767	.830
n-Heptane	.418	.516	.544	.574	.680
1+2 Heptenes	1.33	1.71	1.65	1.78	2.06
C ₇ Isomers	.452	.493	.551	.605	.713
n-Octane	.407	.545	.564	.570	.690
1+2 Octenes	1.23	1.64	1.46	1.43	1.72
C ₈ Isomers	.421	.460	.413	.449	.621
n-Nonane	.408	.477	.478	.553	.624
1+2 Nonenes	1.20	1.37	1.20	1.30	1.46
C ₉ Isomers	.316	.194	.235	.252	.275
n-Decane	.482	.525	.552	.684	.719
1+2 Decenes	1.27	1.30	1.18	1.32	1.43
C ₁₀ Isomers	.407	.205	.266	.328	.358
n-Undecane	.634	.727	.712	.837	.913
1+2 Undecenes	1.51	1.50	1.34	1.47	1.60
C ₁₁ Isomers	.528	.255	.369	.382	.417
C ₂ -C ₄	12.8	14.6	15.7	17.5	17.8
C ₅ -C ₁₁	17.5	19.6	19.8	22.3	23.7
C ₁₂ +	66.4	62.1	60.3	55.6	53.7
Wax ^c	30.3	27.9	28.7	23.0	18.1

^c Unanalyzed wax withdrawn from reactor

Table IV-2.16 Major Events in Run SB-1931.

TOS (h)	Event
	Slurry loading: 283 g n-octacosane, 7.2 g catalyst (<270 mesh)
	Slurry sample withdrawal after the pretreatment: 18 g wax, 0.5 g catalyst
	Wax withdrawal through filter: 9 g of wax
0	Initiate synthesis gas flow
1	Achieved initial process conditions: T=260°C, P=1.48 MPa, SV=2.2 Nl/g-cat/h, (H ₂ /CO)=0.69
15	Reactor was supplied with He during 2 hours due to the fume hood maintenance
63	Spave velocity change from 2.2 to 1.8 Nl/g-cat/h
80	Plug in outlet line – no flow through reactor for 12 hours
138	Spave velocity change from 1.8 to 1.6 Nl/g-cat/h
229	Break in power supply – no syngas flow, no mixing during 4 hours; reactor filled with helium, temperature decreased to 256°C
374	Spave velocity change from 1.6 to 1.2 Nl/g-cat/h
519	Temperature change from 260 to 265°C
691	Slurry sample withdrawal: 43 g wax, 1.0 g catalyst
692	End of run: 267 g wax, 6.2 g catalyst recovered from reactor
	Wax and catalyst removed during the run: 495 g of wax, 0 g of catalyst
	Catalyst recovery: 93%; Wax recovery: 104%

Catalyst pretreatment: H₂ at 250°C

Figure IV-2.15 (H₂+CO) conversion (solid symbols) and volumetric contraction (open symbols) as a function of time on stream for Run SB-1931.

velocity was maintained at 1.2 NI/g-cat/h, and values of the (H₂+CO) conversion were between 80 and 82% (balances 7 and 8). During the last portion of the run (TOS = 520 – 692 h) the reaction temperature was 265°C. Following the initial increase in conversion (84.3% at 525 h) the catalyst deactivated with time. At the end of the run the (H₂+CO) conversion was 75% only.

Water-gas-shift (WGS) activity of the catalyst was high throughout the test. The usage ratio was about 0.6.

Wax and Catalyst Inventories/Withdrawals

High molecular weight products which accumulate in the reactor were withdrawn periodically (approximately every 50 h) through a porous metal filter (0.5 µm pore size), which was placed horizontally to give a static slurry volume of 430 ml. Wax production rate during the test varied between 0.4 and 1.2 g/h, whereas the average production rate was 0.7 g/h.

At the end of the run, 6.2 g of catalyst was recovered from the reactor, and another 0.5 g was removed after reduction for catalyst characterization studies (Table IV-2.16). Catalyst and wax recoveries were: 93 and 104%, respectively.

Catalyst Characterization by XRD and/or MES

MES analysis of the catalyst sample withdrawn from the reactor after hydrogen reduction at 250°C for 4 h, indicates the presence of small superparamagnetic oxide/oxyhydroxide particles. Samples withdrawn from the reactor at 691 h (handled in an inert atmosphere) and at 692 h (exposed to air) were analyzed by XRD, and magnetite and iron carbide(s) were the only phases identified. The following phases were found by MES analysis in the latter sample : superparamagnetic oxides (69%), and χ -carbide (31%).

