Development of Precipitated Iron Fischer-Tropsch Catalysts

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~~Draft~~ Final Technical Report

Texas Engineering Experiment Station Project 32525-44580

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Richard E. Tischer, Project Manager (PETC)

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Abstract

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 (F-T) technology, with its versatile product slate, may be expected to play a major role in production of transportation fuels via indirect coal liquefaction.

Some of the F-T catalysts synthesized and tested at Texas A&M University under DOE Contract No. DE-AC22-89PC89868 were more active than any other known catalysts developed for maximizing production of high molecular weight hydrocarbons (waxes). The objectives of the present contract were to demonstrate repeatability of catalyst performance and reproducibility of preparation procedures of two of these catalysts on a laboratory scale. Improvements in the catalyst performance were attempted through the use of: (a) higher reaction pressure and gas space velocity to maximize the reactor productivity; (b) modifications in catalyst preparation steps; and (c) different pretreatment procedures.

Repeatability of catalyst performance and reproducibility of catalyst synthesis procedure have been successfully demonstrated in stirred tank slurry reactor tests. Reactor space-time-yield was increased up to 48% by increasing reaction pressure from 1.48 MPa to 2.17 MPa, while maintaining the gas contact time and synthesis gas conversion at a constant value. Use of calcination temperatures above 300°C, additional CaO promoter, and/or potassium silicate as the source of potassium promoter, instead of potassium bicarbonate, did not result in improved catalyst performance. By using different catalyst activation procedures we were able to increase substantially the catalyst activity, while maintaining low methane and gaseous hydrocarbon selectivities. Catalyst productivity in runs SA-0946 and SA-2186 was 0.71 and 0.86 gHC/g-Fe/h, respectively, and this represents 45-75% improvement in productivity relative to that achieved in Rheinpreussen's demonstration plant unit (the most successful bubble column slurry reactor performance to date), and sets new standards of performance for "high alpha" iron catalysts.

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I EXECUTIVE SUMMARY

Slurry phase Fischer-Tropsch (F-T) processing is a very promising alternative to conventional vapor phase processes, but additional improvements are needed in the catalyst performance (higher activity, minimization of methane and low molecular weight hydrocarbon yields, and better catalyst stability) in order to accelerate commercialization of this technology. This can be achieved in several ways: (a) through development of new improved catalysts; (b) use of novel reactor configurations; (c) use of suitable catalyst pretreatment (activation) procedures or through combination of these methods, as demonstrated in studies at Texas A&M University (TAMU) sponsored by DOE (Contracts DE-AC22-85PC8011 and DE-AC22-89PC89868). Some of the iron based catalysts synthesized and tested at TAMU, have proven to be more active than any other known iron F-T catalysts developed for maximizing production of high molecular weight hydrocarbons (Bukur et al., 1994).

The overall objectives of this contract are to: (1) demonstrate repeatability of performance and preparation procedure of two high activity, high alpha iron F-T catalysts synthesized at TAMU during the DOE Contract DE-AC22-89PC89868; and (2) seek potential improvements in the catalyst performance through variations in process conditions, pretreatment procedures and/or modifications in preparation steps (e.g. means of introduction of promoters and calcination conditions). The major accomplishments are summarized here.

Repeatability of Performance of Baseline Catalysts

The objective of this task is to verify repeatability of results obtained in stirred tank slurry reactor (STSR) tests of two catalysts designated B (100 Fe/5 Cu/6 K/24 SiO₂ containing 55.4 wt% of iron) and C (100 Fe/3 Cu/4 K/16 SiO₂ containing 59.7 wt% of iron) during the previous DOE Contract DE-AC22-89PC89868. These two catalysts were chosen due to their excellent performance (high syngas conversion and low methane and gaseous hydrocarbons selectivities) in slurry reactor tests. The catalysts from the same preparation batch and the same

pretreatment and process conditions, were employed as in the previous slurry reactor tests of these two catalysts.

Three tests were conducted with each of the two catalysts. In the original tests conducted in 1991 (SB-1931 with the catalyst B, and SB-0261 with the catalyst C) n-octacosane was used as the initial medium. In the four tests conducted during the current contract, Ethylflo 164 oil (a hydrogenated 1-decene homopolymer liquid - C_{30} , obtained from Ethyl Co.) was used as the start-up fluid, due to problems encountered in three initial tests using n-octacosane as the start-up liquid (low activity in all three tests). The effect of reactor set-up (slurry A vs. slurry B reactor system) was investigated in two recent tests with the catalyst C (runs SB-0045 and SA-0705). In general, reproducibility of results in multiple tests of the same catalyst may be regarded as quite satisfactory. The catalyst B (100 Fe/5 Cu/6 K/24 SiO_2) was more stable in the original test (SB-1931) than in the two recent tests (SB-3354 and SB-0665), whereas the opposite trend was observed in tests with the catalyst C (100 Fe/3 Cu/4 K/16 SiO_2). Hydrocarbon product distributions and olefin selectivities in multiple tests with the same catalyst were reproducible.

Performance of catalysts B and C is comparable to, or exceeds, that obtained in the two most successful bubble column slurry reactor (BCSR) tests conducted by Mobil (Kuo, 1985) and Rheinpreussen (Kölbel et al., 1955). In Mobil's run CT-256-13 at synthesis gas conversion of 82%, methane and C_1+C_2 selectivities were 2.7 and 5.6 wt%, respectively, whereas the catalyst productivity was about 0.26 g HC/g-cat/h (Test conditions: 257°C, 1.48 MPa, 2.3 NI/g-Fe/h, $H_2/CO = 0.73$). In Rheinpreussen's demonstration plant unit the C_1+C_2 selectivity was 6.8% at the synthesis gas conversion of 89%, and the catalyst productivity was about 0.33 g HC/g-cat/h (Test conditions: 268°C, 1.48 MPa, 3.1 NI/g-Fe/h, $H_2/CO = 0.67$).

In run SB-3354 with catalyst B (TOS = 97 h) the following results were obtained at 260°C, 1.48 MPa, 3.2 NI/g-Fe/h, $H_2/CO = 0.67$: Methane and $C_1 + C_2$ selectivities were 3.2 and 5.3 wt%, respectively, and the catalyst productivity was 0.26 g HC/g-cat/h at the synthesis gas conversion of 71.5%. The catalyst performance in the original test of the catalyst B (run

SB-1931) was even better, i. e. higher activity and lower methane and gaseous hydrocarbon selectivities were obtained (Bukur et al., 1994).

The performance of catalyst C in run SB-0045 at the reaction pressure of 1.48 MPa and 215 hours on stream, was very similar to that obtained in Mobil's run CT-256-13. However, the productivity of catalyst C was improved at reaction pressure of 2.17 MPa and gas space velocity of 3.4 NI/g-Fe/h (TOS = 336 h). Methane and C_1+C_2 selectivities were 2.6 and 5.4 wt%, respectively, and the catalyst productivity was 0.36 g HC/g-cat/h at the synthesis gas conversion of about 80%. The latter productivity is higher than productivity's obtained in Mobil's and Rheinpreussen's bubble column slurry reactor tests, primarily due to the use of higher reaction pressure and higher gas space velocity in the present study.

Reproducibility of Catalyst Preparation Procedure

Repeatability of performance of catalysts B and C was demonstrated in multiple tests with catalysts from different preparation batches. Three STSR tests were conducted with catalyst B, and four tests with catalyst C. In general, catalysts from different preparation batches had similar performance (activity and selectivity) and reproducibility of catalyst preparation procedure is regarded as satisfactory.

Syngas conversions, methane and C_1+C_2 selectivities obtained in tests with catalysts B and C were similar to those obtained in two tests conducted in slurry bubble column reactors (Mobil's and Rheinpreussen's tests). However, the catalyst productivity in two tests with catalyst C (runs SA-1665 and SB-0045), at 2.17 MPa, was even higher (0.53 or 0.60 g HC/g-Fe/h) than that obtained in Rheinpreussen's test (0.49 g HC/g-Fe/h), whereas at the reaction pressure of 1.48 MPa the catalyst productivity of our catalysts B and C (0.38-0.42 g HC/g-Fe/h) was similar to that obtained in Mobil's study (0.39 g HC/g-Fe/h). Due to complete reactor backmixing in our experiments (stirred tank reactor) it may be expected that the catalyst productivity under the same process conditions would be even higher in a reactor with partial fluid mixing (e.g., bubble column slurry reactor). ✓

The Effect of Basic Oxide Promoter and Source of Potassium

Four catalysts containing CaO promoter with nominal compositions 100 Fe/3 Cu/4 K/x Ca/16 SiO₂ and 100 Fe/5 Cu/5 K/x Ca/24 SiO₂, where x = 2 or 6, were synthesized and tested in fixed bed reactors. The major findings from these tests are that the addition of small amounts of CaO promoter (x = 2) results in the catalyst performance (activity and gaseous hydrocarbon selectivity) similar to that of the baseline catalysts B and C, whereas the addition of a larger amount of CaO (x = 6) results in markedly lower catalyst activity in comparison to the baseline catalysts. Selectivity of the two catalysts with x = 6, is similar to that of the corresponding baseline catalysts. On the basis of these results it was decided to evaluate two catalysts with x = 2 in stirred tank slurry reactors.

The 100 Fe/5 Cu/5 K/2 Ca/24 SiO₂ catalyst was tested in run SA-2405, and its performance was compared to that of the baseline catalyst B in run SB-1295, whereas results from run SB-3115 with the 100 Fe/3 Cu/4 K/2 Ca/16 SiO₂ catalyst were compared with results obtained with the catalyst C in run SA-1665. General trends in tests with the CaO containing catalysts showed some similarities, as well as differences. For example activity of the 100 Fe/5 Cu/5 K/2 Ca/24 SiO₂ catalyst (run SA-2405) was nearly the same as that of the baseline catalyst B (run SB-1295) but its stability with time (deactivation rate) was better, whereas the 100 Fe/3 Cu/4 K/2 Ca/16 SiO₂ catalyst (run SB-3115) was less active (about 15%) than the baseline catalyst C (run SA-1665) and its deactivation rate was higher. At reaction pressure of 1.48 MPa, selectivity of gaseous hydrocarbons on CaO containing catalysts was higher than that of the corresponding baseline catalysts. However, at reaction pressure of 2.17 MPa the gaseous hydrocarbon selectivity decreased on the CaO containing catalysts, and was nearly the same as that of the baseline catalysts at 1.48 MPa. It appears that the selectivity of the CaO promoted catalysts improves at higher reaction pressures, whereas the selectivity of the catalyst C is essentially independent of reaction pressure (at a constant P/SV ratio to maintain a constant value of the gas residence time at different pressures). The addition of CaO promoter did not result in improved performance of the baseline catalysts, but the CaO promoted catalysts may

be suitable for operation at higher reaction pressures. Finally, it is possible that the performance of CaO promoted catalysts may be improved with the use of different pretreatment procedures, but this has not been investigated in the present study.

Some differences in catalyst performance were observed in fixed bed tests of catalysts B (runs FA-1725 and FB-1715) and C (runs FA-1605 and FB-1985) prepared by different methods. In both cases, the activity and methane selectivity of catalysts prepared using potassium silicate as the source of potassium promoter were higher than those of the corresponding baseline catalysts prepared by incipient wetness impregnation using KHCO_3 as the source of potassium promoter. On the other hand, in two slurry reactor tests of catalyst B (SB-1295 - K from KHCO_3 , and SA-3155 - K from K_2SiO_3) it was found that the activity of the catalyst prepared from K_2SiO_3 is about 15 % lower than that of the catalyst prepared by KHCO_3 impregnation, whereas gaseous hydrocarbon selectivities were similar after about 140 h on stream.

On the basis of these results we conclude that the baseline procedure utilizing impregnation of Fe-Cu-SiO₂ precursor with the aqueous solution of KHCO_3 is the preferred method of catalyst preparation. The second procedure, which avoids the impregnation step, provides satisfactory results, and may be used as an alternative.

Pretreatment Effect Research

The effect of different pretreatment procedures on the performance of catalyst C (100 Fe/3 Cu/4 K/16 SiO₂, batch-4) was studied in a STSR. Seven different pretreatment procedures were employed: three with hydrogen as reductant at different temperatures (240-280°C), CO and synthesis gas ($\text{H}_2/\text{CO} = 0.67$) pretreatments at 280°C for 8 hours, TAMU pretreatment, and no pretreatment before testing at 1.48 MPa, 260°C, 1.4-2.3 NI/g-cat/h with synthesis gas with H_2/CO molar feed ratio of 0.67. ✓

Significant improvements in the catalyst activity were obtained through the use of different pretreatment procedures. Our standard reduction procedure with the catalyst C

(hydrogen reduction at 240°C for 2 hours) resulted in the initial activity, expressed in terms of the apparent reaction rate constant, of about 250 mmol/g-Fe/MPa/h. The activity decreased with time and at about 400 h the apparent rate constant reached the value of 220 mmol/g-Fe/MPa/h (run SA-1665) or 140 mmol/g-Fe/MPa/h (run SB-2145). The initial activity of the catalyst reduced with hydrogen at 250°C for 4 hours (run SB-3425) was about 350 mmol/g-Fe/MPa/h, which represents a 40% increase relative to the standard reduction procedure. However, the catalyst activity decreased with time and at about 300 h the apparent rate constant was 250 mmol/g-Fe/MPa/h (similar to the value obtained in run SA-1665).

The CO pretreatment (SA-0946), syngas pretreatment (SA-1626) and TAMU pretreatment (SA-2186) also resulted in improved catalyst activity, relative to the standard reduction procedure. The initial values of the apparent reaction rate constant, after these pretreatments, were 300-400 mmol/g-Fe/MPa/h, corresponding to 20-60% increase in activity relative to the standard procedure. Activity of the CO and TAMU pretreated catalysts increased with time, and at 400 hours the values of the apparent reaction rate constants were 360 and 430 mmol/g-Fe/MPa/h, respectively. As the result of the improvement in the catalyst activity, while maintaining low methane and gaseous hydrocarbon selectivities, the catalyst productivities in these two tests were markedly higher than those obtained in Mobil's and Rheinpreussen's slurry bubble column reactor tests. The catalyst productivity in Rheinpreussen test was 0.49 gHC/g-Fe/h, and those obtained in runs SA-0946 and SA-2186 were 0.71 and 0.86 gHC/g-Fe/h, respectively. This represents 45-75% improvement in catalyst productivity relative to that achieved in Rheinpreussen's demonstration plant unit, and sets new standards of performance for "high alpha" iron catalysts. We believe that the performance of our catalyst B (100 Fe/5 Cu/6 K/24 SiO₂) can be also improved through the use of better pretreatment procedures. ✓

Calcination Effect Research

We have conducted six fixed bed reactor tests, and two slurry reactor tests to investigate the effect of calcination temperature on performance of catalysts B and C during F-T synthesis. Both catalyst B (100 Fe/5 Cu/6 K/24 SiO₂) and C (100 Fe/3 Cu/4 K/16 SiO₂) were tested in fixed bed reactors after calcinations at 400°C and 500°C for 5 h, and after flash calcination at 700°C for 1 h, and in a stirred tank slurry reactor after flash calcination at 700°C for 1 h.

In fixed bed reactor tests, activities, as well as gaseous hydrocarbon selectivities, of catalysts B and C calcined at 400°C and 500°C, were similar to those of catalysts calcined at 300°C (baseline calcination temperature). Catalysts calcined at 700°C for 1 h had lower activity, than the catalysts calcined at temperatures of 300-500°C. Gaseous hydrocarbon selectivity of catalyst C, was not strongly affected by the use of different calcination temperatures, whereas the catalyst B calcined at 700°C had higher gaseous hydrocarbon selectivity than the catalysts calcined at lower temperatures.

The main findings from slurry reactor tests are: (1) The activity of catalysts B and C calcined at 700°C is lower than that of these two catalysts calcined at 300°C; (2) Gaseous hydrocarbon selectivities are higher on catalysts calcined at 700°C; (3) Alpha olefin selectivity of C₁₀+ hydrocarbons was markedly higher on catalysts calcined at 700°C; and (4) Oxygenates yields were about four times higher on the catalysts B and C calcined at 700°C, than on the catalysts calcined at 300°C.

Testing of Alternative Catalysts for Slurry Reactors

Although catalysts B and C have desirable activity and selectivity characteristics, they may not have a sufficient mechanical strength and attrition properties required for utilization in commercial bubble column slurry reactors. This work has been undertaken with the objective to test catalysts with potentially improved mechanical and attrition properties.

Three catalysts 100 Fe/5 Cu/4.2 K/20 Al₂O₃ (run SA-0097), 100 Fe/5 Cu/6 K/139 SiO₂ (SB-0627) and 100 Fe/5 Cu/9 K/139 Al₂O₃ (SB-2337) were evaluated in slurry reactor tests. The alumina containing catalyst 100 Fe/5 Cu/4.2 K/20 Al₂O₃ was chosen, because of its similarity with our baseline catalysts B and C (similar promoter, Cu and K, and binder amounts, except that aluminum oxide was used as the binder instead of silicon oxide). The alumina and silica supported catalysts were chosen because they are expected to have high mechanical strength and high attrition resistance during testing in slurry reactors.

The alumina containing catalyst (SA-0097) was markedly less active and had higher methane and gaseous hydrocarbon selectivities than the baseline catalysts. The silica supported catalyst (100 Fe/5 Cu/6 K/139 SiO₂) deactivated fairly rapidly with time, and had markedly higher gaseous hydrocarbon selectivities than the baseline catalysts B and C. The alumina supported catalyst (100 Fe/5 Cu/6 K/139 Al₂O₃) was the least active, and deactivated rapidly with time-on-stream. Gaseous hydrocarbon selectivities were higher than those obtained in tests with the baseline catalysts B and C, but were lower than those obtained in tests of the other two alternative catalysts. The reasons for fairly rapid loss in activity in tests with the alumina and silica supported catalysts are not understood at the present time. In general the performance of the three alternative catalysts was inferior in comparison to our baseline catalysts. ✓

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II INTRODUCTION

Several technologies are currently available or are under development for conversion of coal-derived synthesis gas to liquid transportation fuels or fuel precursors. Technologies that have been commercially proven include fixed and fluidized bed Fischer-Tropsch synthesis, methanol synthesis (fixed bed and slurry phase), and Mobil's methanol to gasoline (MTG) process. Of these technologies, Fischer-Tropsch (F-T) hydrocarbon synthesis produces the widest slate of products and has been in operation for the longest period. F-T hydrocarbon synthesis was first developed and practiced in Germany during the 1930's and 1940's using cobalt catalysts. Subsequently, the process was commercialized on a large scale by Sasol in South Africa. The Sasol process includes both tubular fixed bed and circulating fluidized bed operation and uses promoted iron catalysts (Dry, 1981).

Of the various indirect liquefaction technologies, Fischer-Tropsch synthesis offers many advantages. While hydrocarbon production is generally non selective and is governed by the so-called Schulz-Flory distribution, the Fischer-Tropsch process has the ability to produce a range of gaseous and liquid hydrocarbon products that can be easily upgraded via conventional refining operations. The fluidized bed reactors at Sasol, for example, maximize gasoline yields while the fixed bed process produces predominantly diesel fuel and hydrocarbon waxes.

In the late 1940's, slurry phase Fischer-Tropsch technology was developed in Germany (Kölbel and Ralek, 1980). Slurry processing provides the ability to more readily remove the heat of reaction, minimizing temperature rise across the reactor and eliminating localized hot spots. As a result of the improved temperature control, yield losses to methane are reduced and catalyst deactivation due to coking is decreased. This, in turn, allows much higher conversions per pass, minimizing synthesis gas recycle, and offers the potential to operate with CO-rich synthesis gas feeds without the need for prior water-gas shift. Due to the simpler reactor design, capital investment in a slurry phase F-T reactor is expected to be

✓
substantially smaller than in conventional fixed or fluidized-bed systems. In May 1993 the commercial Slurry Bed Reactor (5 m in diameter, 22 m high) was commissioned by Sasol, as replacement for its tubular fixed bed reactors (Jager and Espinoza, 1995).