Hydrocarbon and Carbon Number Product Distributions

Hydrocarbon product distribution shifted gradually toward lower molecular weight products with time. For example, methane selectivity increased from 2.5% in

Figure IV-2.16 Carbon number product distribution for Run SB-1931 (TOS=98 h).

balance 1 (42 h) to 3.7% in balance 8 (496 h), while (C₂-C₄) increased from 11 to 14.6% and (C₅-C₁₁) from 18 to 19.6%, whereas C₁₂⁺ selectivity decreased from 68.7 to 62.1% during the same period of time. (C₁+C₂) selectivity was below target value of 7% during first 450 h of testing at 260°C, but this target value was exceeded in balance 8 (500 h on stream) where (C₁+C₂) selectivity was 8.2%.

A typical carbon number product distribution (C₁-C₅₀ carbon number range) is shown in Figure IV-2.16. Experimental data were fitted with a three parameter model of Huff and Satterfield. Some positive deviations from this model are noted in C₁₄-C₁₉ carbon number range (diesel fuel). This type of behavior has been observed in other mass balances during this test, and in tests of some other iron/silica catalysts synthesized in our laboratory.

Concluding Remarks

This has been another successful test of a precipitated iron catalyst containing silicon oxide as a binder. We were able to achieve high values of (H₂+CO) conversion (74-84%), and the catalyst deactivation rate was low in spite of three operational upsets during the test. Also, hydrocarbon selectivity was within the target up to 450 h on stream.

IV-2.8 Run SB-3101 with 100 Fe/5 Cu/8 K/24 SiO₂ Catalyst

The catalyst was tested at : 260°C, 1.48 MPa (200 psig), 1.6 NI/g-cat/h and H₂/CO = 0.64 throughout the entire test. A feed flowrate upset occurred at about 158 h, but it was corrected immediately by increasing slightly the cylinder delivery pressure. The run was terminated after 354 h on stream. Results from six mass balances made during the test are summarized in Table IV-2.17, whereas major events are listed in Table IV-2.18.

Table IV-2.17 Summary of Slurry Reactor Test Results for Run SB-3101.

Period	1	2	3	4	5	6
Date	11/08/91	11/10/91	11/13/91	11/16/91	11/19/91	11/21/91
Time on Stream (h)	39.0	86.0	171.0	243.0	302.0	339.5
Balance Duration (h)	8.0	6.5	11.0	12.0	6.5	11.0
Average Temperature (°C)	260.	260.	260.	260.	260.	260.
Pressure (MPa)	1.48	1.48	1.48	1.48	1.48	1.48
H ₂ /CO Feed Ratio	.645	.645	.650	.650	.650	.639
Space Velocity (NI/g-cat·h) ^a	1.62	1.62	1.62	1.60	1.63	1.63
Space Velocity (NI/g-Fe·h)	3.11	3.11	3.11	3.08	3.14	3.14
GHSV (h ⁻¹) ^b	44.0	44.0	44.0	40.2	40.9	40.9
CO Conversion (%)	78.6	75.2	70.5	67.1	65.0	62.8
H ₂ +CO Conversion (%)	74.4	72.3	67.7	64.1	61.3	60.1
H ₂ /CO Usage	.557	.581	.586	.577	.556	.570
STY (mols H ₂ +CO/g-cat·h) ^a	.054	.052	.049	.046	.044	.044
$P_{CO_2} \cdot P_{H_2} / P_{CO} \cdot P_{H_2O}$	50.5	42.6	26.3	26.1	28.2	32.1
Weight % of Outlet						
H ₂	1.42	1.43	1.62	1.80	2.00	1.91
H ₂ O	.463	.456	.668	.633	.565	.447
CO	20.4	23.6	28.0	31.3	33.7	35.1
CO ₂	59.0	56.6	53.3	50.4	47.2	46.3
Hydrocarbons	9.52	9.69	9.61	9.53	9.10	8.75
Oxygenates	.177	.201	.155	.129	.568	.465
Wax ^c	8.96	7.96	6.63	6.18	6.93	7.04
Yield (g/Nm ³ H ₂ + CO Converted)						
CH ₄	8.37	8.95	9.49	10.7	10.8	11.7
C ₂ -C ₄ Hydrocarbons	29.0	29.0	30.4	33.7	33.1	35.1
C ₅ -C ₁₁ Hydrocarbons	49.6	50.1	51.9	51.5	47.9	48.0
C ₁₂ + Hydrocarbons	111.	107.	99.7	99.1	114.	117.
Wax ^c	96.1	87.8	78.2	76.7	89.2	94.6
Oxygenates	1.90	2.22	1.82	1.60	7.31	6.24
Total	200.	197.	193.	197.	214.	218.
1+2 Olefins/n-Paraffin Ratio						
C ₂	3.34	2.99	2.86	2.74	2.63	2.49
C ₃	6.21	6.22	5.86	5.80	5.75	5.63
C ₄	4.91	5.41	4.86	4.54	4.59	4.44
C ₈	3.18	3.23	2.74	2.58	2.30	2.44
C ₁₀	1.46	2.99	2.92	2.90	3.00	2.40

^a Based on unreduced catalyst^b Based on static slurry volume^c Unanalyzed wax withdrawn from reactor

Table IV-2.17 (cont'd) Summary of Slurry Reactor Test Results for Run SB-3101.

Period	1	2	3	4	5	6
Weight % of Hydrocarbons						
CH ₄	4.22	4.60	4.96	5.49	5.22	5.52
Ethane	1.09	1.10	1.17	1.31	1.24	1.33
Ethylene	3.40	3.08	3.13	3.34	3.06	3.10
Propane	.805	.838	.945	1.04	.975	1.02
Propylene	4.77	4.97	5.28	5.74	5.35	5.48
n-Butane	.709	.773	.887	1.00	.924	.959
1+2 Butenes	3.36	4.04	4.16	4.40	4.09	4.11
C ₄ Isomers	.514	.114	.300	.455	.423	.547
n-Pentane	.722	.771	.926	.973	.960	.937
1+2 Pentenes	3.15	3.37	3.63	3.76	3.52	3.54
C ₅ Isomers	.720	2.43	2.27	2.35	2.13	2.26
n-Hexane	.855	.935	.989	.882	.911	.910
1+2 Hexenes	2.41	2.62	2.62	2.56	2.47	2.60
C ₆ Isomers	.869	1.10	1.05	1.17	1.12	1.16
n-Heptane	.587	.667	.800	.809	.845	.814
1+2 Heptenes	1.80	2.03	2.07	2.08	1.93	1.94
C ₇ Isomers	.612	.885	.819	.794	.663	.724
n-Octane	.550	.578	.749	.756	.746	.656
1+2 Octenes	1.72	1.84	2.02	1.91	1.69	1.57
C ₈ Isomers	.513	.841	.503	.403	.471	.427
n-Nonane	.619	.453	.568	.538	.544	.459
1+2 Nonenes	1.54	1.50	1.77	1.63	1.26	1.09
C ₉ Isomers	.471	.289	.334	.333	.278	.236
n-Decane	1.18	.568	.626	.570	.381	.393
1+2 Decenes	1.70	1.67	1.80	1.63	1.12	.929
C ₁₀ Isomers	1.27	.501	.450	.444	.363	.305
n-Undecane	.674	.549	.638	.600	.349	.335
1+2 Undecenes	1.71	1.81	2.00	1.83	1.09	1.06
C ₁₁ Isomers	1.37	.323	.459	.390	.387	.309
C ₂ -C ₄	14.6	14.9	15.9	17.3	16.1	16.5
C ₅ -C ₁₁	25.0	25.7	27.1	26.4	23.2	22.7
C ₁₂ +	56.1	54.7	52.1	50.8	55.5	55.3
Wax ^c	48.5	45.1	40.8	39.3	43.2	44.6

^c Unanalyzed wax withdrawn from reactor

Table IV-2.18 Major Events in Run SB-3101.

TOS (h)	Event
	Slurry loading: 310 g n-octacosane, 12.5 g catalyst (particle size <270 mesh)
	Catalyst pretreatment: H ₂ at 250°C
	Slurry sample withdrawal: 20.4 g wax, 0.8 g catalyst
	Wax withdrawal through filter: 6.31 g of wax
0	Initiate synthesis gas flow
1	Achieved process conditions: T=260°C, P=1.48 MPa, SV= 1.6 NI/g-cat/h, (H ₂ /CO=0.64)
158	Discovered decrease in feed flow rate and restored to desired flow rate
182	Slurry sample withdrawal: 24.5 g wax, 0.9 g catalyst
352	Slurry sample withdrawal: 49.3 g wax, 1.4 g catalyst
354	End of run: 287 g wax, 8.5 g catalyst recovered from reactor
	Wax/catalyst removed during the run: 400 g of wax, 2.3 g of catalyst
	Catalyst recovery: 92.3%; Wax recovery: 101%

Catalyst Activity and Stability

The catalyst deactivated continuously with time on stream. The (H₂+CO) conversion decreased from initial value of 77% to 60% at 350 h on stream, while volumetric contraction (VC) decreased from 50% to 38% during the same time period. Changes of (H₂+CO) conversion and VC with time on stream are shown in Figure IV-2.17. WGS activity of the catalyst was high, and the (H₂/CO) usage ratio varied between 0.56-0.58.