II-1 Objectives and Scope of Work

The slurry phase F-T processing is a very promising alternative to conventional vapor phase processes, but additional improvements are needed in the catalyst performance (higher activity, minimization of methane and low molecular weight hydrocarbon yields, and better catalyst stability). This can be achieved in several ways: (a) through development of new improved catalysts; (b) use of novel reactor configurations; (c) use of suitable catalyst pretreatment (activation) procedures or through combination of these methods, as demonstrated in studies at Texas A&M University (TAMU) sponsored by DOE (Contracts DE-AC22-85PC8011 and DE-AC22-89PC89868). Some of the iron based catalysts synthesized and tested at TAMU, have proven to be more active than any other known iron F-T catalysts developed for maximizing production of high molecular weight hydrocarbons (Bukur et al., 1994).

The overall objectives of this contract are to: (1) demonstrate repeatability of performance and preparation procedure of two high activity, high alpha iron Fischer-Tropsch catalysts synthesized at TAMU during the DOE Contract DE-AC22-89PC89868; and (2) seek potential improvements in the catalyst performance through variations in process conditions, pretreatment procedures and/or modifications in preparation steps (e.g. means of introduction of promoters and calcination conditions). In order to achieve these objectives the work is divided into a number of tasks, which are described below together with the time schedule for their execution. ✓

Task 1. Project Work Plan (April 1-April 30, 1994)

The objectives of this task are: (1) Prepare in detail all activities which shall be performed for the successful completion of the work for the entire duration of the contract; and (2) Provide a project work chart showing the key personnel/groups planned for each task, and the percentage of their time to be devoted to individual tasks.

Task 2. Engineering, Modification and Training of New Personnel (April 1-September 30, 1994)

The objective of this task is to perform the engineering design, procurement of new equipment, installation of the instruments and auxiliary gas supply lines and to provide training for new personnel prior to catalyst testing in laboratory reactors.

Task 3. Testing of Previously Synthesized Catalysts (October 1, 1994 - March 31, 1995)

The purpose of this task is to verify reproducibility of results obtained previously at TAMU with catalysts designated B (100 Fe/5 Cu/6 K/24 SiO₂) and C (100 Fe/3 Cu/4 K/16 SiO₂). The catalysts from the same preparation batch shall be used, and the same pretreatment and process conditions shall be employed as in the previous slurry reactor tests of these two catalysts.

Task 4. Reproducibility of Catalyst Preparation (October 1, 1994 - September 30, 1995)

The objective of this task is to demonstrate reproducibility of catalyst preparation procedure on a laboratory scale. Catalysts B and C will be synthesized following procedures developed at TAMU. Catalysts with satisfactory physico-chemical properties will be initially tested in a fixed bed reactor for screening purposes (5 day tests). Following this the two catalysts will be tested in a stirred tank slurry reactor (STSR) using standard pretreatment and process conditions. The activity, selectivity, deactivation behavior of these new catalyst batches will be compared to that of the catalysts from the original (existing) batches. ✓

Task 5. The Effect of Source of Potassium and Basic Oxide Promoter (October 1, 1994 - December 31, 1995)

The objective of this task is to determine effects of two different sources of potassium and addition of another promoter on the catalyst performance. Catalysts B and C will be synthesized using potassium silicate solution as the source of potassium promoter, and performance of these catalysts will be compared with that of catalysts synthesized using our standard procedure (i.e. using potassium bicarbonate as the source of potassium promoter).

The effect of CaO promotion on performance of catalysts B and C (two levels of promotion per catalyst) shall be investigated. Synthesized catalysts will be tested first in a fixed bed reactor, and if the satisfactory results are obtained the most promising catalyst formulations will be tested in the STSR.

Task 6. Pretreatment Effect Research (October 1, 1995 - November 30, 1996)

The effect of four different pretreatment procedures, in addition to the baseline procedure, on the performance of catalyst B (or C) will be studied in a STSR. In addition to STSR tests, the pretreatment effects will be studied by thermogravimetric analysis (TGA) , and temperature programmed reduction (TPR). Iron phases in the catalyst will be determined by X-ray powder diffraction (XRPD).

Task 7. Calcination Effect Research (October 1, 1995 - July 31, 1996)

The effect of calcination temperature (300-500°C) on the catalyst physical properties and performance during F-T synthesis shall be studied in a fixed bed reactor and a STSR. In addition to the baseline calcination temperature of 300°C, the calcination temperatures of 400 and 500°C will be employed in a fixed bed reactor with flowing air. Also, the effect of rapid heating (flash calcination) on performance of catalysts B and C shall be investigated. ✓

Task 8. Catalyst Characterization (December 1, 1994 - July 31, 1997)

The goal of this task is to: (a) provide basic characterization of all catalyst prepared (atomic absorption analysis, surface area, X-ray diffraction); (b) determine bulk iron phases after the pretreatment and during Fischer-Tropsch synthesis in slurry reactors by XRD and Mössbauer spectroscopy (at University of Kentucky); and (c) study reduction behavior of iron F-T catalysts by isothermal and temperature programmed reduction (TPR). These studies may lead to activity-structure relationships, and better understanding of the factors which influence catalyst activity, selectivity and longevity.

Task 9. Testing of Alternative Catalysts for Slurry Reactors (January 1 - June 30, 1997)

Although catalysts B and C have desirable activity and selectivity characteristics, they may not have a sufficient mechanical strength and attrition resistance properties required for utilization in commercial bubble column slurry reactors. We propose to evaluate the performance of up to three alternative catalysts containing either silica and/or alumina as a binder/support in the STSR tests. Mechanical strength and attrition resistance of these catalysts will be determined in collaboration with other DOE contractors.

Task 10. Characterization of Product Distribution and Data Analysis (June 1 - August 31, 1997)

The objective of this task is to perform detailed gas chromatographic analysis of selected liquid and wax products collected during the STSR tests (Tasks 3-7 and 9), and provide information on the effects of time on stream (catalyst aging), process conditions, pretreatment conditions and/or catalyst promoters on product distribution.

A brief description of activities conducted under Task 2. Engineering, Modification and Training of New Personnel is provided in the section II-3, whereas results from Tasks 3 - 10 are described in Chapters III-X of this report.

II-3 Engineering Modification and Training of New Personnel

During the course of work on this task we have obtained quotes for major equipment and prepared bid specifications for the following items: Thermal Gravimetric/ Differential Thermal Analyzer (TGA/DTA Apparatus); Temperature Programmed Pulse Chemisorption Unit equipped with thermal conductivity detector for temperature-programmed reduction studies, Carbon Monoxide/ Flammable Gas Detector/Monitor System; Gas cylinder cabinet for storage of toxic and flammable gases and Macintosh computer (Mac Quadra 660 AV 8 MB RAM, 230 MB hard disk) and a Laser printer (Hewlett Packard, 4 ML).

After reviewing the bids the following equipment was purchased: Thermal Gravimetric/ Differential Thermal Analyzer (TGA/DTA Apparatus) - TA Instruments, Carbon Monoxide/ Flammable Gas Detector/Monitor - MSA; Pulse chemisorption, temperature programmed reduction/desorption (TPR/TPD) apparatus (Micromeritics Inc.; TPR/TPD Pulse Chemisorb 2705). All instruments were installed and calibrated with appropriate standards. A gas cylinder cabinet (with CO and H₂ cylinders, or syngas mixture) was connected to a fume hood vent in our Catalyst Characterization Laboratory (Room 35B of Zachry Engineering Center).

During the first six months of the contract tests of the existing gas chromatographs for gas, liquid and hydrocarbon wax product analysis, were completed using the calibration standards. A Carle gas chromatograph, used for analysis of gaseous hydrocarbons, synthesis gas and carbon dioxide, was moved to a laboratory in which our reactors are located (Room 326B). Also, tubing and valves connecting the GC and the two slurry reactors were installed, which will enable us to use it as an on-line gas chromatographic system. Two slurry reactor systems were pressure tested, and mass flow meters were calibrated for future tests. Dr. Xiaosu Lang trained new personnel in the usage of existing computer software for data reduction and analysis, gas chromatographs and fixed bed and slurry reactor systems.

II-4 References

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RESULTS AND DISCUSSION

III Testing of Previously Synthesized Catalysts

The objective of this task is to verify repeatability of results obtained in stirred tank slurry reactor (STSR) tests of two catalysts designated B (100 Fe/5 Cu/6 K/24 SiO₂ containing 55.4 wt% of iron) and C (100 Fe/3 Cu/4 K/16 SiO₂ containing 59.7 wt% of iron) during the previous DOE Contract DE-AC22-89PC89868. These two catalysts were chosen due to good performance (high syngas conversion and low methane and gaseous hydrocarbons selectivities) in slurry reactor tests. The catalysts from the same preparation batch and the same pretreatment and process conditions, were employed as in the previous slurry reactor tests of these two catalysts.

III-1 Catalyst Characterization Studies

Catalysts B and C (both from the first preparation batch) synthesized in our laboratory, and commercial precipitated iron catalyst (LP 33/81) synthesized by Ruhrchemie AG (Oberhausen-Holtien, Germany) were characterized after calcination in air at 300°C for 5 h by elemental chemical analysis, BET surface area (SA), total pore volume (PV) and pore size distribution (PSD). Ruhrchemie catalyst was used initially in fixed bed reactors at Sasol in South Africa, and it represents an useful reference catalyst.

Bulk iron phases in catalysts B and C after the Fischer-Tropsch synthesis in a slurry reactor, were determined by X-ray diffraction (XRD) analysis and/or by Mössbauer effect spectroscopy (MES). The Mössbauer spectra were obtained and analyzed at the University of Kentucky (The Consortium for Fossil Fuel Liquefaction Science). A description of the catalyst synthesis procedure is given in Appendix 1, whereas the catalyst characterization equipment and experimental procedures employed are described in Appendix 2.

Catalyst Composition and Physical Characterization

The catalyst composition and textural properties of catalysts calcined at 300°C are summarized in Table III-1.1. The catalyst compositions were calculated based on the

Table III-1.1 Catalyst Composition and Structural Properties of Fischer-Tropsch Catalysts

Catalyst Code	Amount Prepared, (g)	Composition 100 Fe/x Cu/y K/z SiO ₂	BET Surface Area, m ² /g	Pore Volume, cm ³ /g
100 Fe/3 Cu/4 K/16 SiO ₂ S3416-1	40	3.5/5.8/17 3.0/6.7/16 ^(a) 3.0/5.9/16 ^(b)	257 245 ^(a)	0.66 0.65 ^(a)
100 Fe/5 Cu/6 K/24 SiO ₂ S5624-1	67	5.4/6.2/24 5.1/8.1/26 5.5/6.6/24 ^(c)	235 222 ^(a)	0.71 0.68 ^(a)
100 Fe/5 Cu/4.2 K/24 SiO ₂ Ruhrchemie	n/a	5.6/5.1/31 ^(a) 5/4/27 ^(d)	290	0.62

(a): Bukur (1994).

(b): Analysis conducted at Universal Oil Products Inc.

(c): Analysis conducted at Pittsburgh Energy Technology Center.

(d): Analysis conducted at Sandia National Laboratory.

elemental analysis by atomic absorption spectroscopy (AAS). The results of elemental analysis of all three catalysts show that numerical values for iron, copper and silica are fairly consistent with the corresponding nominal (intended) values, whereas the potassium contents are slightly higher than the nominal values. The BET surface areas were between 222 and 290 m²/g, whereas the pore volume varied from 0.62 cm³/g (Ruhchemie LP 33/81) to 0.71 cm³/g (catalyst B). Multiple measurements of the same property with the same catalyst indicate good reproducibility of results. Ruhchemie catalyst has similar composition as our catalyst B, and its surface area is about 20% higher than that of the catalyst B.

Figure III-1.1 shows the differential pore volumes of catalysts B and C as a function of pore diameter. The data show that the pore volume contribution from larger pores (>10 nm) is very small.

Iron phases in calcined and used catalysts B and C

XRD patterns of calcined catalysts B and C did not exhibit crystallinity, i. e. they are either amorphous or the crystallites are too small (less than 5 nm) to be detected by XRD. The iron phases present in catalysts samples withdrawn from the slurry reactor at the end of several tests are summarized in Table III-1.2. Mössbauer spectroscopy analysis indicates the presence of a significant fraction (38-73%) of iron phase(s) exhibiting superparamagnetic behavior at a room temperature. Kündig et al. (1966) have found that the critical diameter of iron oxide particles for superparamagnetic relaxation at room temperature is about 13.5 nm. In runs SB-0045 and SA-0075 magnetite (Fe₃O₄) was identified by XRD analysis, but not by MES analysis. It is likely that at least a portion of superparamagnetic phase is magnetite. Fe_xC_y designates either a single iron carbide phase (ε'- or χ- carbide) or a mixture of these two carbides. The precise identification of these two types of carbides by XRD analysis is difficult when the signal intensities are low, and other compounds with overlapping peaks are present, such as magnetite and wax. In this report χ-carbide (Fe₃C₂) refers to the so-called

Figure III-1.1 Pore size distributions of catalysts B and C from batch-1.

Table III-1.2 Summary of XRD and MES Results of Used Catalyst Samples

Run Number	Catalyst	Time on Stream (TOS), h	Phases Identified by Mössbauer	Phases Identified by XRD	(H ₂ +CO) (%) Conversion	CH ₄ (mol%)
SB-0045	100 Fe/3 Cu/4 K/16 SiO ₂ S3416-1	400 (EOR)	40% (Spm) and 60% (χ -Fe ₅ C ₂)	Fe ₃ O ₄ , Fe _x C _y and FeCO ₃	78 - 81	2.2 - 2.4
SA-0705	100 Fe/3 Cu/4 K/16 SiO ₂ S3416-1	526 (EOR)	38% (Spm) 10% (FeCO ₃) and 52% (χ -Fe ₅ C ₂)	Fe ₃ O ₄ , Fe _x C _y and FeCO ₃	76 - 78	2.9 - 3.1
SB-3064	100 Fe/5 Cu/6 K/24 SiO ₂ S5624-1	54 (EOR)	73% (Spm) and 27% (Fe ₃ O ₄)	-	8 - 14	8.2 - 11.4
SB-0665	100 Fe/5 Cu/6 K/24 SiO ₂ S5624-1	377 (EOR)	52% (Spm) 46% (ϵ' -Fe _{2.2} C) and 2% (χ -Fe ₅ C ₂)	-	64 - 67	3.5 - 3.7

EOR stands for end of run.

FTS process conditions for 100 Fe/5 Cu/6 K/24 SiO₂, batch-1 catalyst testing are: T = 260°C, P = 1.48 MPa, H₂/CO = 0.67, SV = 1.6 - 2.2 NL/g-cat/h; and for 100 Fe/3 Cu/4 K/16 SiO₂, batch-1 catalyst testing: T = 260°C, P = 1.48 MPa, H₂/CO = 0.67, SV = 1.4 NL/g-cat/h during the first 260 h on stream, P = 2.17 MPa, SV = 2.05 NL/g-cat/h until the end of run.

Fe_xC_y denotes iron carbide phase(s).

Hägg carbide and its XRD pattern reported by Hoffer et al. (1949). ϵ' -carbide ($\text{Fe}_{2.2}\text{C}$) has a pseudo-hexagonal structure and its XRD pattern was first reported by Barton and Gale (1964). The identification of iron phases by Mössbauer spectroscopy was made by utilizing published values of the hyperfine parameters (the isomer shift, the quadruple splitting, and the magnetic hyperfine field) of the Mössbauer spectra.

The following observations are made from results shown in Table III-1.2:

- (1) Syngas conversion was low (8-14%) in run SB-3064; magnetite and superparamagnetic phase (probably iron oxide) were identified at the end of the test. A possible reason for low activity in this test is the presence of impurities (catalyst poisons) in the initial slurry medium. These impurities may have prevented the formation of active iron phases during the reduction and F-T reaction. In all other tests the catalyst was active and the iron carbide phases were identified by Mössbauer and XRD analysis.
- (2) Catalyst B (24 parts of SiO_2 per 100 parts of Fe) contained ϵ' -carbide (SB-0665), whereas in runs SB-0045 and SA-0705 with catalyst C (16 parts of SiO_2 per 100 parts of Fe) χ -carbide was found in the used catalyst samples at the end of the tests. It is not clear whether this is due to differences in silicon oxide loadings, or due to the use of different process conditions in different tests. Namely, in runs SB-0045 and SA-0705 with catalyst C, the catalyst was tested at both 1.48 MPa and 2.17 MPa, whereas in run SB-0665, the catalyst B was tested at 1.48 MPa, only.
- (3) Methane selectivities were lower in tests where χ -carbide was the dominant iron phase (catalyst C), in comparison to the test SB-0665 with catalyst B where ϵ' -carbide was present. ✓

III-2 Reaction Studies with Catalysts B and C

Octacosane (n-C₂₈ paraffin) was used as a start-up slurry medium in the first three tests with catalyst B (runs SB-2764, SB-3064 and SA-0025), but all of them were unsuccessful (low catalyst activity). In the original test of catalyst B (SB-1931) purified n-octacosane was used as the start-up fluid, and high synthesis gas conversion was obtained.

Before loading to the reactor, the n-octacosane (99 % purity, The Humphrey Chemical Company, North Haven, CT) was extracted with tetrahydrofuran (THF) to remove bromotetradecane, since bromine is known to be the catalyst poison. Samples of fresh n-octacosane (before purification with THF), and from the slurry reactor (after the purification) were sent for trace bromine analysis to two different Laboratories. According to analysis done at Galbraith Laboratories, Inc. (Knoxville, TN) the as received n-octacosane had 530 ppm bromine, and the purified one less than 10 ppm bromine. The VHG Labs Inc. (Manchester, NH), using TOX (total organic halogen) method, detected even higher level of impurities. They reported 0.7 wt-% total halogen (as bromine) in the fresh n-octacosane, and less than 0.005 wt% (50 ppm) in the purified sample. Both results show that the amount of bromine was substantially reduced with THF washing. However, it can not be ruled out that the residual ppm level of bromine had a detrimental effect on the catalyst activity. The trace of sulfur was also detected by Galbraith Laboratories in used octacosane samples. Therefore, we believe that the presence of impurities in n-octacosane had resulted in catalyst poisoning in the three unsuccessful tests with the catalyst B. After these three unsuccessful tests, we decided to abandon n-octacosane as the start-up liquid medium, and we began using the Ethylflo 164 oil (a hydrogenated 1-decene homopolymer liquid - C₃₀, obtained from Ethyl Co.). Ethylflo 164 oil was used in all subsequent slurry reactor tests throughout this contract.

III-2.1 Stirred Tank Slurry Reactor Tests of Catalyst B (100 Fe/5 Cu/6 K/24 SiO₂)

Two successful tests of catalyst B designated SB-3354 and SB-0665 were performed in a slurry reactor B. The catalyst was reduced with H₂ at 250°C, 0.8 MPa (100 psig), 4000

cm³/min for 4 h. The same reduction conditions were employed in the original test of this catalyst (SB-1931). In all three tests the process conditions were: 260°C, 1.48 MPa, gas space velocity (SV) of 1.2-2.2 NI/g-cat/g using synthesis gas with molar feed ratio H₂/CO = 0.67-0.69. In each test, 7-10 g of catalyst with particle size less than 53 µm (270 mesh) was suspended in the start-up liquid to form a 2.4-3.6 wt% slurry.