Wax and Catalyst Withdrawals/Inventories

Wax was withdrawn periodically through a porous sintered metal filter with nominal pore size of 0.5 μm . No catalyst was found in the withdrawn wax. The wax production rate decreased from 1.4 to 1.0 g/h as the catalyst deactivated with time.

At the end of the run, 8.5 g of catalyst was recovered from the reactor slurry. Another estimated 2.4 g of catalyst was removed from the reactor during the test with slurry samples for catalyst characterization. Catalyst recovery was about 92%, whereas wax recovery was 101% based on the amounts of catalyst and wax charged into the reactor.

Catalyst Characterization by XRD and/or MES

A slurry sample withdrawn from the reactor after hydrogen reduction at 250°C for 4 h contained a small amount of catalyst which was insufficient for XRD analysis. The iron phases in this sample were determined by MES analysis. Superparamagnetic oxide/oxyhydroxide was the most dominant phase (96%) in the sample, the remainder being the metallic iron. Samples withdrawn from the reactor at 182 and 352 h on stream contained magnetite and iron carbide(s) phases, whereas iron carbide(s) was the only phase found in a sample withdrawn at 354 h on stream (XRD analysis). The MES analysis of the last two samples (352 and 354 h) reveals the presence of superparamagnetic oxide phase (probably magnetite based on XRD analysis) and ϵ' -carbide, in approximately equal amounts.

Figure IV-2.17 (H₂+CO) conversion (solid symbols) and volumetric contraction (open symbols) as a function of time on stream for Run SB-3101.

Figure IV-2.18 Carbon number product distribution for Run SB-3101 (TOS=243 h).

Hydrocarbon and Carbon Number Product Distributions

Hydrocarbon product distribution shifted gradually toward lower molecular weight products with time on stream. For example, at 40 h on stream, hydrocarbon selectivity was: (CH₄) = 4.2, (C₂–C₄) = 14.6, (C₅–C₁₁) = 25 and C₁₂⁺ = 56.2 wt%, while at 340 h, it became (CH₄) = 5.5%, (C₂–C₄) = 16.5, (C₅–C₁₁) = 23, and C₁₂⁺ = 55 wt%.

A typical carbon number product distribution is shown in Figure IV-2.18 in the form of ASF plot. This plot is based on products collected overhead (i.e. the wax from the reactor was not analyzed).

IV-2.9 Comparison of Catalyst Performance

Results illustrating performance of iron-silica catalysts synthesized in our laboratory are summarized in Table IV-2.19. None of the catalysts have met all of the activity targets listed in Table IV-2.2. The initial syngas conversions in five of the eight tests were above 80% (81-88%), but were nevertheless somewhat less than the target value of 88%. Also, these conversions could not be maintained over a long period of time due to catalyst deactivation. Catalyst productivity target of 2.6 Nm³(H₂+CO) reacted /kg-Fe/h was met in two of the tests (Runs SB-2832 and SB-1931). The water gas shift activity of all catalysts was high, and the usage ratio was less than 0.65.

Initial values of the apparent first order reaction rate constant were above 250 mmol/g-Fe/h/MPa in all tests except in Run SB-2270. In the latter test the initial value of the apparent rate constant was only 180 mmol/g-Fe/h/MPa. Low activity of the catalyst in this test may be attributed to low reduction temperature (220°C for 2h), i.e. low degree of reduction of the catalyst. Also, the activity of the catalyst used in Run SB-1910 (100 Fe/5 Cu/4.2 K/8 SiO₂) was lower than that of the other two catalysts containing 8 parts of silicon oxide per 100 parts of iron (Runs SA-1371 and SB-0931), due to lower degree of reduction (shorter duration of reduction and/or lower reduction

Table IV-2.19 Summary of Slurry Reactor Test Results of Iron-Silica Catalysts Synthesized at TAMU.