Activity and Stability

Changes in synthesis gas, (H₂+CO), conversion and (H₂/CO) usage ratio with time-on-stream (TOS) are shown in Figure III-2.1. In the original run SB-1931 (with n-octacosane as the start-up liquid), (H₂+CO) conversion was stable with time (Figure III-2.1a). However, in the two recent runs SB-3354 and SB-0665 (with Ethylflo 164 oil as the initial slurry medium) the catalyst deactivated during the first 150 h of testing. Initial conversions in all three tests were similar (H₂+CO conversion was between 72 and 78%), but the initial space velocities were different in these tests (2.2 NI/g-cat/h in run SB-1931, 2.0 NI/g-cat/h in run SB-0665 and 1.8 NI/g-cat/h in run SB-3354). Comparison of conversion values at the same gas space velocity (at 1.8 and 1.6 NI/g-cat/h) reveals that the catalyst was most active in run SB-1931 (the highest conversions) and the least active in run SB-0665 (the lowest conversions).

Comparison of catalyst activity in terms of syngas conversion is not meaningful when the reaction conditions are not the same. In such a case an apparent reaction rate constant provides a better basis for comparison of the catalyst activity. In this study the apparent reaction rate constant was calculated assuming that the rate of (H₂+CO) disappearance has a first-order dependence on hydrogen partial pressure :

$$k = \frac{1000 \cdot SV \cdot X_{H_2+CO}}{22.4 \cdot P_{H_2} \cdot w_{Fe}} \text{ (mmol (H}_2\text{+CO) converted/g-Fe/h/MPa)}$$

where: SV = gas space velocity (NL/g-cat/h); X_{H_2+CO} is syngas conversion; P_{H_2} = partial pressure of hydrogen (MPa); w_{Fe} = mass fraction of iron in the catalyst (-).

The apparent rate constant as a function of time-on-stream for three runs with catalyst B is shown in Figure III-2.2. As can be seen from this figure, initial activities in all three tests were about the same, $k = 340\text{--}350$ mmol/g-Fe/h/MPa. In run SB-1931, the apparent rate constant gradually decreased from 350 to 300 mmol/g-Fe/h/MPa over a 400 hour period. However, in run SB-3354, the rate constant decreased from 340 to 250 mmol/g-Fe/h/MPa during the first 150 h of testing. It was stable at this value during the next 150 hours of testing at SV = 1.6 NL/g-cat/h; and then decreased further to 200 mmol/g-Fe/h/MPa during testing at SV = 1.2 NL/g-cat/h. In run SB-0665, the initial value of the apparent rate constant was 350 mmol/g-Fe/h/MPa at 20 h, but the rate constant decreased from 350 to 250 mmol/g-Fe/h/MPa in 120 hours, and then stabilized at 220 mmol/g-Fe/h/MPa between 180 and 370 h of testing.

Water gas shift (WGS) activity of the catalyst is related to (H_2/CO) usage ratio (UR), partial pressure quotient $K_P = P_{CO_2}P_{H_2}/P_{CO}P_{H_2O}$ and per cent CO conversion to carbon dioxide (CO_2 selectivity). Lower values of the usage ratio, or higher values of K_P or CO_2 selectivity imply higher WGS activity. In runs SB-3354 and SB-0665, the usage ratio was fairly stable at 0.56-0.58 (see Figure III-2.1b) during the entire test. The usage ratio in run SB-1931 was usually above 0.60, and increased to 0.62 at about 500 h on stream, i. e. the catalyst's WGS activity was lower than in runs SB-3354 and SB-0665.

Hydrocarbon Selectivity and Carbon Number Distribution

Methane and $C_1 + C_2$ hydrocarbons (methane + ethane + ethylene) selectivities are shown in Figure III-2.3. Low selectivities of methane and $C_1 + C_2$ hydrocarbons obtained in run SB-1931 were also observed in runs SB-3354 and SB-0665. For example, selectivities to methane and $C_1 + C_2$ hydrocarbons during run SB-3354, were similar to those obtained in run SB-1931 (2.5-3 mol% and 5-6 mol%, respectively); whereas the corresponding values in

Figure III-2.1 Changes in (a) (H_2+CO) conversion and (b) H_2/CO usage ratio with time and process conditions in STSR tests of the 100 Fe/5 Cu/6 K/24 SiO₂ catalyst.

Figure III-2.2 Apparent first order reaction rate constant as a function of time (100 Fe/5 Cu/6 K/24 SiO₂ catalyst).

(100 Fe/5 Cu/6 K/24 SiO₂ catalyst).

Figure III-2.3 Methane (a) and (C₁+C₂) hydrocarbon selectivity (b) as a function of time

run SB-0665 were slightly higher (e. g. 2.5-3.6 mol% and 5-7 mol%, respectively). Gaseous hydrocarbon selectivities ($C_2 - C_4$) (Table III-2.1) varied between 10 and 12.5 wt% in runs SB-1931 and SB-3354, but were higher in run SB-0665 (12-15 wt%).

In run SB-1931, hydrocarbon product distribution shifted gradually toward lower molecular weight products with time (see Table III-2.1). For example, methane selectivity increased from 2.5 wt% (42 h) to 3.7 wt% (496 h), while $C_2 - C_4$ selectivity increased from 11 to 14.6 wt% (between 98 and 208 hours on stream), whereas C_{19+} selectivity decreased from 58 to 49 wt% (also between 98 and 208 h). In runs SB-3354 and SB-0665, hydrocarbon product distribution during the first 100 h on stream was very similar to that obtained in run SB-1931 (Table III-2.1), but after about 100 h on stream the product distribution in these two tests did not change significantly with time. Some differences in hydrocarbon product distributions were observed in these three runs. For example, gasoline range hydrocarbons ($C_5 - C_{11}$) selectivity in run SB-1931 was between 13.2 and 19.6 wt%, whereas in run SB-0665 it varied between 16.3 and 23 wt%. The gasoline range hydrocarbons in run SB-3354 varied between 16.9 and 19.2 wt%, which is similar to that obtained in run SB-1931.

Carbon number distributions obtained in tests with catalyst B, are shown in Figure III-2.4 in the form of Anderson - Schulz - Flory (ASF) plots (log of mole fraction vs. carbon number). Data for individual mass balances at $SV = 1.6$ NI/g-cat/h and similar TOS were chosen for comparison (The effect of time-on-stream and process conditions on the carbon number distribution was negligible in all three tests). Positive deviations from ASF distribution are noted in all three tests in $C_{10} - C_{22}$ carbon number range. We are not certain whether this is due to the intrinsic catalytic selectivity, or due to experimental errors (e.g. loss of products and/or errors in analysis). The same behavior was obtained in several other mass balances in each of these three tests. Experimental data in Figure III-2.4 were fitted with a three parameter model of Huff and Satterfield (1984):

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

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 2 sites, respectively. The model parameters were estimated by a nonlinear regression (products of carbon number range C_{10} - C_{20} were excluded from calculations). Numerical values of the parameters are as follows: $\alpha_1 = 0.61$, $\alpha_2 = 0.93$, and $\beta = 0.76$.

Olefin Selectivity

Primary products of Fischer-Tropsch synthesis are 1-olefins and to a smaller extent, n -paraffins. Alpha olefins may undergo secondary reactions, such as hydrogenation, isomerization and readsorption. The olefin content, defined as $100 \times \text{olefin}/(\text{olefin} + \text{paraffin})$, is a measure of catalyst's hydrogenation activity. Weight percent olefin content variation with carbon number (up to C_{15}) is illustrated in Figure III-2.5a. The ethene content is low, since it readsorbs much more readily than the other low molecular weight olefins resulting in hydrogenation and/or chain growth initiation to higher molecular weight products. The olefin content reaches a maximum at C_3 - C_4 , and then decreases with increase in carbon number. The olefin contents were similar in runs SB-1931 and SB-3354, whereas slightly lower values were obtained in run SB-0665.

Ratio of 2-olefins/(1+2)- linear olefins is indicative of catalyst's isomerization activity. This ratio usually increases with carbon number, especially for hydrocarbons in the liquid phase (C_7+). The 2-olefin contents were similar in all three runs (Figure III-2.5b), although the 2-olefin content in run SB-1931 was slightly lower than that obtained in runs SB-3354 and SB-0665.

Table III-2.1 Performance of 100 Fe/5 Cu/6 K/24 SiO₂ (batch-1) Catalyst^a in Slurry Reactor Tests

Test designation	SB-1931				SB-3354			SB-0665		
Test conditions										
Temperature, °C	260	260	260	260	260	260	260	260	260	260
Pressure, MPa	1.48	1.48	1.48	1.48	1.48	1.48	1.48	1.48	1.48	1.48
Space velocity, NI/g-cat/h ^b	2.2	1.8	1.6	1.2	1.8	1.6	1.2	2.0	1.8	1.6
Feed H ₂ /CO ratio	0.67	0.67	0.67	0.67	0.67	0.67	0.67	0.67	0.67	0.67
Time on stream, h	42	98	208	496	97	288	384	38	110	290
CO conversion, %	78.2	78.4	81.4	83.9	76.0	74.4	79.4	76.2	71.1	69.2
(H ₂ +CO) conversion, %	74.0	75.1	77.3	80.3	71.5	70.6	74.2	71.5	67.0	65.4
STY, mmol (H ₂ +CO)/g-cat/h ^b	71	68	56	43	57	50	40	63	54	47
k, mmol/g-Fe/h/MPa ^c	346	370	304	280	282	249	226	328	284	215
(H ₂ /CO) usage ratio	0.60	0.62	0.60	0.60	0.57	0.57	0.56	0.56	0.57	0.58
K _p = P _{CO2} ·P _{H2} /P _{CO} ³ /P _{H2O}	24	10	11	17	27	22	32	22	20	20
% CO converted to CO ₂	47.6	46.4	46.8	45.1	48.6	48.3	48.1	48.3	47.8	48.2
Hydrocarbon selectivity, wt%										
CH ₄	2.5	2.8	2.8	3.7	3.2	3.5	3.5	3.0	4.1	4.2
C ₂ -C ₄	10.9	10.2	10.7	14.6	12.4	12.9	12.6	12.3	15.3	15.5
C ₅ -C ₁₁	18.0	13.2	13.5	19.6	18.5	19.2	16.9	16.3	22.9	22.7
C ₁₂ -C ₁₈		14.3	23.7		13.7	18.8	18.1		22.1	17.8
C ₁₂ ⁺	68.6	72.8	73.0	62.1	65.9	64.4	67.2	68.4	55.7	57.6
C ₁ +C ₂	5.4	5.7	6.1	8.1	6.4	6.9	6.9	6.1	8.0	8.2
Yield, g/Nm ³ (H ₂ +CO) Converted										
Hydrocarbons	212	217	213	206	207	206	210	209	193	199
Oxygenates	2.5	3.6	4.6	3.1	6.3	5.6	3.8	4.6	9.2	10.0
Catalyst productivity, g HC/g-cat/h ^b	0.34	0.33	0.27	0.20	0.26	0.23	0.19	0.29	0.23	0.21

^a Iron content of this catalyst (0.554 g-Fe/g-cat)^b Based on unreduced catalyst^c Apparent rate constant for a first order reaction in hydrogen

Figure III-2.4 Carbon number product distribution in S'FSR tests of the 100 Fe/5 Cu/6 K/24 SiO₂ catalyst.

Figure III-2.5 Olefin content (a) and 2-olefin content (b) dependence on carbon number (100 Fe/5 Cu/6 K/24 SiO₂ catalyst).

III-2.2 Stirred Tank Slurry Reactor Tests of Catalyst C (100 Fe/3 Cu/4 K/16 SiO₂)

Two new slurry phase tests were conducted with catalyst C from batch 1. These two runs were carried out in two different reactor systems, run SA-0705 was made in the slurry reactor A and run SB-0045 in the slurry reactor B. The reduction conditions employed in the original test of this catalyst (SB-0261) and in run SA-0705 were the same (H₂ at 240°C, 0.8 MPa (100 psig), 7500 cc/min for 2 h). In the test SB-0045 the reduction was carried out at a higher temperature (250°C, instead of 240°C), whereas the remaining conditions were the same. In all three tests the catalyst was tested at: 260°C, 1.48 MPa, 1.4-2.0 NI/g-cat/h using synthesis gas with molar feed ratio H₂/CO = 0.67-0.69. About 7-20 g of catalyst of particle size less than 53 µm (270 mesh) was suspended in the start-up fluid to form a 2.3-7 wt% slurry.

Catalyst Activity and Stability

Changes in (H₂+CO) conversion and H₂/CO usage ratio with time are shown in Figure III-2.6. During the first 100 hours of testing at the baseline conditions: 260°C, 1.48 MPa, and 1.4 NI/g-cat/h, the syngas conversions were similar in all three tests. After 100 h, the syngas conversion started to decline in run SB-0261, and reached 76% at 150 h on stream. Between 160 and 240 h on stream the catalyst was tested at 263°C (results not shown), and upon returning to the baseline conditions the conversion was about 67%. After that, the catalyst became stable and the conversion did not change with time. On the other hand, in runs SB-0045 and SA-0705 the catalyst was quite stable up to 250 h, and the syngas conversion was about 81%. After that, in both tests, the reaction pressure and gas space velocity were increased proportionally to 2.17 MPa and 2.05 NI/g-cat/h, respectively, in order to maintain the constant gas residence time. In both cases, the conversion decreased slightly to about 79%, and in run SA-0705 the syngas conversion decreased from 79 to 75 %

Figure III-2.6 Changes in (a) (H₂+CO) conversion and (b) H₂/CO usage ratio with time and process conditions in STSR tests of the 100 Fe/3 Cu/4 K/16 SiO₂ catalyst.

during the next 260 h of testing at higher reaction pressure. The reactor space-time-yield (STY) increased by about 40% during testing at 2.17 MPa and 2.05 NI/g-cat/h (Table III-2.2).

Good reproducibility of catalyst activity is also reflected in Figure III-2.7, in which the apparent reaction rate constant in all three tests varied between 250-270 mmol/g-Fe/h/MPa during the initial 100 h on stream. Constant activity and low deactivation rate were observed during the next 150 hours of testing in runs SB-0045 and SA-0705. In the original test (SB-0261), the catalyst began to deactivate after about 100 h on stream. However, it became stable again at about 250 hours ($k = 170$ mmol/g-Fe/h/MPa).

In the two recent tests (SB-0045 and SA-0705) of catalyst C, the reaction pressure and space velocity were increased to 2.17 MPa and 2.05 NI/g-cat/h, respectively, at about 250 hours. The apparent rate constant in run SB-0045 remained almost constant (about 255 mmol/g-Fe/h/MPa), whereas in run SA-0705 it decreased from 256 to 240 mmol/g-Fe/h/MPa at 525 hours on stream.

Water gas shift activity in all three tests was high and very reproducible (Figure III-2.6b). The usage ratio was between 0.55 and 0.57 in all three tests.

Hydrocarbon Selectivity and Carbon Number Distribution

Methane and gaseous hydrocarbon selectivities obtained in runs SB-0261 and SB-0045 were similar (Figure III-2.8 and Table III-2.2), whereas slightly higher selectivities of low molecular weight hydrocarbons were obtained in run SA-0705. For example, methane selectivity varied between 2 and 3 mol% in the latter test, whereas in the two tests conducted in the reactor B it was between 1.9 and 2.4 mol%. Also, $C_2 - C_4$ selectivity was between 9.3 - 11.3 wt% (Table III-2.2) in tests conducted in the slurry B system, whereas it was 12.5-14 wt% in the test SA-0705.

Hydrocarbon product distributions for C_5+ products in all three tests were similar (Table III-2.2). For example, the fraction of gasoline range hydrocarbons ($C_5 - C_{11}$) was generally between 11-14 wt%. Numerical values for diesel range hydrocarbons ($C_{12} - C_{18}$)

Figure III-2.7 Apparent first order reaction rate constant as a function of time (100 Fe/3 Cu/4 K/16 SiO₂ catalyst).

Figure III-2.8 Methane (a) and (C₁+C₂) hydrocarbon selectivity (b) as a function of time (100 Fe/3 Cu/4 K/16 SiO₂).

Table III-2.2 Performance of 100 Fe/3 Cu/4 K/16 SiO₂ (batch-1) Catalyst^a in Slurry Reactor Tests

Test designation	SB-0261			SB-0045			SA-0705		
Test conditions									
Temperature, °C	260	260	260	260	260	260	260	260	260
Pressure, MPa	1.48	1.48	1.48	1.48	1.48	2.17	1.48	1.48	2.17
Space velocity, NL/g-cat/h ^b	1.4	1.4	1.4	1.4	1.4	2.0	1.4	1.4	2.0
Feed H ₂ /CO ratio	0.67	0.67	0.67	0.67	0.67	0.67	0.67	0.67	0.67
Time on stream, h	92	356	523	95	215	336	88	197	364
CO conversion, %	87.4	72.4	72.6	87.1	86.7	85.0	87.5	86.9	83.8
(H ₂ +CO) conversion, %	81.4	67.4	67.9	81.0	80.8	79.9	81.4	81.1	79.1
STY, mmol (H ₂ +CO)/g-cat/h ^b	50	42	39	51	51	73	51	51	72
k, mmol/g-Fe/h/MPa ^c	251	165	161	254	256	255	256	255	252
(H ₂ /CO) usage ratio	0.57	0.56	0.57	0.55	0.56	0.57	0.55	0.56	0.57
K _p = P _{CO2} ·P _{H2} /P _{CO} /P _{H2O}	24	21	26	41	39	21	36	40	26
% CO converted to CO ₂	49.2	48.5	49.4	49.8	49.8	48.5	48.9	48.6	48.5
Hydrocarbon selectivity, wt%									
CH ₄	2.7	2.2	2.2	2.7	2.9	2.6	3.5	3.7	3.6
C ₂ -C ₄	11.3	9.7	9.3	10.4	10.4	10.7	12.5	13.0	14.3
C ₅ -C ₁₁	14.0	13.0	8.9	13.2	14.0	14.5	12.3	11.4	12.4
C ₁₂ -C ₁₈	17.9	24.5	20.9	14.8	17.8			18.0	18.2
C ₁₂ ⁺	70.7	75.6	76.2	73.5	72.7	72.3	67.6	71.8	69.7
C ₁ +C ₂	5.2	5.2	4.9	5.7	5.9	5.7	7.1	7.5	7.4
Yield, g/Nm ³ (H ₂ +CO) Converted									
Hydrocarbons	196.8	200.8	205.5	197.7	206.9	203.0	203.3	205.8	202.6
Oxygenates	2.2	2.0	1.8	2.5	3.2	3.4	2.6	2.2	2.6
Catalyst productivity, g HC/g-cat/h ^b	0.22	0.19	0.18	0.23	0.24	0.36	0.23	0.24	0.33

^a Iron content of this catalyst (0.597 g-Fe/g-cat)^b Based on unreduced catalyst^c Apparent rate constant for a first order reaction in hydrogen

and C₁₉+ products were not as reproducible as those for the gasoline range hydrocarbons, but for majority of mass balances the corresponding selectivities were about 18 wt% and 51-55 wt%, respectively.

Typical carbon number distribution obtained in run SB-0045 is shown in Figure III-2.9. Positive deviations from ASF distribution are noted in C₁₀ - C₂₀ carbon number range. The same type of irregularity was observed in tests with catalyst B (Figure III-2.4). Experimental data were fitted with a three parameter model, and the model prediction is shown as a solid line. The estimated values of parameters are as follows: $\alpha_1 = 0.59$; $\alpha_2 = 0.95$, and $\beta = 0.75$.

Olefin Selectivity

Total olefin and 2-olefin contents as a function of carbon number are shown in Figure III-2.10. Total olefin contents (Figure III-2.10a) were similar in all three runs and small deviations in results may be attributed to experimental errors. Also, 2-olefin contents (Figure III-2.10b) were similar in all three runs up to C₁₂, but significantly higher 2-olefin contents of C₁₃+ hydrocarbons were obtained in run SB-0261 than in the other two tests.