Run ID	SA-1371	SB-0931	SB-1910	SB-0261	SB-2270	SB-2832	SB-1931	SB-3101
Catalyst Composition (Fe/Cu/K/SiO ₂)	100/3/3/8	100/3/4/8	100/5/4.2/8	100/3/4/16	100/5/4.2/16	100/5/4.2/16	100/5/6/24	100/5/8/24
ACTIVITY PARAMETERS								
(H ₂ +CO) (%)	52-84	55-88	42-63	63-83	34-73	67-81	74-81	60-74
CO (%)	56-90	58-93	46-70	65-90	35-75	71-88	78-85	63-79
UR (-)	.55-.59	.54-.61	.54-.69	.53-.60	.59-.69	.58-.62	.59-.60	.55-.58
k (mmol/g-Fe/h/MPa) at 260°C	180-330	170-320	90-270	120-255	80-180	200-270	260-350	200-290
Nm ³ (H ₂ +CO)/kg-Fe/h	1.8-2.4	1.1-2.1	1.4-1.8	1.3-2.0	1.4-1.6	1.7-2.9	1.7-3.0	1.9-2.3
DR (%/day)	3.3	2.1	4.1	1.4	3.1	0.9	1.3	2.1
SELECTIVITY								
g HC/Nm ³ (H ₂ +CO) reacted	190-210	~200	185-208	195-215	205-217	205-217	203-218	194-212
g C ₃ +/Nm ³ (H ₂ +CO) reacted	~180	~188	~186	~194	~191	~191	~199	~183
(C ₁ +C ₂), wt. %	9.1-11.5	5.3-7.1	6.6-7.2	3.5-6.4	6.7-9.2	8.1-9.8	5.4-8.2	8.5-9.9
CH ₄	4.6-6.4	2.5-3.4	3.1-3.8	1.6-2.8	3.3-4.5	4.4-5.3	2.5-3.7	4.2-5.5
C ₂ -C ₄	18-21	10.6-12.5	13-13.6	8-13	13-19	15.2-17.4	10-14.6	14.6-17.3
C ₅ -C ₁₁	30-36	16-21.7	21-29	12-16	12-19	20.6-29.8	13-18	22.7-27.1
C ₁₂	37-45	65-70	54-62	69-77	57-71	48.3-59.3	62-74	51-57

temperature). Silicon oxide is known to inhibit reduction of iron (Bukur et al., 1990b) and in order to compensate for this we have used higher reduction temperatures for catalysts with higher silica contents. As a result the initial activities of the catalysts containing 8 and 24 parts of SiO₂ were similar (300-350 mmol/g-Fe/h/MPa).

Catalyst deactivation rates listed in Table IV-2.19 were estimated using the following expression:

$$DR = [1 - k(t)/k(t_0)] \times 100/t$$

where: DR – deactivation rate in (%/day); k(t) and k(t₀) – reaction rate constants at time t and t₀, respectively; t – time in days; t₀ – time at which the first mass balance was conducted (usually, after about 40 h on stream).

Deactivation rates calculated in this way varied between 0.9 and 4.1% per day. In general, catalysts with the lowest silica content (8 parts of SiO₂ per 100 parts of Fe) had higher deactivation rates. The estimated deactivation rates in all tests, except Run SB-2832, were higher than the target value of 1% per day. However, the above procedure provides a conservative estimate, since the deactivation rate is based on the initial catalyst activity. In some cases the catalyst activity goes through a maximum (induction period) before it starts decreasing or leveling off.

All of our catalysts have either met most or all of the selectivity targets listed in Table IV-2.2. Hydrocarbon productivity targets have been exceeded in all eight tests (both for total hydrocarbon products produced and C₃⁺ hydrocarbons). The requirement that (C₁+C₂) selectivity be less than 8 wt%, was satisfied in four tests (see Table IV-2.19).

Results from STSR tests of the best three precipitated iron catalysts synthesized in our laboratory are shown in Figures IV-2.19 and IV-2.20. Variations in (H₂+CO) conversion with TOS for these three catalysts are shown in Figure IV-2.19. Process conditions in all tests were: 260°C, 1.48 MPa, H₂/CO=0.66-0.70, whereas gas space velocity varied between 2.2 and 3.4 NI/g-Fe/h (see Figure IV-2.19 for details). In two of

Figure IV-2.19 Variations in (H₂+CO) conversion with time on stream in STSR tests of precipitated iron catalysts synthesized at TAMU.

Figure IV-2.20 Selectivities of methane and (C₁+C₂) hydrocarbons in STSR tests of precipitated iron catalysts synthesized at TAMU.

the tests (Runs SB-0931 and SB-0261) process conditions were varied during the test, however results from these periods are not shown. Three types of catalyst behavior were observed in these tests. Catalyst with nominal composition 100 Fe/3 Cu/4 K/8 SiO₂ (SB-0931) had initially high conversion (~ 88%), but its activity decreased gradually with TOS. During the test of catalyst 100 Fe/3 Cu/4 K/16 SiO₂ (SB-0261) the (H₂+CO) conversion was initially about 81% decreasing to 76% at 150 h on stream. Between 160 and 240 h the catalyst was tested at 265°C (results not shown in Figure IV-2.19), and it continued to deactivate. Upon returning to the baseline conditions, the activity became stable as evidenced by nearly constant value of (H₂+CO) conversion (66-68%) between 240 and 530 h on stream. In the test of catalyst 100 Fe/5 Cu/6 K/24 SiO₂ (SB-1931) gas space velocity was decreased twice to obtain higher conversions. At a constant gas space velocity (3.4 and 3.0 NI/g-Fe/h) the activity increased slightly with time up to about 390 h. During the last portion of the test (400-500 h) at gas space velocity of 2.3 NI/g-Fe/h the catalyst exhibited some deactivation.

Performance of all three catalysts was somewhat below specified target values for activity (Table IV-2.2). For example, the (H₂+CO) conversions were between 68 and 88% and catalyst productivity varied between 1.5 and 2.5 Nm³ (H₂+CO) converted/kg-Fe/h, whereas the corresponding target values are 88% and 2.6, respectively. It should be noted that these measures do not necessarily reflect the intrinsic catalyst activity. For a given catalyst these two measures (conversion and catalyst productivity) depend on the reactor type (e.g. fixed bed, STSR or bubble column slurry reactor-BCSR) and process conditions employed.

Selectivities of methane and (C₁+C₂) hydrocarbons obtained in tests of these three catalysts are shown in Figure IV-2.20. In tests SB-0931 and SB-1931 selectivities of methane and (C₁+C₂) hydrocarbons increased gradually with TOS, whereas in the test SB-0261 these two selectivities passed through a maximum at about 150 h. Methane selectivity of all three catalysts was less than 3% (mole %

carbon basis), whereas (C_1+C_2) selectivity was less than 7% throughout the entire test. The latter value is within the specified target performance.

Comparison of performance of the catalyst with nominal composition 100 Fe/5 Cu/6 K/24 SiO₂ with other catalysts tested in our laboratory and elsewhere, is presented in Table IV-2.20. As can be seen the performance of this catalyst is very similar to that of the best Mobil's catalyst in the wax mode of operation (Kuo, 1985). The latter catalyst was tested in a bubble column slurry reactor, the behavior of which approaches that of a plug flow reactor. Our catalyst is significantly more active than the Mobil's catalyst used in run CT-256. We have chosen an apparent first order reaction rate constant evaluated at a common temperature of 260°C, as a measure of catalyst activity. Data obtained at other reaction temperatures were converted to 260°C assuming the activation energy of 90 kJ/mol. STSR was modeled as a perfectly mixed flow reactor, whereas the rate constant from a BCSR was estimated using a model which assumes that the gas phase is in plug flow and the liquid is unmixed (Bukur, 1983). This catalyst is also more active than the Ruhrchemie, UCI and UOP (Abrevaya et al., 1991) catalysts, and it produces less methane and gaseous hydrocarbons than these catalysts.

IV.2-10 Summary

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/Nm³(H₂+CO) reacted and more than 166 g C₃+/Nm³(H₂+CO) reacted. Four of the catalysts have met the requirement that methane + ethane + ethylene selectivity be less than 8% 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 Nm³(H₂+CO) reacted/(kg-Fe·h) has been met in two tests, whereas

Table IV-2.20 Catalyst Performance in Slurry Bed Reactors

Catalyst Designation	TAMU	Ruhrchemie	UCI	UOP	Mobil's Run**
Run ID	SB-1931	SA-0888	SA-3391	(1991)	CT-256-13
Process Conditions:					
Temp. (°C)	260	250	265	265	257
Pressure (MPa)	1.48	1.48	2.10	2.10	1.48
SV (NI/g-Fe/h)	2.2-3.4	3.8	2.4	2.4	2.3
Feed (H ₂ /CO)	0.66-0.69	0.67	0.7	0.7	0.73
TOS (h)	40-520	0-343	227-322	15-370	475
% (H ₂ +CO) Conv.	74-84	40-43	73-80	69	82
Usage Ratio	0.56-0.62	0.74-0.84	0.58-0.62	0.57	0.59
Rate Const at 260°C (rel)	100	88	40	33	49-70
Hydrocarbon Selectivities (wt-%):					
CH ₄	3.0	4.7	4.4		2.7
C ₂ -C ₄	10.5	20.6	16.5		11.1
C ₅ -C ₁₁	16.0	23.2	23.6		18.1
C ₁₂ +	70.5	51.5	55.5		68.1
C ₁ +C ₂	6.1	10.8	9.2		5.6
Hydrocarbon Selectivities (mol-%):					
CH ₄	2.7		3.9	4.5	
C ₁ +C ₂	5.8		8.7	5.8*	