Concluding Remarks on Multiple Tests with Catalysts B and C

Three tests were conducted with each of the two catalysts. In the original tests conducted in 1991 (SB-1931 with the catalyst B, and SB-0261 with the catalyst C) n-octacosane was used as the initial medium. In the four tests conducted during the current contract, Ethylflo 164 oil was used as the start-up fluid, due to problems encountered in three initial tests using n-octacosane as the start-up liquid (low activity in all three tests). The effect of reactor set-up (slurry A vs. slurry B reactor system) was investigated in two recent tests with the catalyst C (runs SB-0045 and SA-0705). In general, reproducibility of results in multiple tests of the same catalyst may be regarded as quite satisfactory. The catalyst B (100 Fe/5 Cu/6 K/24 SiO₂) was more stable in the original test (SB-1931) than in the two recent tests (SB-3354 and SB-0665), whereas the opposite trend was observed in tests with

Figure III-2.9 Carbon number product distribution in STSR tests of the 100 Fe/3 Cu/4 K/16 SiO₂ catalyst.

Figure III-2.10 Olefin content (a) and 2-olefin content (b) dependence on carbon number (100 Fe/3 Cu/4 K/16 SiO₂ catalyst).

the catalyst C (100 Fe/3 Cu/4 K/16 SiO₂). Hydrocarbon product distributions and olefin selectivities in multiple tests with the same catalyst were also reproducible.

Performance of catalysts B and C is comparable to, or exceeds, that obtained in the two most successful bubble column slurry reactor (BCSR) tests conducted by Mobil (Kuo, 1985) and Rheinpreussen (Kölbel et al., 1955). In Mobil's run CT-256-13 at synthesis gas conversion of 82%, methane and C₁ + C₂ selectivities were 2.7 and 5.6 wt%, respectively, whereas the catalyst productivity was about 0.26 g HC/g-cat/h (Test conditions: 257°C, 1.48 MPa, 2.3 NI/g-Fe/h, H₂/CO = 0.73). In Rheinpreussen's demonstration plant unit the C₁ + C₂ selectivity was 6.8% at the synthesis gas conversion of 89%, and the catalyst productivity was about 0.33 g HC/g-cat/h (Test conditions: 268°C, 1.48 MPa, 3.1 NI/g-Fe/h, H₂/CO = 0.67).

In run SB-3354 with catalyst B (TOS = 97 h) the following results were obtained at 260°C, 1.48 MPa, 3.2 NI/g-Fe/h, H₂/CO = 0.67: Methane and C₁ + C₂ selectivities were 3.2 and 5.3 wt%, respectively, and the catalyst productivity was 0.26 g HC/g-cat/h at the synthesis gas conversion of 71.5%. The catalyst performance in the original test of the catalyst B (run SB-1931) was even better (see Table III-2.1), i. e. higher activity and lower methane and gaseous hydrocarbon selectivities were obtained.

The performance of catalyst C in run SB-0045 is illustrated in Table III-2.1. For example, at the reaction pressure of 1.48 MPa and 215 hours on stream, its performance was very similar to that obtained in Mobil's run CT-256-13. However, the performance of catalyst C was better at reaction pressure of 2.17 MPa and gas space velocity of 3.4 NI/g-Fe/h (TOS = 336 h). Methane and C₁ + C₂ selectivities were 2.6 and 5.4 wt%, respectively, and the catalyst productivity was 0.36 g HC/g-cat/h at the synthesis gas conversion of about 80%.

III-3 References

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IV Reproducibility of Catalyst Preparation

The objective of this task is to verify reproducibility of catalyst synthesis procedure on a laboratory scale. Four new batches of catalyst with nominal composition 100 Fe/5 Cu/6 K/24 SiO₂ (catalyst B; S5624) and three new batches of catalyst with nominal composition 100 Fe/3 Cu/4 K/16 SiO₂ (catalyst C; S3416) were synthesized, characterized by different techniques (Section IV-1), and some of them were tested in slurry reactors (Section IV-2).

IV-1 Catalyst Characterization Studies

Several batches (90 to 405 g) of catalysts B and C were synthesized using the procedure developed in our laboratory (Appendix 1). Different batches of the catalyst with the same nominal composition are designated with the serial number (catalyst code) followed by an Arabic numeral designating the specific batch (e.g., S3416-2 refers to batch-2 of catalyst with nominal composition 100 Fe/3 Cu/4 K/16 SiO₂). Synthesized catalysts were characterized by atomic absorption spectroscopy (AAS), BET surface area (SA), pore volume (PV), pore size distribution (PSD) measurements, temperature-programmed reduction (TPR) and isothermal reduction.

Catalyst Composition and Textural Properties

The catalyst composition was determined by AAS using a Varian Spectra AA-30 spectrophotometer. Detailed description of experimental equipment and procedures is provided in Appendix 2. Results of elemental analysis are shown in Table IV-1.1, and major findings are summarized below:

- (1) For catalyst C, both the copper and the silica contents agree well among different batches, however, potassium content of batch-2 (3.6 parts by weight (pbw) of K per 100 pbw of Fe), batch-3 (3.5 pbw of K per 100 pbw of Fe) and batch-4 (3.6 pbw of K per 100 pbw of Fe) catalysts is significantly lower than that of batch-1 (5.8 - 6.7 pbw of K per 100 pbw of Fe). The actual potassium content of the catalysts synthesized during the current contract (batches 2 to 4) is closer to the nominal one, than that of batch-1 (synthesized during the

Table IV-1.1 Elemental Analysis and Textural Properties of Synthesized Catalysts

Nominal Composition Designation	Amount Prepared (g)	Composition 100 Fe x Cu/y K/z SiO ₂	BET Surface Area (m ² /g)		Pore Volume cm ³ /g
			Single point	BET plot	
100 Fe/3 Cu/4 K/16 SiO ₂					
S3416-1	40	3.5 / 5.8 / 17 3.0 / 6.7 / 16(a) 3.0 / 5.9 / 16(b)		257 245 (a)	0.66 0.65 (a)
S3416-2	101	3.1 / 3.6 / 19	316	315	0.43
S3416-2 (c)		3.5 / 6.5 / 18			
S3416-3 (d)	173	2.9 / 3.5 / 16	262	291	0.43
S3416-3 (c)		3.2 / 6.9 / 20			
S3416-4	215	3.1 / 3.6 / 19	310	306	0.45
100 Fe/5 Cu/6 K/24 SiO ₂					
S5624-1	67	5.4 / 6.2 / 24 5.1 / 8.1 / 26(a) 5.5 / 6.6 / 24(e)	202	235 222 (a)	0.71 0.68 (a)
S5624-2	90	5.4 / 5.1 / 22	228	238	0.23
S5624-3	240	4.8 / 5.2 / 24	258	284	0.51
S5624-4	200	5.2 / 6.5 / 23	295	299	0.48
S5624-5	405	5.2 / 7.8 / 29		287	0.54

(a): Bukur (1994).

(b): measurements conducted at UOP.

(c): additional amount of K was added to obtain a better agreement with the actual K content of the original catalyst (S3416-1).

(d): contains 0.34 wt% sodium (Na/Fe = 0.006 by mass).

(e): measurements conducted at PETC, DOE.

previous contract). However, in order to obtain the desired catalytic performance, additional potassium was added by impregnation to the catalyst from batches 2 and 3, to obtain about 6.5-6.9 pbw of K per 100 pbw of Fe. Results obtained from measurements conducted at different laboratories with the same catalyst batch (S3416-1) are in good agreement.

(2) For catalyst B the potassium content of batches 2 - 5 varies from 5.1 to 7.8 pbw of K per 100 pbw of Fe, and the copper content varies between 4.8 to 5.5 pbw of Cu per 100 pbw of Fe. The copper content of these catalysts is close to the desired nominal value. The potassium content of batches 4 and 5 is slightly higher than the nominal amount, but is comparable to that of the batch-1 catalyst. The silica contents are similar for batches 2 to 4, and comparable to the value obtained for batch-1 catalyst. The silica content (29 pbw of SiO_2 per 100 pbw of Fe) of batch-5 is slightly higher than the nominal value.

(3) A relatively high sodium content in the catalyst S3416-3 is due to the use of washing water which was not purified properly. Its potential impact on catalytic results is expected to be small, since sodium can also serve as an alkali promoter.

Surface areas and pore volumes were measured by physical adsorption of nitrogen at 77 K using Micromeritics Digisorb 2600 instrument, and values obtained are summarized in Table IV-1.1. Surface areas obtained from the single-point BET method on a Micromeritics Pulse Chemisorb 2705 instrument are also included for comparison purposes. Differential pore volume distributions (PSD) obtained by nitrogen adsorption are shown in Figure IV-1.1. From the surface area and pore volume size distribution results, it can be seen that:

- (1) The surface areas obtained from the single-point BET method are close to those obtained from the multi-point BET plot (with relative error less than 10 %).
- (2) The BET surface areas of catalyst C (for batches from 1 to 4) vary between 245 to 310 m^2/g , and those of catalyst B (for batches from 1 to 5) are between 222 and 299 m^2/g . The maximum variation in BET areas among different batches is about 20%. Also, multiple measurements with the same catalyst (batch-1) were in good agreement.

Figure IV-1.1 Pore size distributions of iron catalysts from different batches:(a) Catalyst C (100 Fe/3 Cu/4 K/16 SiO₂) and (b) Catalyst B (100 Fe/5 Cu/6 K/24 SiO₂).

(3) Pore volumes for all new batches (2 - 5) are lower than those of catalysts synthesized during the previous contract (batch-1 in both series), even though the surface areas are similar as indicated.

(4) Pore diameters (Figure IV-1.1) of synthesized catalysts are between 2 and 20 nm. For the catalyst B series, the pore size distributions of catalysts from batches 1 and 5 are similar, and both have two major pore diameters. One is a mesopore with the pore diameter of 2.5 nm, and the other is a macropore with the pore diameter of about 10 nm. However, the pore size distribution of batch-2 catalyst is quite different, and it exhibits a very narrow pore size distribution with dominant pore diameters between 2.5 and 4 nm. For the catalyst C series, all four batches show similar pore size distributions and have two dominant pore diameters. The mesopores are about 2.5 nm in diameter, and the macropores have dominant pore diameters between 4 and 10 nm.

(5) Micropores with pore diameters less than 1.5 nm may exist in the catalysts investigated, but they are beyond the detectable limit of the technique employed.

Reduction Behavior of Catalysts

Reduction behavior of synthesized catalysts was studied in both temperature-programmed mode (TPR method) and isothermal mode of operation. In the latter mode of operation, the temperature was ramped from a room temperature to a desired reduction temperature at a rate of 5°C/min either in helium (TGA unit) or in a mixture of hydrogen and nitrogen (TPR unit), and then held constant.

Temperature Programmed Reduction (TPR)

Temperature-programmed reduction (TPR) studies were performed using a 5% H₂ / 95% N₂ mixture as a reductant. In a typical TPR experiment about 20 mg of catalyst was packed in a quartz reactor and purged with helium to remove the moisture from the catalyst sample. Then the catalyst sample was heated in a flow of 5%H₂/95%N₂ (flow rate = 40 ml/min) from room temperature to 800-900°C at a rate of 20°C/min. The degree of reduction

values are calculated from measured hydrogen consumption, and calibration data with standard CuO sample.

Peak positions (temperature values corresponding to maxima in hydrogen consumption) and degree of reduction values from TPR experiments with catalysts C and B from different batches are summarized in Table IV-1.2. Figures IV-1.2(a) and IV-1.2(b) show the TPR profiles of catalyst C (batch-2 to batch-4) and B (batch-2 to batch-5), respectively. From Figure IV-1.2 it is clear that the reduction of iron oxide proceeds in two steps namely, the reduction of Fe_2O_3 to Fe_3O_4 (first step) and Fe_3O_4 to Fe (second step). For catalyst C samples the first stage reduction peaks are located (Figure IV-1.2a) between 302 to 326°C and the second stage reduction peaks are located between 530 and 585°C. The degree of reduction for the first stage is about 23 - 26%, and total degree of reduction is between 79 and 96% (Table IV-1.2).

Similarly, catalyst B also has two peaks, one at 300 - 315°C and the second one at 570 - 580°C (Figure IV-1.2b). The degree of reduction for the first stage reduction is about 23 - 27% and the total degree of reduction varies between 88 and 98%. It is interesting to note that for both catalysts, B and C, the degree of reduction values for the first stage of reduction (23-27%) are considerably higher than the theoretical value corresponding to the reduction of Fe_2O_3 to Fe_3O_4 (i. e. 12.5%) indicating that part of iron Fe^{2+} is reduced to metallic iron at lower temperatures (300-326°C).

Similarity of peak positions and degree of reduction values of catalysts from different batches is indicative of good reproducibility of catalyst preparation, which was confirmed in stirred tank slurry reactor tests of these catalysts (Section IV-2).

Table IV-1.2 Temperature Programmed and Isothermal Reduction Results with Catalysts B and C from Different Batches

Sample	TPR Peak Position, °C#		Degree of Reduction, (%)		Degree of Reduction, (%) Isothermal Reduction	
	First Stg.	Second Stg.	First stage	Total	TPR unit(*)	TGA unit (**)
100 Fe/3 Cu/4 K/16 SiO ₂ , S3416-2	320	585	25	87	24	88
100 Fe/3 Cu/4 K/16 SiO ₂ , S3416-2+K(2)	302	538	23	79	25	70
100 Fe/3 Cu/4 K/16 SiO ₂ , S3416-3+K(2)	306	530	23	96	25	83
100 Fe/3 Cu/4 K/16 SiO ₂ , S3416-4	326	576	26	84	23	82
100 Fe/5 Cu/6 K/24 SiO ₂ , S5624-2	310	578	23	98	22	89
100 Fe/5 Cu/6 K/24 SiO ₂ , S5624-3	300	580	24	88	24	79
100 Fe/5 Cu/6 K/24 SiO ₂ , S5624-4	302	570	23	96	21	78
100 Fe/5 Cu/6 K/24 SiO ₂ , S5624-5	313	570	27	89	24	79

Sample wt = 10 to 20 mg, reducing gas = 5%H₂/95%N₂, flow rate = 40 cc/.min, ramp = 20°C/min, temperature range = room temp to 800°C.

* Sample wt = 400 to 500 mg, reducing gas = 5%H₂/95% N₂, flow rate = 40 cc/min, ramp = 5°C/min, temperature range = room temperature to 280°C and then, maintained at 280°C for 8 h.

** Sample wt = 20 mg, reductant hydrogen, flow rate 40 cc/min, heated in helium flow to 280°C, heating rate = 5°C/min and reduced in hydrogen at 280°C for 8 h.

Figure IV-1.2 TPR profiles of iron catalysts from different batches: (a) Catalyst C (100 Fe/3 Cu/4 K/16 SiO₂) and (b) Catalyst B (100 Fe/5 Cu/6 K/24 SiO₂).

Isothermal Reduction Behavior

In isothermal reductions conducted in the TPR unit, the temperature was ramped at a constant rate of 5°C/min to a final temperature of 280°C in a flow of 5% H₂/95% N₂ mixture. Then the catalyst sample was maintained at this temperature for 8 h in a flow of 5% H₂/95% N₂ (40 ml/min). The degree of reduction as a function of time was calculated from measured hydrogen consumption, and calibration with standard CuO sample.

In isothermal reductions conducted in the TGA unit, the catalyst sample was purged with helium (40 ml/min) and the temperature was ramped at a rate of 5°C/min from room temperature to 280°C. Then the helium flow was switched to hydrogen (99.995% purity) and the temperature was maintained at 280°C for a total period of 8 h. The degree of reduction was calculated from experimental weight loss vs. time data, and the theoretical weight loss based on the known composition and mass of a sample.

Figures IV-1.3a and IV-1.3b show the isothermal reduction behavior (in TPR unit) of catalyst C and catalyst B in diluted hydrogen as a function of reduction time. The final degree of reduction values (i.e. at the end of eight hour reduction period) are between 21 and 25% for all catalysts. These values are similar to those obtained for the first stage of reduction in the TPR mode of reduction.

Final degrees of reduction in pure hydrogen (TGA unit) for catalysts B and C were significantly higher than those obtained in 5% hydrogen stream. For example, for catalyst C the final degree of reduction in pure hydrogen varied between 70% (S3416-2+K(2) batch) and 82-85% for all other batches (Figure IV-1.4a), whereas for catalyst B the final degree of reduction in pure hydrogen was 89% (S5624-2 batch), and about 80% for the other three batches (Figure IV-1.4b).

The above results are consistent with the ones obtained during the temperature programmed reduction (Table IV-1.2), and they indicate that there are no significant differences in the reduction behavior among catalysts from different batches.

Figure IV-1.3 Isothermal reduction behavior of iron catalysts from different batches (TPR unit): (a) Catalyst C (100 Fe/3 Cu/4 K/16 SiO₂) and (b) Catalyst B (100 Fe/5 Cu/6 K/24 SiO₂).

Figure IV-1.4 Isothermal reduction behavior of iron catalysts from different batches (TGA unit): (a) Catalyst C (100 Fe/3 Cu/4 K/16 SiO₂) and (b) Catalyst B (100 Fe/5 Cu/6 K/24 SiO₂).

Iron Phases in Reduced and Used Catalysts

XRD and MES results of pretreated and used catalyst samples are summarized in Tables IV-1.3 and IV-1.4. In general there is a good agreement between XRD and MES results with regard to identity of iron phases in a given sample. Occasional discrepancies in the phase identification are due to the following factors. A significant fraction of iron has not been positively identified by Mössbauer spectroscopy, i. e. it is in the form of small crystallites (less than about 13 nm) which exhibit superparamagnetic behavior at room temperature (Spm phase in Tables IV-1.3 and IV-1.4). On the other hand, XRD can identify phases with crystallites larger than about 4 nm and thus some phases are identified by XRD (e.g. magnetite or metallic iron), but not by MES analysis. Another source of discrepancy, is the difficulty in discriminating between ϵ' - and χ - carbide with XRD analysis, so that occasionally an iron carbide may be identified as ϵ' -carbide (Fe_{22}C) by XRD analysis, whereas MES analysis identifies this phase as a χ -carbide (Fe_5C_2).

Figure IV- 1.5(a) shows XRD patterns of reduced (in H_2 at 240°C for 2 h and TOS = 0 h) catalyst C from batches 2 to 4. Both magnetite (Fe_3O_4) and α -Fe were identified by XRD in reduced catalysts from preparation batches 2 and 3. The MES results (Table IV-1.3) for these two samples indicate the presence of α -Fe(5-12%), as well as magnetite (7%) for batch-3 catalyst only (SA-2175), and 81% to 95% superparamagnetic (Spm) phase. The catalyst from batch-4 was primarily in the form of magnetite (Figure IV-1-5a and Table IV-1.3). From these results it appears that the catalyst C is not reduced completely and that only a small fraction of iron is in the form of either magnetite or metallic iron.