*CH₄+C₂H₆ only

**Slurry Bubble Column Reactor Test

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 (hydrocarbon wax).

IV.2-11 References

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V. RECOMMENDATIONS FOR FURTHER STUDY

Several catalysts synthesized at TAMU during the current contract have met most of the DOE target performance criteria. Some of these catalysts are more active than any other known Fischer-Tropsch catalysts developed for production of high molecular weight hydrocarbons, and their deactivation with time is rather moderate. A research program to demonstrate repeatability of catalyst performance in a stirred tank slurry reactor, reproducibility of preparation procedures on a laboratory scale, followed up by catalyst production scale-up in collaboration with a catalyst manufacturer is recommended. A successful completion of this program would provide a state-of-the-art precipitated iron catalyst for future process evaluation studies in the DOE owned Alternative Fuel Development Unit (a bubble column reactor of 0.6 m in diameter, 6 m tall) located at LaPorte, Texas.

Further improvements in the catalyst performance (activity, selectivity, and/or stability) are needed to accelerate commercialization of Fischer-Tropsch technology based on coal derived synthesis gas. This may be achieved through further research on (a) the use of different pretreatment procedures; (b) the use of higher reaction pressure and gas space velocity to increase the reactor productivity; and (c) modifications in catalyst preparation steps.

As shown in this contract, and elsewhere, pretreatment conditions (nature of reductant, temperature, duration and gas flow rate during the pretreatment) can be used to alter catalyst activity, selectivity, and stability. The pretreatment conditions chosen in this study (with iron-silica catalysts) are not necessarily the optimal ones. A comprehensive catalyst characterization studies are needed to gain understanding of the underlying reasons for differences in catalyst performance following different pretreatments.

In several tests with different catalysts, we have shown that the reactor productivity (space-time-yield) can be improved by using higher reaction pressure and gas space velocities. A penalty seems to be in a higher rate of catalyst deactivation, but this needs to be examined over a long period of time.

Also, we recommend studies on the effects of basic oxides as promoters (e.g. MnO, MgO and/or CaO), sources of potassium, and calcination conditions on the catalyst performance.

Finally, the studies on the effect of reactor type: stirred tank slurry reactor (STSR) vs. bubble column slurry reactor (BCSR) are recommended. The space-time-yield and product distribution in a STSR may be significantly different than those in a laboratory BCSR operating under the same process conditions. At high syngas conversions ($\geq 80\%$) a catalyst in the STSR is exposed to a hydrogen rich syngas, and methane selectivities are expected to be higher than in the BCSR.

VI. Acknowledgments

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Appendix I. Fixed Bed and Slurry Reactors and Product Analysis System

Fixed Bed Reactors and Operating Procedures

A simplified flow diagram of a fixed bed reactor system is shown in Figure A-1. Inert (N₂ or He) and (H₂, CO, premixed synthesis gas) are delivered to the reactor through thermal mass flow controllers equipped with a digital meter readout. Two traps are located upstream of the flow controllers, one filled with alumina and heated to 300°C so as to decompose any carbonyls and the other filled with Cu/alumina catalyst to remove trace oxygen. The reactor is made of 1/2" OD stainless steel 316 tubings of 15 or 30 cc volume heated externally via heating blocks. Bed temperatures are monitored through six radially installed thermocouples. The reactor effluent passes through a high pressure trap maintained at 140-210°C, a heated back pressure regulator, and a low pressure trap immersed in ice bath. The gas effluent from the low pressure trap can be sampled for analysis via the sample port and the flow rate is measured by a wet test meter as well as a soap bubble meter.

The catalyst is crushed and sieved to the desired particle size range before loading into the reactor. Reactor is then pressurized and leak tested overnight with He and brought to activation conditions under He atmosphere. Depending upon the activation route being used, the appropriate gas or gas blend is introduced and a temperature program initiated. Following activation, any process parameters not at run condition are adjusted and the flow of synthesis gas is initiated.

Material balance periods are typically 4-8 h duration. Reactor effluent is diverted to tared sample traps (high and low pressure). During this period gas flow rate is measured and gas effluent analyzed periodically. At the completion of the balance, product flow is diverted to the waste traps. The steady state product traps are removed from the system and are allowed to equilibrate at room temperature and their weight

recorded. The contents of the traps are then drained and separated into aqueous and organic layers.

Product Analysis System

A versatile analytical and computerized data handling system consisting of four gas chromatographs linked to a data acquisition system is used for product analysis (Figure A-2). In the gas effluent from the reactor unreacted H_2 , CO and product CO_2 and C1-C5 hydrocarbon gases are analyzed on the Carle AGC-400 Series gas chromatograph. Small amounts of C_6 and higher hydrocarbons and light oxygenates that are not condensed in the cold trap are analyzed by a Varian 3400 GC. The liquid product is separated into aqueous and organic fractions. The aqueous layer is analyzed for C1-C6 alcohols, C2-C4 aldehydes, C3-C6 ketones and carboxylic acids. The water content is determined by Karl-Fischer titrator. The organic fraction is analyzed in a Sigma 1 GC for C4-C30 hydrocarbons, C4-C11 alcohols, C3-C6 ketones, and C2-C6 aldehydes. The wax fraction is dissolved in CS_2 or other organic solvents and is analyzed on the Varian 3400 for hydrocarbons up to C50.

Several integrators are used to collect and integrate the data from all the GC's. The results are then transferred to a HP-9000 series minicomputer for further analysis and reduction. The mass balance program uses pull up templates to prompt the operator to enter the needed information. The calibration data for each GC are stored in databases files. The program is designed to handle up to 50 classes of products with up to 100 members in each class. Five types of streams: feed gas, aqueous liquid product, organic liquid product, reactor tail gas, and reactor wax are considered by the program. Using measured sample weights, the program can calculate individual species flow rates and arrive at total inlet and outlet weight and mole fractions of all identified compounds. The material balance program calculates mass and atomic balance closures, yields, and selectivities of products, and lumps products according to carbon

numbers. The program also calculates the Schulz-Flory chain growth parameter and produces Schulz-Flory plots.

Slurry Reactors and Operating Procedure

Two continuous 1 liter stirred slurry-phase reactors were used for catalyst testing and the schematic representation of one of these units is shown in Fig. A-3. Inlet CO and H₂ streams are passed through a series of oxygen removal, drying and carbonyl removal traps. The gas flow rate and H₂ to CO feed ratio are controlled using a mass flow controller for each feed gas. Alternatively, premixed synthesis gas at a fixed H₂ to CO feed ratio may be used, in which case only a single mass flow controller is required. The reactor is fully baffled, and the gas inlet point is directly beneath the flat-bladed impeller to maximize gas shear.

Products, together with unreacted syngas, are taken overhead through a heated partial reflux condenser, maintained at a temperature of about 200°C to return vaporized slurry oil to the reactor and minimize the carryover of high boiling products. The slurry level in the reactor is controlled by withdrawing accumulated slurry oil at the end of each mass balance period. The rise in slurry level is due to the accumulation of high molecular weight products in the reactor during synthesis. By determining the amount of slurry oil withdrawn to maintain a constant level at a particular set of process conditions, the higher molecular weight hydrocarbons that do not distill with the gas phase product can be quantitatively included in the material balance. This procedure is essential for obtaining an accurate overall product distribution.

During the system startup, or during an unsteady period, the reactor effluent passes through the unsteady state trap, which operates at ambient temperature and system pressure. The gas flows through the back pressure regulator to an unsteady state ice trap, and then to the system outlet where the gas flowrate is measured. During a mass balance period, the flow is diverted through the high and low pressure steady

Figure A-3. Slurry Reactor System Schematic

state traps. The high pressure steady state trap is operated at 60–100°C and system pressure, and the low pressure trap is operated at 0°C and ambient pressure. Before draining, the pressure in the high pressure trap is relieved through the ice trap to minimize product loss due to flashing.

The whole system is designed to run continuously and automatically when unattended. After any change in process parameters, the reactor system is allowed to equilibrate for at least 14 to 16 hours before obtaining material balances over an additional 6–8 hour period. Due to the complexity of the Fischer-Tropsch product, equilibration of the reactor and the product collection system and a flexible quantitative analysis scheme incorporating all product, including waxes, are required to produce good mass balances and prevent misleading results.

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