Figure IV-1.5(b) shows XRD patterns of reduced (in H_2 at 250°C for 4 h and TOS = 0 h) catalyst B from batches 4 and 5. The results indicate that the samples contain poorly crystalline magnetite (Fe_3O_4) and α -Fe suggesting that the particles are too small or less crystalline. However, MES results of these samples show that the reduced

Table IV-1.3 Summary of X-ray Diffraction and MES Analysis of Used Samples (Catalyst C:100 Fe/3 Cu/4 K/16 SiO₂)

Run Number	Catalyst	Time on Stream (TOS), h	Phases Identified by Mössbauer	Phases Identified by XRD
SB-0045	100 Fe/3 Cu/4 K/16 SiO ₂ batch-1	400 (EOR)	70% (Spm) and 30% (χ -Fe ₅ C ₂)	Fe ₃ O ₄ , ϵ' -Fe ₂₂ C and FeCO ₃
SA-0705	100 Fe/3 Cu/4 K/16 SiO ₂ batch-1	526 (EOR)	38% (Spm), 10% (FeCO ₃) and 52% (χ -Fe ₅ C ₂)	Fe ₃ O ₄ , ϵ' -Fe ₂₂ C and FeCO ₃
SB-2695	100 Fe/3 Cu/4 K/16 SiO ₂ batch-2	0 142 142 (EOR)	95% (Spm), and 5% (α -Fe) 47% (Spm), 24% (Fe ₃ O ₄), and 29% (ϵ' -Fe ₂₂ C) 49% (Spm), 23% (Fe ₃ O ₄), and 28% (Fe ₅ C ₂)	Fe ₃ O ₄ , and α -Fe Fe ₃ O ₄ , and ϵ' -Fe ₂₂ C Fe ₃ O ₄ , and ϵ' -Fe ₂₂ C
SA-2715	100 Fe/3 Cu/4 K/16 SiO ₂ batch-3	0 138	81% (Spm), 7% (Fe ₃ O ₄), and 12% (α -Fe) 43% (Spm), 13% (Fe ₃ O ₄), and 44% (Fe ₅ C ₂)	Fe ₃ O ₄ , and α -Fe Fe ₃ O ₄ , ϵ' -Fe ₂₂ C and FeCO ₃
SA-1665	100 Fe/3 Cu/4 K/16 SiO ₂ batch-4	500	61% (Spm), 7% (Fe ₃ O ₄), 27% (ϵ' -Fe ₂₂ C) and 5% (Fe ₅ C ₂)	Fe ₃ O ₄ and ϵ' -Fe ₂₂ C
SB-2145	100 Fe/3 Cu/4 K/16 SiO ₂ batch-4	0 67 145 213 401 402 (EOR)	69 (Spm), and 31% (Fe ₃ O ₄) 48 (Spm), 24% (Fe ₃ O ₄), 14% (ϵ' -Fe ₂₂ C) and 14% (Fe ₅ C ₂) 63 (Spm) and 37% (ϵ' -Fe ₂₂ C) 65 (Spm) and 35% (ϵ' -Fe ₂₂ C) 55 (Spm) and 45% (ϵ' -Fe ₂₂ C) 54 (Spm), 3% (Fe ₃ O ₄), 39% (ϵ' -Fe ₂₂ C) and 4% (Fe ₅ C ₂)	Fe ₃ O ₄ Fe ₃ O ₄ , and ϵ' -Fe ₂₂ C Fe ₃ O ₄ , and ϵ' -Fe ₂₂ C Fe ₃ O ₄ , and ϵ' -Fe ₂₂ C Fe ₃ O ₄ , and ϵ' -Fe ₂₂ C Fe ₃ O ₄ , and ϵ' -Fe ₂₂ C

EOR stands for end of the run sample which was exposed to air; TOS = 0 h means reduced sample.

FTS process conditions for slurry tests with catalyst C (100 Fe/3 Cu/4 K/16 SiO₂) were: T = 260°C, P = 1.48 - 2.17 MPa, H₂/CO = 0.67, SV = 1.4 - 2.1 NI/g-cat/h.

Table IV-1.4 Summary of X-ray Diffraction and MES Analysis of Used Samples (Catalyst B:100 Fe/5 Cu/6 K/24 SiO₂)

Run Number	Catalyst	Time on Stream (TOS), h	Phases Identified by Mössbauer	Phases Identified by XRD
SB-3064	100 Fe/5 Cu/6 K/24 SiO ₂ batch-1	54 (EOR)	73% (Spm) and 27% (Fe ₃ O ₄)	-
SB-0665	100 Fe/5 Cu/6 K/24 SiO ₂ batch-1	377 (EOR)	52% (Spm) 46% (ε'-Fe _{2.2} C) and 2% (χ-Fe ₅ C ₂)	-
SB-1295	100 Fe/5 Cu/6 K/24 SiO ₂ batch-3	353 (EOR)	30% (Spm), 68% (ε'-Fe _{2.2} C) and 2% (χ-Fe ₅ C ₂)	Fe ₃ O ₄ and ε'-Fe _{2.2} C
SA-2615	100 Fe/5 Cu/6 K/24 SiO ₂ batch-4	0 119 119 (EOR)	92 (Spm) and 8% (α-Fe) 83 (Spm) and 17% (ε'-Fe _{2.2} C) 74 (Spm) and 26% (ε'-Fe _{2.2} C)	Fe ₃ O ₄ , and α-Fe Fe ₃ O ₄ , and ε'-Fe _{2.2} C Fe ₃ O ₄ , and ε'-Fe _{2.2} C
SB-2585	100 Fe/5 Cu/6 K/24 SiO ₂ batch-5	0 120 120 (EOR)	95% (Spm) and 5% (α-Fe) 75% (Spm), 20% (ε'-Fe _{2.2} C) and 5% (χ-Fe ₅ C ₂) 68% (Spm), 27% (ε'-Fe _{2.2} C) and 5% (χ-Fe ₅ C ₂)	Fe ₃ O ₄ , and α-Fe Fe ₃ O ₄ , and ε'-Fe _{2.2} C Fe ₃ O ₄ , and ε'-Fe _{2.2} C

EOR stands for end of the run sample which was exposed to air; TOS = 0 h means reduced sample.

FTS process conditions for slurry tests with catalyst B (100 Fe/5 Cu/6 K/24 SiO₂) were: T = 260°C, P = 1.48 - 2.17 MPa, H₂/CO = 0.67, SV = 1.4 - 2.1 NI/g-cat/h.

Figure IV-1.5a XRD patterns of reduced (TOS = 0 h) catalysts from slurry tests with catalyst C (100 Fe/3 Cu/4 K/16 SiO₂) from different batches: (A) SB-2695, batch-2; (B) SA-2715, batch-3; and (C) SB-2145, batch-4.

Figure IV-1.5b XRD patterns of reduced (TOS = 0 h) catalysts from slurry tests with catalyst B (100 Fe/5 Cu/6 K/24 SiO₂) from different batches: (A) SB-2615, batch-4; (B) SB-2585, batch-5.

samples contain superparamagnetic (Spm) and α -Fe phases only and no magnetite was detected in the reduced samples by MES.

Figure IV-1.6 illustrates changes in bulk iron phases with time on stream during run SB-2145 with catalyst C from batch-4. Only magnetite was found (Figure IV-1.6a) in the sample withdrawn immediately after the reduction (TOS = 0 h). During the F-T synthesis (Figure IV-1.6b to IV-1.6e) magnetite and ϵ '-Fe_{2.2}C (pseudo-hexagonal iron carbide) were identified in used catalyst samples. The fraction of magnetite decreased with time (as evidenced by a decrease in size of a peak at about $2\theta = 35$), while the fraction of ϵ '-carbide phase increased with time on stream (increase in size of a peak at about $2\theta = 43$). During the same period of time, the catalyst activity continued to decline with time on stream (see Section IV-2.2).

Figure IV-1.6 Changes in bulk iron phases with time on stream during run SB-2145 with catalyst C (100 Fe/3 Cu/4 K/16 SiO_2 , batch-4): (A) TOS = 0 h; (B) TOS = 67 h; (C) TOS = 145 h; (D) TOS = 213 h and (E) TOS = 401 h.

IV-2 Reaction Studies

Repeatability of performance of catalysts B and C was demonstrated in multiple tests with catalysts from different preparation batches. Three STSR tests were conducted with catalyst B, and four tests with catalyst C. Results from these tests and comparisons of catalyst performance are described below.

IV-2.1 Stirred Tank Slurry Reactor Tests of Catalyst B

Three new tests with the catalyst B from batch-3 (run SB-1295), batch-4 (run SA-2615) and batch-5 (run SB-2585) were conducted in slurry reactors. In each of the tests, about 10 g of catalyst with particle size less than 53 μm (270 mesh) was suspended in Durasyn 164 oil (a new trade name for hydrogenated 1-decene homopolymer liquid - C_{30} , obtained from Albemarle Co.) to form a 3.4 wt% slurry. Similar slurry concentrations were used in three tests with the catalyst B from batch-1 (runs SB-1931, SB-3354 and SB-0665). In all six tests, the catalyst was reduced with H_2 at 250°C, 0.8 MPa (100 psig), 4000-7500 cm^3/min for 4 hours. Tests SB-2855 and SA-2615 lasted about 120 h, whereas the remaining tests were of longer durations. Initial catalyst behavior during the first 120 h of testing at 260°C, 1.48 MPa, space velocity of 1.8 NL/g-cat/h using synthesis gas with molar feed ratio $\text{H}_2/\text{CO} = 0.67$ will be discussed first, followed by discussion of results obtained in some of the tests which lasted longer than 120 hours.

Comparison of catalyst activity in terms of (H_2+CO) conversion and the apparent first order rate constant, k , obtained in six STSR tests with the 100 Fe/5 Cu/6 K/24 SiO_2 catalyst is given in Figure IV-2.1. Syngas conversions in all six tests are within 10% of the mean value of conversion, i. e. $71 \pm 6\%$. Catalyst from batch-5 (run SB-2585) was the least active (66-71 % conversion), whereas the catalyst from batch-4 (SA-2615) was the most active (74-77 % conversion). Comparison of catalyst activity in terms of the apparent first order

Figure IV-2.1 Synthesis gas conversion (a) and apparent reaction rate constant (b) as a function of time for STSR tests of catalyst B.

reaction rate constant, k , is shown in Figure IV-2.1b. Catalyst deactivation was observed in all six tests. The lowest deactivation rate was obtained in run SB-1931 with batch-1 catalyst, however, this low deactivation rate was not observed in two other tests of the same catalyst (runs SB-3354 and SB-0665). At about 100 h on stream numerical values of the apparent rate constant were between 248 mmol/g-Fe/h/MPa (SB-2585) and 301 mmol/g-Fe/h/MPa (run SA-2615).

Methane and C_1+C_2 selectivities are shown in Figure IV-2.2a and Figure IV-2.2b, respectively. Similar values of selectivities were obtained in all three tests of the catalyst from batch-1 (runs SB-1931, SB-3354, and SB-0665), and in run SB-2585 with batch-5 catalyst, whereas higher values were obtained in tests with batch-3 (SB-1295) and batch-4 (SA-2615) catalysts. A possible reason for higher methane and C_1+C_2 selectivities obtained in run SB-1295 is that potassium content of batch-3 catalyst is lower than that of the other batches (5.2 K per 100 Fe (batch-3) vs. 6.2 - 7.8 K per 100 Fe in other batches). However, the catalyst from batch-4 (SA-2615) had higher potassium loading (6.5 K per 100 Fe) than the catalyst from batch-3, and yet its methane and C_1+C_2 selectivities were higher.

Results from testing at a lower gas space velocity of 1.6 NL/g-cat/h (the other process conditions being the same as during the first 120 h on stream) are shown in Figures IV-2.3 and IV-2.4. Synthesis gas conversion (i.e. catalyst activity) was fairly stable in all three tests (two with batch-1, and one with batch-3 catalyst) and was between 65 and 75% (Figure IV-2.3). Methane and C_1+C_2 selectivities were also stable with time and varied between 3-4 mol% and 6-8 mol%, respectively (Figure IV-2.4). Catalyst from batch-3 (SB-1295) produced more gaseous hydrocarbons than batch-1 catalyst, which was also observed during the first 120 h of testing (Figures IV-2.2).

Figure IV-2.2 Methane selectivity (a) and (C₁+C₂) hydrocarbon selectivity (b) as a function of time for STSR tests of catalyst B.

Figure IV-2.3 Synthesis gas conversion as a function of time for STSR tests of catalyst B.

Figure IV-2.4 Methane selectivity (a) and (C₁+C₂) hydrocarbon selectivity (b) as a function of time for STSR tests of catalyst B.

Hydrocarbon Product Distribution

Lumped hydrocarbon distribution, activity parameters and product yields during the first 120 hours of testing of catalyst B from four preparation batches are shown in Table IV-2.1. In runs SB-3354 (batch-1 catalyst) and SB-2585 (batch-5 catalyst) methane and gaseous hydrocarbon (C_2-C_4) selectivities were lower than in other tests. Gasoline fraction (C_5-C_{11} hydrocarbons) was about 22% of total hydrocarbons, and diesel fraction ($C_{12}-C_{18}$ hydrocarbons) varied from 14 to 22%.

Olefin selectivities in tests with catalysts from batches 3-5 were similar to those obtained in tests with batch-1 catalyst (runs SB-1931, SB-3354 and SB-0065). Total olefin content and 2-olefin content dependence on carbon number for three tests with batch-1 catalyst were shown previously in Figure III-2.5.

IV-2. 2 Stirred Tank Slurry Reactor Tests of Catalyst C

About 10 g (runs SB-2695, SA-2715 and SA-1665) or 30 g (in run SB-2145) of catalyst C together with Durasyn 164 oil was loaded to a slurry reactor, so that the slurry concentration was about 3.4 wt% in tests SB-2695 (batch-2 catalyst), SA-2715 (batch-3 catalyst) and SA-1665 (batch-4 catalyst) and about 9.7 wt% in run SB-2145 (batch-4 catalyst). Similar slurry concentrations (2.3-7 wt%) were used in three tests with the catalyst C from batch-1 (runs SB-0261, SB-0045 and SA-0075). Pretreatment conditions (H_2 at $240^\circ C$, 0.8 MPa, $7500\text{ cm}^3/\text{min}$ for 2 h) were the same in all tests. Results obtained during the first 120 h of testing at $260^\circ C$, 1.48 MPa, 1.4 NL/g-cat/h using synthesis gas with molar feed ratio $H_2/CO = 0.67$ are discussed first, followed by discussion of results obtained in some of the tests which lasted longer than 120 hours.

Catalyst activity was similar in all seven tests. For example, syngas conversions (Figure IV-2.5a) were between 78 and 84 % (i.e., $81 \pm 3\%$), whereas values of the apparent reaction rate constant (Figure IV-2.5b) were between 225 and 290 mmol/g-Fe/h/MPa (mean value of about 250 mmol/g-Fe/h/MPa).

Table IV-2.1 Performance of 100 Fe/5 Cu/6 K/24 SiO₂ Catalyst^a from Different Batches in Slurry Reactor Tests

Test designation Batch-#	SB-3354 1	SB-0665 1	SB-1295 3	SA-2615 4	SB-2585 5
Test conditions					
Temperature, °C	260	260	260	260	260
Pressure, MPa	1.48	1.48	1.48	1.48	1.48
Space velocity, NI/g-cat/h ^b	1.8	1.8	1.8	1.8	1.8
Feed H ₂ /CO ratio	0.67	0.67	0.67	0.67	0.67
Time on stream, h	97	110	122	87	102
CO conversion, %	76.0	71.1	74.3	77.7	69.6
(H ₂ +CO) conversion, %	71.5	67.0	69.6	73.6	66.0
STY, mmol (H ₂ +CO)/g-cat/h ^b	57	54	57	59	53
k, mmol/g-Fe/h/MPa ^c	282	284	259	299	248
(H ₂ /CO) usage ratio	0.57	0.57	0.56	0.58	0.57
K _p = P _{CO2} · P _{H2} /P _{CO} /P _{H2O}	27	20	39	22	
% CO converted to CO ₂	48.6	47.8	48.9	47.9	48.7
Hydrocarbon selectivity, wt%					
CH ₄	3.2	4.1	4.4	5.5	2.9 ^d
C ₂ -C ₄	12.4	15.3	15.6	19.0	12.0 ^d
C ₅ -C ₁₁	18.5	22.9	21.8	23.2	
C ₁₂ -C ₁₈	13.7	22.1	18.4		
C ₁₂ ⁺	65.9	57.7	58.2	52.3	
C ₁ +C ₂	6.4	8.0	8.3	10.5	6.0 ^d
Yield, g/Nm ³ (H ₂ +CO) Converted					
Hydrocarbons	207	193	205	202	
Oxygenates	6.3	9.2	6.9	5.1	
Catalyst productivity, g HC/g-cat/h ^b	0.26	0.23	0.26	0.27	

^a Iron content of this catalyst (0.554 g-Fe/g-cat)^b Based on unreduced catalyst^c Apparent rate constant for a first order reaction in hydrogen^d in mol%

Figure IV-2.5 Synthesis gas conversion (a) and apparent reaction rate constant (b) as a function of time for STSR tests of catalyst C.

Methane (Figure IV-2.6a) and C_1+C_2 selectivities (Figure IV-2.6b) were also similar in all seven tests. At about 100 h on stream, the mean value of methane selectivity from all seven tests is 2.6 %, whereas the minimum value is 2.1 % (SA-2715) and maximum 3.1 % (runs SB-2145 and SA-0705). Also, the mean value of C_1+C_2 selectivity at about 100 h on stream is 5.7 %, whereas the minimum and the maximum are: 4.8 % (SA-2715) and 6.5 % (SA-0705), respectively. Lower methane and gaseous hydrocarbon selectivities obtained in tests with catalysts from batches 1-3, in comparison to the catalyst from batch-4, are consistent with higher potassium loading of these catalysts.

High syngas conversions and low gaseous hydrocarbon selectivities were obtained after 120 h on stream in tests which lasted 400-520 hours (Figures IV-2.7 and IV-2.8). Catalyst from batch-4 (runs SB-2145 and SA-1665) deactivated more rapidly than the catalyst from batch-1 (runs SB-0045 and SA-0075). Methane selectivity was between 2.5 and 3.5 mol% in all four tests, and C_1+C_2 selectivity varied between 5.5 and 7 mol% (Figure IV-2.8).

Hydrocarbon Product Distribution

Lumped hydrocarbon distribution, activity parameters and product yields during the first 120 hours of testing of catalyst C from four preparation batches are shown in Table IV-2.2. Methane and gaseous hydrocarbon (C_2-C_4) selectivities were low in all seven tests, and the fraction of liquid plus wax hydrocarbons (C_5+ hydrocarbons) was greater than 85% of total hydrocarbons produced. Gasoline fraction (C_5-C_{11} hydrocarbons) was about 10-18% of total hydrocarbons, and diesel fraction ($C_{12}-C_{18}$ hydrocarbons) varied from 15 to 18%. The amount of wax produced was significant in all tests, and yields of oxygenates were small.

Olefin selectivities in tests with catalysts from batches 2-4 were similar to those obtained in tests with batch-1 catalyst (runs SB-0261, SB-0045 and SA-0705). Total olefin content and 2-olefin content dependence on carbon number for three tests with batch-1 catalyst were shown previously in Figure III-2.10.

Figure IV-2.6 Methane selectivity (a) and (C₁+C₂) hydrocarbon selectivity (b) as a function of time for STSR tests of catalyst C.

Figure IV-2.7 Synthesis gas conversion as a function of time for STSR tests of catalyst C.

Table IV-2.2 Performance of 100 Fe/3 Cu/4 K/16 SiO₂ Catalyst^a from Different Batches in Slurry Reactor Tests

Test designation Batch #	SB-0261 1	SB-0045 1	SA-0705 1	SB-2695 2	SA-2715 3	SA-1665 4	SB-2145 4
Test conditions							
Temperature, °C	260	260	260	260	260	260	260
Pressure, MPa	1.48	1.48	1.48	1.48	1.48	1.48	1.48
Space velocity, NI/g-cat/h ^b	1.4	1.4	1.4	1.4	1.4	1.4	1.4
Feed H ₂ /CO ratio	0.67	0.67	0.67	0.67	0.67	0.67	0.67
Time on stream, h	92	95	88	98	88	112	40
CO conversion, %	87.4	87.1	87.5	83.3	87.2	84.1	82.2
(H ₂ +CO) conversion, %	81.4	81.0	81.4	77.6	81.6	79.0	77.2
STY, mmol (H ₂ +CO)/g-cat/h ^b	50	51	51	49	50	49	48
k, mmol/g-Fe/h/MPa ^c	251	254	256	218	240	248	222
(H ₂ /CO) usage ratio	0.57	0.55	0.55	0.55	0.55	0.57	0.56
K _p = P _{CO2} P _{H2} /P _{CO} P _{H2O}	24	41	36		38	33	37
% CO converted to CO ₂	49.2	49.8	48.9	49.1	48.5	48.9	48.4
Hydrocarbon selectivity, wt%							
CH ₄	2.7	2.7	3.5	2.2 ^d	2.4	3.2	3.1
C ₂ -C ₄	11.3	10.4	12.5	10.8 ^d	9.3	12.3	11.9
C ₅ -C ₁₁	14.0	13.2	12.3		10.1	12.0	17.7
C ₁₂ -C ₁₈	17.9	14.8					
C ₁₂ ⁺	70.7	73.5	67.6		78.2	72.6	67.3
C ₁ +C ₂	5.2	5.7	7.1	5.1 ^d	5.2	6.5	6.2
Yield, g/Nm³(H₂+CO) Converted							
Hydrocarbons	197	198	203		201	204	198
Oxygenates	2.2	2.5	2.6		2.5	2.4	3.9
Catalyst productivity, g HC/g-cat/h ^b	0.22	0.23	0.23		0.22	0.22	0.21

^a Iron content of this catalyst (0.597 g-Fe/g-cat)^b Based on unreduced catalyst^c Apparent rate constant for a first order reaction in hydrogen^d in mol%

Concluding Remarks on Tests of Catalysts B and C from Different Batches

In general, catalysts from different preparation batches had similar performance (activity and selectivity) and reproducibility of catalyst preparation procedure is regarded as satisfactory.

Table IV-2.3 summarizes performance of catalysts B and C, and precipitated iron catalysts (Fe-Cu-K) used in Mobil's slurry bubble column reactor and Rheinpreussen's demonstration plant unit. The latter two studies are regarded as the most successful examples of the slurry reactor performance. Process conditions in all tests were similar, with the exception of the use of higher reaction pressure (2.17 MPa) during later periods of two tests with catalyst C.

In Mobil's run CT-256-13 at synthesis gas conversion of 82%, methane and C_1+C_2 selectivities were 2.7 and 5.6 wt%, respectively, whereas the catalyst productivity was 0.39 g HC/g-Fe/h. In Rheinpreussen's demonstration plant unit the C_1+C_2 selectivity was 6.8% at synthesis gas conversion of 89%, and the catalyst productivity was 0.49 g HC/g-Fe/h.

Syngas conversions, methane and C_1+C_2 selectivities obtained in tests with catalysts B and C were similar to those obtained in two tests conducted in slurry bubble column reactors. However, the catalyst productivity in two tests with catalyst C, at 2.17 MPa, was even higher (0.53 or 0.60 g HC/g-Fe/h) than that obtained in Rheinpreussen's test (0.49 g HC/g-Fe/h), whereas at the reaction pressure of 1.48 MPa the catalyst productivity of our catalysts B and C (0.38-0.42 g HC/g-Fe/h) was similar to that obtained in Mobil's study (0.39 g HC/g-Fe/h). Due to complete reactor backmixing in our experiments (stirred tank reactor) it may be expected that the catalyst productivity under the same process conditions would be even higher in a reactor with partial fluid mixing (e.g., bubble column slurry reactor).

Table IV-2.3 Catalyst Performance in Slurry Reactor Tests

Catalyst designation Run ID	B (batch-1) SB-3354	B (batch-3) SB-1295	C (batch-1) SB-0045	C (batch-4) SA-1665	Mobil ^a CT-256-13 Kuo (1985)	Rheinpreussen ^a Kölbel et al. (1955)
Test conditions						
Temperature, °C	260	260	260	260	257	268
Pressure, MPa	1.48	1.48	1.48	1.48	1.48	1.20
Space velocity, NI/g-Fe/h	3.2	2.9	2.3	3.4	2.3	3.1
Feed H ₂ /CO ratio	0.67	0.67	0.67	0.67	0.73	0.67
Time on stream, h	288	243	215	336	475	
(H ₂ +CO) conversion, %	74	70.4	80.8	79.9	82	89
(H ₂ /CO) usage ratio	0.57	0.56	0.56	0.57	0.59	0.63
Hydrocarbon selectivities, wt%						
CH ₄	3.5	4.5	2.9	2.6	2.7	3.2 ^b
C ₂ -C ₄	12.9	16.3	10.4	10.7	11.1	31.3
C ₅ -C ₁₁	19.2	22.9	14.0	14.5	18.1	53.6
C ₁₂ ⁺	64.4	56.2	72.8	72.3	68.1	11.9
C ₁ +C ₂	6.9	8.9	5.9	5.7	5.6	6.8
Yields						
Nm ³ /kg-Fe/h	2.0	2.0	1.9	2.7	1.9	2.8
g HC/Nm ³ (H ₂ +C)	206	199	207	203	206	178
g C ₃ ⁺ /Nm ³ (H ₂ +C)	192	181	195	191	195	166
g HC/g-Fe/h	0.42	0.40	0.40	0.60	0.39	0.49

^a Slurry bubble column reactor test.^b CH₄ + C₂ H₆

IV-3 References

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V The Effect of Source of Potassium and Basic Oxide Promoter

The objective of this task is to determine effects of two different sources of potassium and addition of another promoter on performance of catalysts B and C. In our standard catalyst preparation procedure silicon oxide is introduced by addition of a dilute potassium silicate (K_2SiO_3) solution to the iron/copper precipitate. This procedure introduces potassium in the excess of the desired amount. Potassium is completely removed by washing of the precipitate. Addition of the desired amount of potassium promoter is accomplished via "incipient wetness" method, using $KHCO_3$ dissolved in water. An obvious alternative to the above procedure is to utilize potassium from K_2SiO_3 as the source of potassium, i.e. discontinue with washing when the residual amount of potassium equals the desired amount of promoter. Catalysts B and C were synthesized using potassium silicate as the source of the potassium promoter, and performance of these catalysts was compared with those synthesized using our usual procedure (Section IV-2).

In many of the older German preparation procedures basic oxides such as: MnO , MgO and CaO were used as promoters (Anderson, 1956). In particular, calcium oxide was used as a standard promoter in Ruhrchemie catalysts, and Kölbel stated that CaO increases catalyst activity and possibly causes the increase in molecular weight of the product (Anderson, 1956; p.133). The effect of CaO promotion on the performance of catalysts B and C (two levels of promotion per catalyst) was investigated in this task. Synthesized catalysts were characterized (Section IV-1) and tested first in a fixed bed reactor, and the two most promising catalyst formulations were tested in the STSR (Section IV-2).

V-1 Catalyst Characterization Studies

Six new catalysts (four containing CaO as a promoter, and two using potassium silicate solution as the source of potassium promoter) were synthesized. The synthesized catalyst were characterized by atomic absorption spectroscopy (AAS), BET surface area

(SA) and pore size distribution (PSD) measurements, and reduction behavior under temperature programmed and isothermal conditions.

Elemental Analysis

The CaO containing catalysts were prepared by impregnation of Fe-Cu-SiO₂ precursor from batch-3. For catalyst C series (100 Fe/3 Cu/4 K/x Ca/16 SiO₂) the copper (2.9-3.2 pbw of Cu per 100 pbw of Fe), and calcium (2.2 and 6.3 pbw of Ca per 100 pbw of Fe) contents are close to the nominal amounts (Table V-1.1). Their potassium (4.6-4.8 pbw of K per 100 pbw of Fe) and silica (17-22 pbw of SiO₂ per 100 pbw of Fe) contents are slightly higher than the nominal compositions. Similarly, for catalyst B series (100 Fe/5 Cu/6 K/x Ca/24 SiO₂) the copper, potassium and calcium contents are close to the nominal values but the silica content is higher than the corresponding nominal amount (24 pbw of SiO₂ per 100 pbw of Fe).

Catalysts C (S3416-4-K) and B (S5624-5-K) were prepared from Fe-Cu-SiO₂ precursors from batch-4 and batch-5, respectively, using potassium silicate as the source of both potassium and silicon oxide promoters. The excess potassium was removed by washing of the Fe-Cu-SiO₂ precursors (Appendix 1). Both potassium and silicon oxide contents of these two catalysts were higher than the corresponding nominal amounts.

BET Surface Area and Pore Volume

Surface areas obtained from single-point method are similar to those obtained from the BET plot (multiple point) method (Table V-1.1). Catalysts containing 6 pbw of Ca per 100 pbw of Fe (S3416-3+6 Ca and S5624-3+6 Ca) have surface areas of 73-105 m²/g, and those containing 2 pbw of Ca per 100 pbw of Fe (S3416-3+2 Ca and S5624-3+2 Ca) have surface areas between 190 and 221 m²/g, whereas the surface area of the corresponding catalysts without CaO is about 290 m²/g. The pore volume of the catalysts with 6 parts of Ca per 100 parts of Fe is 0.26-0.30 cm³/g, whereas the baseline catalysts B and C have pore volumes between 0.43 and 0.51 cm³/g. These results show that the addition of calcium

Table V-1.1

Effect of Calcium Addition and Source of Potassium on the Textural Properties of Iron Catalysts

Catalyst Code	Amount Prepared (g)	Composition 100 Fe/w Ca x Cu/y K/z SiO ₂	BET Surface Area (m ² /g)		Pore Volume cm ³ /g
			Single point	BET plot	
S3416-3	173	/ 2.9 / 3.5 / 18	262	291	0.43
S3416-3+2 Ca	12	<u>2.2</u> / 3.2 / 4.8 / 17	190	190	0.36
S3416-3+6 Ca	13	<u>6.3</u> / 3.2 / 4.6 / 22	106	105	0.30
S3416-4	215	/ 3.1 / 3.6 / 19	310	306	0.45
S3416-4-K	20	/ 3.2 / 5.6 / 21	312 ^a	277	0.41
S5624-3	240	/ 4.8 / 5.2 / 24	258	284	0.51
S5624-3+2 Ca	13	<u>2.2</u> / 5.5 / 5.0 / 22	224	221	0.46
S5624-3+6 Ca	14	<u>6.1</u> / 5.1 / 5.3 / 31	100	73.2	0.26
S5624-5	405	/ 5.2 / 7.8 / 29		287	0.54
S5624-5-K	34	/ 5.2 / 6.6 / 30	300 ^a	270	0.59

^a : Catalyst dried at 120°C, others were calcined at 300°C for 5 h.

Nominal (intended) catalyst compositions:

S3416-3-2Ca 100 Fe/2 Ca/3 Cu/4 K/16 SiO₂S3416-3-6Ca 100 Fe/6 Ca/3 Cu/4 K/16 SiO₂S5624-3-2Ca 100 Fe/2 Ca/5 Cu/6 K/24 SiO₂S5624-3-6Ca 100 Fe/6 Ca/5 Cu/6 K/24 SiO₂

decreases the surface area and pore volume of the baseline catalysts and that this effect is more pronounced at a higher level of CaO promotion.

Catalysts C (S3416-4-K) and B (S5624-5-K) prepared from Fe-Cu-SiO₂ precursors from batch-4 and batch-5, respectively, using potassium silicate as the source of both potassium and silicon oxide promoters, have similar surface areas and pore volumes as the baseline catalysts C and B prepared by impregnation of Fe-Cu-SiO₂ precursors with potassium bicarbonate.

Pore Size Distributions

Figures V-1.1(a) and V-1.1(b) show the effect of potassium source on the pore size distribution (PSD) of catalyst C (batch-4) and catalyst B (batch-5). Pore size distributions of the catalysts originating from the same Fe-Cu-SiO₂ precursor are similar.

Figure V-1.2 shows the effect of calcium addition on the pore size distribution of catalysts C and B. It is found that the addition of calcium oxide promoter results in a shift towards larger pores. These results again suggest that the calcium oxide plays significant role in controlling the catalyst structure and texture.

Reduction Behavior

The effect of calcium addition on the reduction behavior of catalyst C (batch-3) is shown in Figure V-1.3(a). The catalyst has two dominant peaks at about 306 and 530°C corresponding to the reduction of Fe₂O₃ to Fe₃O₄ (first stage) and Fe₃O₄ to Fe (second stage), respectively. With the addition of CaO, both reduction peaks shifted to higher temperatures. The first reduction peak is located at about 321°C and the second peak is located at 609°C for the catalyst with 6 pbw of Ca per 100 pbw of Fe. These results indicate that the addition of calcium retards the onset of iron reduction for both stages of the reduction, and causes the broadening of both reduction peaks.

Figure V-1.1 Effect of potassium source on the pore size distributions of (a) Catalyst C (100 Fe/3 Cu/4 K/16 SiO_2) and (b) Catalyst B (100 Fe/5 Cu/6 K/24 SiO_2).

Figure V-1.2 Effect of calcium addition on the pore size distributions of (a) Catalyst C (100 Fe/3 Cu/4 K/16 SiO₂, batch-3) and (b) Catalyst B (100 Fe/5 Cu/6 K/24 SiO₂, batch-3).

Figure V-1.3 Effect of calcium addition on TPR profiles of catalysts B and C.

Similarly, with catalyst B (batch-3) the reduction peaks are located at about 300°C and 580°C (Figure V-1.3b) corresponding to the first and the second stage of reduction, respectively. In the case of the CaO containing catalyst (S5624-3+6 Ca) the peak positions are shifted to higher temperatures (at 332°C and 650°C). These results suggest that the addition of calcium retards the reduction of iron oxide.

Isothermal reduction experiments were conducted in thermal gravimetric (TGA) unit with pure hydrogen as reductant at 280°C for 8 hours. The final degree of reduction values of catalysts C and B, without CaO promoter, were significantly higher (83 and 79%) than the corresponding values obtained with catalysts containing 6 pbw of Ca per 100 pbw of Fe (68 and 49%). These results confirm that the addition of CaO inhibits reduction of iron in baseline catalysts C and B. In the temperature programmed mode of reduction, the final degree of reduction (at 800°C) values were between 88 and 96% for all four catalysts (Table V-1.2).

Iron Phases in Used Catalysts

Used catalyst samples from studies on the effect of source of potassium promoter and addition of CaO promoter in fixed bed and slurry reactors were analyzed by XRD and MES and results are summarized in Table V-1.3.

Used catalysts B and C, without CaO promoter, from fixed bed reactor tests contained only ϵ' -Fe_{2.2}C (samples from both top and bottom portions of the reactor). In two tests with catalysts containing 6 pbw of Ca per 100 pbw of Fe (FA-1705 and FB-1515) magnetite and ϵ' -carbide were identified by both XRD and MES analysis. Activity of the catalysts containing 6 pbw of Ca per 100 pbw of Fe was markedly lower than that of the baseline catalysts B and C (Section V-2.1).

In slurry reactor tests SB-3155 (100 Fe/3 Cu/4 K/2 Ca/16 SiO₂ catalyst) and SA-2405 (100 Fe/5 Cu/6 K/2 Ca/24 SiO₂ catalyst) both magnetite and ϵ' -carbide were identified by

Table V-1.2 Effect of Calcium Addition on the Reduction Behavior of Catalysts B and C

Catalyst	Reduction Temperature Range, °C	Peak Position, °C##		Degree of Reduction, (%)		Degree of Reduction, (%) Isothermal TGA unit
		1st Stage	2nd Stg.	1st stage	Total	
100 Fe/3 Cu/6 K/16 SiO ₂ S3416-3+2 K	RT to 800	306	530	23	96	83
100 Fe/3 Cu/4 K/6 Ca/16 SiO ₂ S3416-3+6 Ca	RT to 1000	321	609	16	96 (92)#	68
100 Fe/5 Cu/6 K/24 SiO ₂ S5624-3	RT to 800	300	580	24	88	79
100 Fe/5 Cu/6 K/6 Ca/24 SiO ₂ S5624-3+6 Ca	RT to 1000	316	645	12	100 (90)#	49

The value in the parenthesis represent the %DR value calculated for the reduction temperature range of RT to 800°C.

Sample wt = 10 to 20 mg, reducing gas = 5%H₂/95%N₂, flow rate = 40 cc/.min, ramp = 20°C/min, temperature range = room temp to 800°C.

* Sample wt = 400 to 500 mg, reducing gas = 5%H₂/95% N₂, flow rate = 40 cc/min, ramp = 5°C/min, temperature range = room temperature to 280°C and then, maintained at 280°C for 8 h.

Table V-1.3 Iron Phases in Used Catalysts from Fixed Bed and Slurry Reactor Tests

Run Number	Catalyst	Time on Stream (TOS), h	Phases Identified by Mössbauer	Phases Identified by XRD
FA-1605	100 Fe/3 Cu/4 K/16 SiO ₂ S3416-4, KHCO ₃ source	120 (top) 120 (bot)	49% (Spm) and 51% (ϵ' -Fe _{2.2} C) 50% (Spm) and 50% (ϵ' -Fe _{2.2} C)	ϵ' -Fe _{2.2} C ϵ' -Fe _{2.2} C
FB-1985	100 Fe/3 Cu/4 K/16 SiO ₂ S3416-4, K ₂ SiO ₃ source	120 (top) 120 (bot)	53% (Spm) and 47% (ϵ' -Fe _{2.2} C) 49% (Spm) and 51% (ϵ' -Fe _{2.2} C)	ϵ' -Fe _{2.2} C ϵ' -Fe _{2.2} C
SB-3115	100 Fe/3 Cu/4 K/2 Ca/ 16 SiO ₂ S3416-3+2 Ca	354	49% (Spm), 8% (Fe ₃ O ₄) and 42% (ϵ' -Fe _{2.2} C)	Fe ₃ O ₄ and ϵ' -Fe _{2.2} C
FA-1525	100 Fe/3 Cu/4 K/2 Ca/ 16 SiO ₂ S3416-3+2 Ca	120 (EOR)	-	ϵ' -Fe _{2.2} C
FB-1515	100 Fe/3 Cu/4 K/6 Ca/ 16 SiO ₂ S3416-3+6 Ca	140 (top) 140 (bot)	44 (Spm), 9% (Fe ₃ O ₄) and 47% (ϵ' -Fe _{2.2} C) 40 (Spm), 16% (Fe ₃ O ₄) and 44% (ϵ' -Fe _{2.2} C)	Fe ₃ O ₄ and ϵ' -Fe _{2.2} C Fe ₃ O ₄ and ϵ' -Fe _{2.2} C
FB-1715	100 Fe/5 Cu/6 K/24 SiO ₂ S5624-3, KHCO ₃ source	119 (top) 119 (bot)	40% (Spm) and 60% (ϵ' -Fe _{2.2} C) 42% (Spm) and 58% (ϵ' -Fe _{2.2} C)	ϵ' -Fe _{2.2} C ϵ' -Fe _{2.2} C
FA-1795	100 Fe/5 Cu/6 K/24 SiO ₂ S5624-5, K ₂ SiO ₃ source	120 (top) 120 (bot)	34% (Spm) and 66% (ϵ' -Fe _{2.2} C) 34% (Spm) and 66% (ϵ' -Fe _{2.2} C)	ϵ' -Fe _{2.2} C ϵ' -Fe _{2.2} C
SA-3155	100 Fe/5 Cu/6 K/24 SiO ₂ S5624-5, K ₂ SiO ₃ source	0 400	79% (Spm) and 21% (α -Fe) 62% (Spm) and 34% (ϵ' -Fe _{2.2} C)	Fe ₃ O ₄ and α -Fe ϵ' -Fe _{2.2} C
SA-2405	100 Fe/5 Cu/6 K/2 Ca/24 SiO ₂ S5624-3+2 Ca	0 550 693 693 EOR	81% (Spm) and 19% (α -Fe) 44% (Spm), 6% (Fe ₃ O ₄), 40% (ϵ' -Fe _{2.2} C) and 10% (χ -Fe ₅ C ₂) 58% (Spm), 39% (ϵ' -Fe _{2.2} C) and 3% (χ -Fe ₅ C ₂) 50% (Spm), 45% (ϵ' -Fe _{2.2} C) and 5% (χ -Fe ₅ C ₂)	Fe ₃ O ₄ and α -Fe Fe ₃ O ₄ and ϵ' -Fe _{2.2} C Fe ₃ O ₄ and ϵ' -Fe _{2.2} C Fe ₃ O ₄ and ϵ' -Fe _{2.2} C
FA-1705	100 Fe/5 Cu/6 K/6 Ca/24 SiO ₂ S5624-3+6 Ca	120 (top) 120 (bot)	43% (Spm), 22% (Fe ₃ O ₄) and 35% (ϵ' -Fe _{2.2} C) 26% (Spm), 33% (Fe ₃ O ₄) and 41% (ϵ' -Fe _{2.2} C)	Fe ₃ O ₄ and ϵ' -Fe _{2.2} C Fe ₃ O ₄ and ϵ' -Fe _{2.2} C

EOR stands for end of the run sample which was exposed to air; TOS = 0 h means reduced sample.

FTS process conditions for slurry tests were: T = 260°C, P = 1.48 - 2.17 MPa, H₂/CO = 0.67, SV = 1.4 - 2.2 NI/g-cat/h.

FTS process conditions for fixed bed tests were: T = 250°C, P = 1.48 MPa, H₂/CO = 0.67, SV = 2.0 NI/g-cat/h.

XRD, whereas MES analysis of samples from run SA-2405 at 693 h reveals the presence of ϵ' -carbide (39%), small amount of χ - Fe_5C_2 (3%), and significant amount of an iron phase exhibiting superparamagnetic behavior (58% Spm). At least a portion of the latter phase is magnetite (small crystallites less than about 10 nm in diameter). Bulk iron composition of the sample which was exposed to air (EOR) in run SA-2405 is very similar to that of the sample withdrawn from the reactor at 693 hours without exposure to air.

V-2 Reaction Studies

Eight fixed bed reactor tests were conducted; two with baseline catalysts B and C; two with catalysts B and C prepared using potassium silicate as the source of potassium promoter, and four with catalysts containing CaO promoter. On the basis of results from fixed bed reactor tests, three catalysts were selected for testing in slurry reactors. Two of these tests were made with catalysts containing CaO promoter (runs SA-2405 and SB-3115) and one with the catalyst B prepared using potassium silicate as the source of potassium promoter (SA-3155). Nominal catalyst compositions, test and catalyst codes, as well as the general purpose of each of these tests are given in Table V-2.1.

V-2.1 Fixed Bed Reactor Tests of Modified Catalysts B and C

Four of the synthesized catalysts containing CaO promoter, and two catalysts prepared using potassium silicate as the source of potassium promoter were tested in a fixed bed reactor to determine their activity and selectivity during Fischer-Tropsch synthesis. About 3 g of the catalyst (30 to 60 mesh particle size) diluted 1:7 (reactor B) or 1:9 (reactor A) by volume with glass beads (the same size as the catalyst) was used in fixed bed reactor tests. Prior to F-T synthesis the catalysts were reduced in-situ with hydrogen at atmospheric pressure, 7500 cm³/min and either 240°C for 2 h (catalysts containing 16 parts of SiO₂ per 100 parts of Fe on a mass basis), or 250°C for 4 h (catalysts containing 24 parts of SiO₂ per 100 parts of Fe on a mass basis). After the conditioning period of about 24 h, during which the reaction temperature was gradually increased from 210 to 250°C, all catalysts were 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 0.67. Test duration was 120 - 140 h including the conditioning period.

Performance of catalysts having 16 parts by weight (pbw) of SiO₂ per 100 pbw of Fe and containing either CaO promoter (runs FA-1525 and FB-1515), or being prepared using K₂SiO₃ as the source of potassium (FB-1895) is compared with that of the baseline catalyst (catalyst C from batch 4; run FA-1605) in Figures V-2.1 and V-2.2. The syngas conversions

Table V-2.1 Fixed Bed and Stirred Tank Slurry Reactor Tests of Catalysts under Task 5

Test Code	Catalyst Composition / Catalyst Code	Test purpose
FA-1605	100 Fe/3 Cu/4 K/16 SiO ₂ S3416-4	Baseline catalyst
FB-1895	100 Fe/3 Cu/4 K/16 SiO ₂ S3416-4-K	Effect of potassium source Fixed bed test
FA-1525	100 Fe/3 Cu/4 K/2 Ca/16 SiO ₂ S3416-3-2Ca	Effect of CaO promoter Fixed bed test
FB-1515	100 Fe/3 Cu/4 K/6 Ca/16 SiO ₂ S3416-3-6Ca	Effect of CaO promoter Fixed bed test
FB-1715	100 Fe/5 Cu/6 K/24 SiO ₂ S5624-3	Baseline catalyst Fixed bed test
FB-1795	100 Fe/5 Cu/6 K/24 SiO ₂ S5624-5-K	Effect of potassium source Fixed bed test
FB-1425	100 Fe/5 Cu/6 K/2 Ca/24 SiO ₂ S5624-3-2Ca	Effect of CaO promoter Fixed bed test
FA-1705	100 Fe/5 Cu/6 K/6 Ca/24 SiO ₂ S5624-3-6Ca	Effect of CaO promoter Fixed bed test
SB-3115	100 Fe/3 Cu/4 K/2 Ca/16 SiO ₂ S3416-3-2Ca	Effect of CaO promoter Slurry reactor test
SA-2405	100 Fe/5 Cu/6 K/2 Ca/24 SiO ₂ S5624-3-2Ca	Effect of CaO promoter Slurry reactor test
SA-3115	100 Fe/5 Cu/6 K/24 SiO ₂ S5624-5-K	Effect of CaO promoter Slurry reactor test

Figure V-2.1 Effect of source of potassium and CaO promoter on (a) synthesis gas conversion and (b) H₂/CO usage ratio in fixed bed reactor tests with catalysts containing 16 parts of SiO₂ per 100 parts of Fe.

decreased with increase in CaO promotion. The activity of the catalyst with lower amount of CaO promoter (run FA-1525 with the 100 Fe/3 Cu/4 K/2 Ca/16 SiO₂ catalyst) was similar to that of the baseline catalyst (run FA-1605), whereas the activity (syngas conversion) of the catalyst containing 6 pbw of Ca per 100 pbw of Fe (FB-1515) was markedly lower (Figure V-2.1a). This may be due to significantly lower surface area of the latter catalyst in comparison to the other catalysts (Table V-1.1). The syngas conversion in run FB-1895 (Catalyst C prepared using K₂SiO₃ as the source of potassium) was about 80 %. By comparison, the baseline catalyst C synthesized using KHCO₃ as the source of potassium (FA-1605) was less active (syngas conversion of about 72 %). Usage ratios in all four tests were similar (about 0.6), indicating similar water-gas-shift activities (Figure V-2.1b).

Methane (Figure V-2.2a) and gaseous (C₂ - C₄) hydrocarbon selectivities (Figure V-2.2b) were slightly higher on the CaO promoted catalysts, than on the baseline catalyst. Methane selectivity in run FB-1895 was between 6 and 7 mol%, and gaseous (C₂ - C₄) hydrocarbon selectivity was between 20 and 22 mol%. The baseline catalyst C had lower methane selectivity (5.1 - 5.9 mol%), and its (C₂ - C₄) hydrocarbon selectivity (21 - 24 mol%) was slightly higher than that obtained in run FB-1895.

Performance of catalysts having 24 pbw of SiO₂ per 100 pbw of Fe and containing either CaO promoter (runs FB-1425 and FA-1705), or being prepared using K₂SiO₃ as the source of potassium (FA-1795) is compared with that of the baseline catalyst (catalyst B from batch 3; run FB-1715) in Figures V-2.3 and V-2.4. As in the case of tests with catalysts containing 16 parts by weight (pbw) of SiO₂ per 100 pbw of Fe, the syngas conversions decreased with increase in CaO promotion. The activity of the catalyst with lower amount of CaO promoter (run FB-1425 with the 100 Fe/5 Cu/5 K/2 Ca/24 SiO₂ catalyst), and of the catalyst B prepared using K₂SiO₃ as the source of potassium (FA-1795) was similar to that of the baseline catalyst B from batch 3 (FB-1715), whereas the activity (syngas conversion) of the 100 Fe/5 Cu/6 K/6 Ca/24 SiO₂ catalyst (run FA-1705) was markedly lower (Fig. V-2.3a). This may be due to significantly lower surface area of the latter catalyst in comparison to the

Figure V-2.2 Effect of source of potassium and CaO promoter on (a) methane selectivity and (b) (C₂ - C₄) hydrocarbon selectivity in fixed bed reactor tests with catalysts containing 16 parts of SiO₂ per 100 parts of Fe.

Figure V-2.3 Effect of source of potassium and CaO promoter on (a) synthesis gas conversion and (b) H₂/CO usage ratio in fixed bed reactor tests with catalysts containing 24 parts of SiO₂ per 100 parts of Fe.

Figure V-2.4 Effect of source of potassium and CaO-promoter on (a) methane selectivity and (b) (C₂ - C₄) hydrocarbon selectivity in fixed bed reactor tests with catalysts containing 24 parts of SiO₂ per 100 parts of Fe.

other catalysts (Table V-1.1). Usage ratios (Figure V-2.3b) in run FA-1705 were higher than in the other three tests, indicating lower WGS activity.

Methane (Figure V-2.4a) and gaseous ($C_2 - C_4$) hydrocarbon selectivities (Figure V-2.4b) on the CaO promoted catalysts and on the catalyst B prepared using K_2SiO_3 as the source of potassium, were slightly higher than those obtained with the baseline catalyst B.

V-2. 2 Continuous Stirred Tank Reactor Tests of Modified Catalysts B and C

Two catalysts containing 2 pbw of Ca per 100 pbw of Fe (100 Fe/3 Cu/2 Ca/4 K/16 SiO_2 and 100 Fe/5 Cu/5 K/2 Ca/24 SiO_2) were evaluated in a STSR, to determine the impact of CaO promotion on the long term catalyst stability (deactivation). The effect of potassium source on the catalyst performance was also studied in slurry phase reactor test, run SB-3155 with 100 Fe/5 Cu/ 6 K/24 SiO_2 catalyst. For these three tests about 9.5 g of the catalyst was loaded into a slurry reactor with Durasyn 164 oil as a start-up liquid to form 3.3 wt% slurry. Catalysts were reduced with hydrogen, at 0.8 MPa, 7500 cm^3/min , and 250°C for 4 h (catalysts containing 24 parts of SiO_2 per 100 parts of Fe on a mass basis) or 240°C for 2 h (catalysts containing 16 parts of SiO_2 per 100 parts of Fe).

V-2. 2. 1 Effect of CaO Promotion on Performance of Catalyst C

Changes in synthesis gas conversion and apparent reaction rate constant with time on stream in tests of the 100 Fe/3 Cu/2 Ca/4 K/16 SiO_2 catalyst (run SB-3115) and the baseline catalyst C from preparation batch-4 (run SA-1665) are shown in Figure V-2.5. The Fe-Cu- SiO_2 precursors for these two catalysts were from two different batches. The CaO containing catalyst was prepared by impregnation of Fe-Cu- SiO_2 precursor from batch-3 first with calcium acetate followed by impregnation with potassium bicarbonate. However, since the test results from different batches of baseline catalyst C were reproducible (Section IV-2), data from run SA-1665 can be used to evaluate the effect of CaO promotion. Run SA-1665 lasted about 500 h, but only the data from first 400 h are shown here.

Figure V-2.5 Effect of CaO promoter on (a) synthesis gas conversion and (b) apparent reaction rate constant in STSR tests with catalysts containing 16 parts of SiO_2 per 100 parts of Fe.

Figure V-2.5 shows that the CaO containing catalyst tested in run SB-3115 had lower activity, i.e. lower syngas conversion and the apparent reaction rate constant, than the catalyst C in run SA-1665. The CaO containing catalyst started to deactivate around 220 h on stream, whereas the catalyst C in run SA-1665 was fairly stable during 400 h of testing.

Also, the CaO containing catalyst had higher methane (Figure V-2.6a) and C_2-C_4 (Figure V-2.6b) hydrocarbon selectivities during testing at 1.48 MPa. After the pressure was increased to 2.17 MPa (while proportionally increasing the gas space velocity to 2.0 NI/g-cat/h) in run SB-3115, the methane and gaseous hydrocarbons selectivities started to decrease (170 - 220 h), and then remained stable (220 - 350 h). The hydrocarbon selectivity of the CaO containing catalyst depends on the reaction pressure (at constant P/SV ratio), whereas gaseous hydrocarbon selectivity was independent of pressure in run SA-1665 with catalyst C.

Olefin and 2-olefin selectivities for runs SA-1665 and SB-3115 are shown in Figure V-2.7. The addition of CaO promoter resulted in a decrease of the total olefin content and in increase of the 2-olefin content, at the reaction pressure of 1.48 MPa. After the pressure was increased from 1.48 MPa to 2.17 MPa in run SB-3115, the total olefin content increased and 2-olefin content decreased, and olefin selectivities became similar to those obtained in run SA-1665 with the baseline catalyst C.

Hydrocarbon and Carbon Number Product Distributions

Lumped hydrocarbon distribution, activity parameters and product yields obtained in runs SA-1665 and SB-3115 are shown in Table V-2.2. The CaO promoted catalyst produced more lower molecular products than the baseline catalyst C. For example at the reaction pressure of 1.48 MPa the gasoline fraction (C_5-C_{11} hydrocarbons) in run SB-3115 was about 38% of total hydrocarbons, whereas in run SA-1665 it was 12% only. Upon increasing the reaction pressure to 2.17 MPa in run SB-3115 the fractions of gaseous hydrocarbons and gasoline fraction (C_5-C_{11} hydrocarbons) decreased, and the fraction of higher molecular weight hydrocarbons ($C_{12}+$) increased.

Figure V-2.6 Effect of CaO promoter on (a) methane selectivity and (b) (C₂ - C₄) hydrocarbon selectivity in STSR tests with catalysts containing 16 parts of SiO₂ per 100 parts of Fe.

Figure V-2.7 Effect of CaO promoter on (a) olefin content and (b) 2-olefin content as a function of carbon number for catalysts containing 16 parts of SiO₂ per 100 parts of Fe.

Table V-2.2 Performance of the Baseline and CaO Promoted Catalyst C in Slurry Reactor Tests

Test designation	SA-1665		SB-3115	
Catalyst	100 Fe/3 Cu/4 K/16 SiO ₂ (K from KHCO ₃) ^a		100 Fe/3 Cu/4 K/2 Ca/16 SiO ₂ (K from KHCO ₃) ^b	
Test conditions				
Temperature, °C	260	260	260	260
Pressure, MPa	1.48	2.17	1.48	2.17
Space velocity, NI/g-cat/h	1.4	2.0	1.4	2.0
Feed H ₂ /CO ratio	0.67	0.67	0.67	0.67
Time on stream, h	112	361	121	288
CO conversion, %	84.1	80.1	72.2	65.7
(H ₂ +CO) conversion, %	79.0	75.8	68.8	62.9
STY, mmol (H ₂ +CO)/g-cat/h	49	69	43	58
k, mmol/g-Fe/h/MPa ^c	238	222	194	166
(H ₂ /CO) usage ratio	0.57	0.58	0.59	0.60
$K_p = P_{CO_2} \cdot P_{H_2} / P_{CO} \cdot P_{H_2O}$	33	26	31	14
% CO converted to CO ₂	48.9	48.4	48.4	47.4
Hydrocarbon selectivity, wt%				
CH ₄	3.2	3.1	5.4	4.4
C ₂ -C ₄	12.3	13.9	17.5	16.9
C ₅ -C ₁₁	12.0	17.9	37.8	29.3
C ₁₂ -C ₁₈			22.8	18.9
C ₁₂ ⁺	72.5	65.1	43.3	49.4
C ₁ +C ₂	6.6	5.8	9.7	8.9
Yield, g/Nm ³ (H ₂ +CO) Converted				
Hydrocarbons	204	203	198	190
Oxygenates	2.4	5.9	7.6	17.1
Catalyst productivity, g HC/g-cat/h	0.22	0.32	0.19	0.25

^a Iron content of this catalyst (0.597 g-Fe/g-cat)^b Iron content of this catalyst (0.587 g-Fe/g-cat)^c Apparent rate constant for a first order reaction in hydrogen

Carbon number distribution at 121 h on stream in run SB-3115 was fitted with a three parameter model of Huff and Satterfield, and the estimated values of parameters were as follows: $\alpha_1 = 0.71$; $\alpha_2 = 0.90$, and $\beta = 0.90$.

V-2. 2. 2 Effect of CaO Promotion and Potassium Source on Performance of Catalyst B

Activity comparisons between the baseline catalyst B from batch-3 (SB-1295), modified catalyst B containing CaO promoter (precursor from batch-3; run SA-2405) and catalyst B prepared using potassium silicate as the source of potassium promoter (precursor from batch-5; run SA-3155) are made in Figure V-2.8a (in terms of syngas conversions) and Figure V-2.8b (in terms of the apparent reaction rate constant). During the first 120 h on stream, the catalyst B was slightly more active than the CaO containing catalyst (higher apparent rate constant), whereas after that the latter catalyst had higher activity. This is primarily due to the fact that the CaO containing catalyst (SA-2405) maintained its activity better than the catalyst B (SB-1295). The CaO containing catalyst deactivated slowly during testing at 2.17 MPa (240-400 hours on stream). The catalyst B prepared using K_2SiO_3 as potassium source was less active than the baseline catalyst B. The syngas conversions and apparent reaction rate constant in run SA-3155 were lower than those obtained in run SB-1295, whereas the H_2/CO usage ratio was higher indicating lower WGS reaction activity (Table V-2.3).

During testing at 1.48 MPa (200 psig) the baseline catalyst B had either similar (first 30-40 h on stream) or lower methane (Figure V-2.9a), and C_2-C_4 (Figure V-2.9b) hydrocarbon selectivities than the CaO containing catalyst. However, when the pressure was increased to 2.17 MPa (at 237 h on stream) in run SA-2405, methane and gaseous hydrocarbon selectivities started to decrease and at 300 h were similar to those obtained in test SB-1295 (here the system pressure is still 1.48 MPa). The data show that hydrocarbon selectivities of the CaO containing catalyst are dependent upon the reaction pressure, and this was also observed in run SB-3115 with the 100 Fe/3 Cu/2 Ca/4 K/16 SiO_2 catalyst. During the first 100 h on stream, methane and gaseous hydrocarbon selectivities in run SA-3155 (K

Figure V-2.8 Effect of source of potassium and CaO promoter on (a) synthesis gas conversion and (b) apparent reaction rate constant in STSR tests with catalysts containing 24 parts of SiO₂ per 100 parts of Fe.

Figure V-2.9 Effect of source of potassium and CaO promoter on (a) methane selectivity and (b) (C₂ - C₄) hydrocarbon selectivity in STSR tests with catalysts containing 24 parts of SiO₂ per 100 parts of Fe (for the description of symbols see Figure V-2.8).

from K_2SiO_3) were significantly lower than in run SB-1295, but these differences in selectivity diminished with time and gaseous hydrocarbon selectivities in the two tests were similar after 140 h (Figure V-2.9). Gaseous hydrocarbon selectivities in run SA-3155 were not affected by reaction pressure (i.e. they were nearly the same during operation at 1.48 MPa and 2.17 MPa).

Olefin and 2-olefin selectivities obtained in runs SB-1295, SA-2405 and SA-3155 are shown in Figure V-2.10. As can be seen from this Figure, the addition of CaO promoter resulted in a decrease of the total olefin content and in an increase of the 2-olefin content during operation at reaction pressure of 1.48 MPa. The total olefin and 2-olefin contents in run SA-2405 during operation at 2.17 MPa were very similar to those in run SB-1295 at 1.48 MPa. The same type of behavior was also observed in run SB-3115 with the 100 Fe/3 Cu/2 Ca/4 K/16 SiO_2 catalyst. Olefin selectivities in run SA-3155 with catalyst B (K from K_2SiO_3) were essentially the same as those obtained in run SB-1295 with the baseline catalyst B (K from $KHCO_3$).

Hydrocarbon and Carbon Number Product Distributions

A typical carbon number distribution obtained in tests SB-1295 and SA-3155 with catalyst B is shown in Figure IV-2.11. Positive deviations from ASF distribution are noted in run SB-1295 for C_{10} - C_{22} carbon number range, but were virtually absent in run SA-3155. Experimental data from both tests were fitted with a three parameter model of Huff and Satterfield, and the estimated values of parameters were as follows: $\alpha_1 = 0.68$; $\alpha_2 = 0.91$; and $\beta = 0.74$.

Lumped hydrocarbon distribution, activity parameters and product yields obtained in runs SB-1295, SA-2405 and SA-3155 are shown in Table V-2.3. The catalyst activity, productivity, and hydrocarbon selectivities in run SA-2405 with the 100 Fe/5 Cu/5 K/2 Ca/24 SiO_2 catalyst at 2.17 MPa (300 psig) were very good. The highest oxygenates yield was obtained in run SA-3155 (8-9 g/Nm³ (H_2 +CO) converted).

Figure V-2.10 Effect of source of potassium and CaO promoter on (a) olefin content and (b) 2-olefin content as a function of carbon number for catalysts containing 24 parts of SiO₂ per 100 parts of Fe.

Figure V-2.11 Effect of source of potassium on carbon number product distribution in STSR tests of catalyst B.

Table V-2.3 Performance of the Baseline and Modified Catalyst B in Slurry Reactor Tests

Test designation Catalyst	SB-1295 100 Fe/5 Cu/6 K/24 SiO ₂ (K from KHCO ₃) ^a		SA-2405 100 Fe/5 Cu/6 K/2 Ca/24 SiO ₂ (K from KHCO ₃) ^b		SA-3155 100 Fe/5 Cu/6 K/24 SiO ₂ (K from K ₂ SiO ₃) ^a	
Test conditions						
Temperature, °C	260	260	260	260	260	260
Pressure, MPa	1.48	1.48	1.48	2.17	1.48	2.17
Space velocity, NI/g-cat/h	1.8	1.6	1.8	2.6	1.8	1.8
Feed H ₂ /CO ratio	0.67	0.67	0.67	0.67	0.67	0.67
Time on stream, h	122	338	192	455	192	383
CO conversion, %	74.3	70.3	72.8	66.3	63.1	65.0
(H ₂ +CO) conversion, %	69.6	66.6	69.1	64.1	61.1	64.1
STY, mmol (H ₂ +CO)/g-cat/h	57	47	55	75	49	51
k, mmol/g-Fe/h/MPa ^c	259	208	266	240	220	167
(H ₂ /CO) usage ratio	0.56	0.57	0.58	0.61	0.61	0.64
K _p = P _{CO2} ·P _{H2} /P _{CO} ·P _{H2O}	39	31.5	27	10	6	9
% CO converted to CO ₂	48.9	49.1	49.1	48.3	46.6	45.9
Hydrocarbon selectivity, wt%						
CH ₄	4.4	4.5	6.5	3.7	5.2	5.0
C ₂ -C ₄	15.6	16.1	21.3	15.8	17.6	18.3
C ₅ -C ₁₁	21.8	18.8	28.6	20.9	27.2	26.8
C ₁₂ -C ₁₈	18.4					14.8
C ₁₂ ⁺	58.2	60.6	43.6	59.6	50.0	50.0
C ₁ +C ₂	8.3	8.9	11.8	7.8	10.5	9.3
Yield, g/Nm ³ (H ₂ +CO) Converted						
Hydrocarbons	205	199	195	197	199	189
Oxygenates	6.9	6.5	5.1	5.1	8.9	8.1
Catalyst productivity, g HC/g-cat/h	0.26	0.21	0.24	0.33	0.22	0.22

^a Iron content of this catalyst (0.554 g-Fe/g-cat)^b Iron content of this catalyst (0.549 g-Fe/g-cat)^c Apparent rate constant for a first order reaction in hydrogen

Concluding Remarks on the Effect of CaO Promotion and Source of Potassium

Four catalysts containing CaO promoter with nominal compositions 100 Fe/3 Cu/4 K/x Ca/16 SiO₂ and 100 Fe/5 Cu/5 K/x Ca/24 SiO₂, where x = 2 or 6, were synthesized and tested in fixed bed reactors. The major findings from these tests are that the addition of small amounts of CaO promoter (x = 2) results in the catalyst performance (activity and gaseous hydrocarbon selectivity) similar to that of the baseline catalysts B and C, whereas the addition of a larger amount of CaO (x = 6) results in markedly lower catalyst activity in comparison to the baseline catalysts. Selectivity of the two catalysts with x = 6, is similar to that of the corresponding baseline catalysts. On the basis of these results it was decided to evaluate two catalysts with x = 2 in stirred tank slurry reactors.

The 100 Fe/5 Cu/5 K/2 Ca/24 SiO₂ catalyst was tested in run SA-2405, and its performance was compared to that of the baseline catalyst B in run SB-1295, whereas results from run SB-3115 with the 100 Fe/3 Cu/4 K/2 Ca/16 SiO₂ catalyst were compared with results obtained with the catalyst C in run SA-1665. General trends in tests with the CaO containing catalysts showed some similarities, as well as differences. For example activity of the 100 Fe/5 Cu/5 K/2 Ca/24 SiO₂ catalyst (run SA-2405) was nearly the same as that of the baseline catalyst B (run SB-1295) but its stability with time (deactivation rate) was better, whereas the 100 Fe/3 Cu/4 K/2 Ca/16 SiO₂ catalyst (run SB-3115) was less active (about 15%) than the baseline catalyst C (run SA-1665) and its deactivation rate was higher. At reaction pressure of 1.48 MPa, selectivity of gaseous hydrocarbons on CaO containing catalysts was higher than that of the corresponding baseline catalysts. However, at reaction pressure of 2.17 MPa the gaseous hydrocarbon selectivity decreased on the CaO containing catalysts, and was nearly the same as that of the baseline catalysts at 1.48 MPa. It appears that the selectivity of the CaO promoted catalysts improves at higher reaction pressures, whereas the selectivity of the catalyst C is essentially independent of reaction pressure (at a constant P/SV ratio to maintain a constant value of the gas residence time at different pressures). The addition of CaO promoter did not result in improved performance of the

baseline catalysts, but the CaO promoted catalysts may be suitable for operation at higher reaction pressures. Finally, it is possible that the performance of CaO promoted catalysts may be improved with the use of different pretreatment procedures, but this has not been investigated in the present study.

Some differences in catalyst performance were observed in fixed bed tests of catalysts B (runs FA-1725 and FB-1715) and C (runs FA-1605 and FB-1985) prepared by different methods. In both cases, the activity and methane selectivity of catalysts prepared using potassium silicate as the source of potassium promoter were higher than those of the corresponding baseline catalysts prepared by incipient wetness impregnation using KHCO_3 as the source of potassium promoter. On the other hand, in two slurry reactor tests of catalyst B (SB-1295 - K from KHCO_3 , and SA-3155 - K from K_2SiO_3) it was found that the activity of the catalyst prepared from K_2SiO_3 is about 15 % lower than that of the catalyst prepared by KHCO_3 impregnation, whereas gaseous hydrocarbon selectivities were similar after about 140 h on stream.

On the basis of these results we conclude that the baseline procedure utilizing impregnation of Fe-Cu-SiO₂ precursor with the aqueous solution of KHCO_3 is the preferred method of catalyst preparation. The second procedure, which avoids the impregnation step, provides satisfactory results, and may be used as an alternative.

V-3 References

- Anderson, R. B., 1956, Catalysts for the Fischer-Tropsch Synthesis In *Catalysis*; Emmett, P. H. Ed.; Van Nostrand-Reinhold: New York., Vol. IV, pp. 29-255.

VI Pretreatment Effect Research

Studies at PETC (Pennline et al., 1987; Zarochak and McDonald, 1986, 1987) and in our laboratory with several precipitated iron catalysts (Bukur et al., 1989; 1995a-d; 1996) have shown that pretreatment procedure may have a marked effect on subsequent catalyst performance during Fischer-Tropsch synthesis in fixed bed and slurry bed reactors. Pretreatment conditions (nature of reductant, temperature, duration and gas flow rate) can be used to alter catalyst activity, hydrocarbon products selectivities and/or to provide a long term stability. The knowledge acquired during these studies was utilized to select the baseline pretreatment conditions in the STSR tests of catalysts B and C. However, the pretreatment conditions chosen were not necessarily the optimal ones. Further improvements in the catalyst performance could be potentially achieved through the use of a better pretreatment procedure.

The effect of different pretreatment procedures on the performance of catalyst C (100 Fe/3 Cu/4 K/16 SiO₂, batch-4) was studied in a STSR, and results from these tests are described in Section VI-2. In addition to STSR tests, the reduction behavior of catalysts B (100 Fe/5 Cu/6 K/24 SiO₂, batch-3) and C was studied by thermogravimetric analysis (TGA). Iron phases in the pretreated catalysts and catalysts withdrawn from slurry reactor tests were determined by XRD and Mössbauer effect spectroscopy (Section VI-1)

VI-1 Catalyst Characterization Studies

In order to simulate the actual pretreatment conditions followed in Fischer-Tropsch synthesis, isothermal reduction/or pretreatment experiments were conducted with catalysts B, C and Ruhrchemie (100 Fe/5 Cu/4.2 K/25 SiO₂). After each isothermal pretreatment the catalysts were passivated (see Appendix 2) and characterized by XRD, and in some cases their surface areas were determined by single point BET measurements (Micromeritics Pulse Chemisorb 2705 unit). Iron phases in pretreated and used catalysts from slurry reactor tests were determined by XRD and Mössbauer effect spectroscopy (MES).

Surface Areas and XRD Analysis of Pretreated Catalysts

Table VI-1.1 summarizes results from surface area and XRD analysis measurements of pretreated and passivated catalysts C and B. The high surface area ($\sim 290 \text{ m}^2/\text{g}$) of calcined catalysts C or B is reduced to $50\text{--}115 \text{ m}^2/\text{g}$ when they are subjected to different reducing gases such as H_2 , CO or syngas. The loss in surface area is due to the collapse of pore structure during iron oxide reduction to metallic iron or to iron carbides.

Metallic iron ($\alpha\text{-Fe}$) was the only crystalline phase found in hydrogen reduced catalysts B, C and Ruhrchemie (reductions at 240°C to 280°C for 8 h). Catalyst B reduced in hydrogen first at 250°C for 4 h (baseline reduction procedure), and then exposed to syngas at 260°C ($\text{H}_2/\text{CO} = 0.67$) for 4 h, contains $\epsilon\text{'-Fe}_{2.2}\text{C}$. This phase was also found in the catalyst C reduced in hydrogen first at 240°C for 2 h (baseline reduction procedure), and then exposed to syngas at 260°C ($\text{H}_2/\text{CO} = 0.67$) for 6 h. These two pretreatments simulate pretreatment conditions employed in slurry reactors, followed by F-T synthesis at 260°C (baseline reaction temperature in slurry reactor tests). Results show that $\epsilon\text{'-Fe}_{2.2}\text{C}$ phase is formed rapidly under these conditions. On the other hand, when the catalysts B and C are exposed to syngas directly at 260°C (or at 280°C) for 8 h, the χ -carbide ($\chi\text{-Fe}_5\text{C}_2$) phase is formed instead (Table VI-1.1).

After the pretreatment of catalysts B and C with CO or syngas ($\text{H}_2/\text{CO} = 0.67$) at either 260°C or 280°C for 8 hours the $\chi\text{-Fe}_5\text{C}_2$ phase was the only phase detected by XRD.

TGA Measurement Results

In isothermal reductions conducted in the TGA unit, the catalyst sample was purged with helium (40 ml/min) and the temperature was ramped at a rate of 5°C/min from room temperature to a desired pretreatment temperature. Then the helium flow was switched to reductant gas (hydrogen, carbon monoxide or synthesis gas with $\text{H}_2:\text{CO}$ molar ratio of 2:3) and the temperature was maintained constant for a fixed period of time (up to 8 h). The degree

Table VI-1.1 BET Surface Area and XRD Measurement Results of Reduced and Passivated Samples of Catalyst C (100 Fe/3 Cu/4 K/16 SiO₂, batch-4) and Catalyst B (100 Fe/5 Cu/6 K/24 SiO₂, batch-3)*

Catalyst Id	Reduction Conditions	Single-Point BET** Surface Area, m ² /g	Iron Phases found in the Reduced and Passivated Samples			
			α -Fe	Fe ₃ O ₄	ϵ' -Fe ₂₂ C	χ -Fe ₅ C ₂
100 Fe/3 Cu/4 K/16 SiO ₂	H ₂ , 240°C for 8 h	-	+			
100 Fe/3 Cu/4 K/16 SiO ₂	H ₂ , 250°C for 8 h	116	+			
100 Fe/5 Cu/6 K/24 SiO ₂	H ₂ , 250°C for 8 h	109	+			
Ruhrchemie catalyst	H ₂ , 280°C for 8 h	-	+			
100 Fe/3 Cu/4 K/16 SiO ₂	H ₂ , 240°C for 2 h, then syngas, 260°C for 6h	-			+	
100 Fe/5 Cu/6 K/24 SiO ₂	H ₂ , 250°C for 4 h, then in syngas at 260°C for 4 h	-			+	
100 Fe/3 Cu/4 K/16 SiO ₂	syngas, 280°C for 8 h	53				+
100 Fe/5 Cu/6 K/24 SiO ₂	syngas, 280°C for 8 h	83				+
100 Fe/3 Cu/4 K/16 SiO ₂	syngas, 260°C for 8 h	-				+
100 Fe/5 Cu/6 K/24 SiO ₂	syngas, 260°C for 8 h	-				+
100 Fe/3 Cu/4 K/16 SiO ₂	CO, 250°C for 8 h	-				+
100 Fe/5 Cu/6 K/24 SiO ₂	CO, 250°C for 8 h	-				+
100 Fe/3 Cu/4 K/16 SiO ₂	CO, 280°C for 8 h	-				+
100 Fe/5 Cu/6 K/24 SiO ₂	CO, 280°C for 8 h	82				+

* Passivated under controlled conditions at room temperature.

** Degassed the samples at 200°C for 1.5 h prior to the N₂ adsorption measurements.

of reduction was calculated from experimental weight loss vs. time data, and the theoretical weight loss based on the known composition and mass of a sample.

Figure VI-1.1 shows the effect of reduction temperature (240 to 280°C) on the reduction behavior of catalyst C in the TGA unit in pure hydrogen under isothermal conditions. The degree of reduction of catalyst C at 240 and 250°C in hydrogen increased gradually with time and after 8 hours was about 60%. During reduction at 280°C the degree of reduction increased rapidly during the first 100 minutes of hydrogen exposure and then leveled off with further exposure to hydrogen. The degree of reduction was about 65% after the first 100 minutes of reduction period, and about 80% at the end of reduction period (after ~450 minutes in hydrogen). These results show that the reduction of iron catalysts increases with the increase of reduction temperature. Even though these results indicate that the reduction is not complete, the XRD analysis of passivated samples revealed only the presence of metallic iron.

Figure VI-1.2 shows the effect of reduction temperature (250 and 280°C) on the reduction behavior of catalyst B (100 Fe/5 Cu/6 K/24 SiO₂, batch-3) in hydrogen. As expected the final degree of reduction is higher at higher reduction temperature (80% at 280°C vs. 60% at 250°C). From Figures VI-1.1 and VI-1.2 it appears that the reduction behavior of catalysts C and B is similar at both reduction temperatures of 250°C and 280°C. However, the reduction behavior of the Ruhrchemie catalyst at 280°C is similar to that of catalyst B or C reduced at 250°C. Apparently, the catalysts B and C (synthesized in our laboratory) are easier to reduce than the Ruhrchemie catalyst.

Figure VI-1.3 illustrates the effect of temperature (250 and 280°C) on the weight changes of catalyst C during CO pretreatment. Note that the catalyst had lost about 3-4% of initial sample weight during the heating in helium (from room temperature to a reduction temperature) due to removal of adsorbed moisture. The weight loss is rapid during the first 100 minutes of exposure to CO. The resulting weight loss may be due to three different reactions occurring simultaneously on the catalyst surface/or in the bulk. The possible reactions are reduction of iron oxide to metallic iron or magnetite, carbon deposition (via

Figure VI-1.1 Effect of reduction temperature on the reduction behavior of catalyst C (100 Fe/3 Cu/4 K/16 SiO₂, batch-4) in hydrogen under isothermal conditions in TGA apparatus.

Figure VI-1.2 Effect of reduction temperature on the reduction behavior of catalyst B(100 Fe/5 Cu/6 K/24 SiO₂, batch-3) and the Ruhrchemie catalyst in hydrogen under isothermal conditions in TGA apparatus.

Figure VI-1.3 Effect of reduction temperature on the reduction behavior and weight changes of catalyst C (100 Fe/3 Cu/4 K/16 SiO₂, batch-4) in CO under isothermal conditions in TGA apparatus.

Boudoudart reaction: $2 \text{ CO} \rightarrow \text{CO}_2 + \text{CO}$); and carbide formation (i.e. carburization). Theoretical weight loss for the total conversion of iron oxide (Fe_2O_3) to: (a) metallic iron is about 25%; (b) $\chi\text{-Fe}_5\text{C}_2$ is about 20%; and about 3.3% for the formation of magnetite ($\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4$). The observed weight loss (>13%) at 280°C suggests that the reduction and carburization processes are predominant during the first 100 minutes of CO exposure. During the later stages of CO exposure the catalyst weight decreased slowly up to about 200 minutes, and then started to increase with time, which indicates that all three reactions (reduction, carbon deposition and carbide formation) are occurring simultaneously. The observed increase in weight (after ~200 minutes) suggests that the carbon deposition became the dominant reaction, even though the carbide formation and reduction processes were incomplete. The loss of weight during the CO pretreatment at 250°C was more gradual, and it has continued until the end of the reduction period.

Both catalyst B and Ruhrchemie catalyst lost weight rapidly during the initial periods of CO exposure at 280°C (Figure VI-1.4). The weight loss during the first 100 minutes of CO exposure was about 12% for both the catalysts, and the reduction behavior with time was similar with both catalysts. After that, both catalysts started to gain weight slowly with time due to the dominance of carbon deposition reaction. The continued weight loss of catalyst B during the CO pretreatment at 250°C suggests that the reduction of iron oxide and the carbide formation are incomplete (since both reactions are associated with the weight loss).

Changes in weight of catalysts B and C during pretreatments with synthesis gas ($\text{H}_2/\text{CO} = 0.67$) at 260°C and 280°C are shown in Figure VI-1.5. Both catalysts had lost about 3-4% of the initial sample weight during heating in He flow from room temperature to the pretreatment temperature, due to removal of adsorbed moisture. The weight loss (7-13%) was rapid during the first 100 minutes of exposure to the syngas, suggesting that oxide reduction and carburization reactions are predominant and incomplete. During the later stages of syngas exposure the catalyst weight did not change rapidly, which is an indication that all three

Figure VI-1.4 Effect of reduction temperature on the reduction behavior and weight changes of catalyst B (100 Fe/5 Cu/6 K/24 SiO₂, batch-3) and the Ruhrchemie catalyst in CO under isothermal conditions in TGA apparatus.

Figure VI-1.5 Comparison of reduction behavior and weight changes of catalyst C (100 Fe/3 Cu/4 K/16 SiO₂, batch-4) and catalyst B (100 Fe/5 Cu/6 K/24 SiO₂, batch-3) in syngas (H₂/CO = 0.67) under isothermal conditions in TGA apparatus.

reactions (reduction of iron oxides; carbon deposition and carbide formation) were occurring simultaneously. However, a gradual increase in weight was observed in all the cases, and this suggests that carbon deposition became the dominant reaction, even though the carbide formation and iron oxide reduction were incomplete.

Figure VI-1.6 illustrates the weight loss behavior of catalysts B and C exposed first to hydrogen (at 250°C for 4 h - catalyst B; or at 240°C for 2 h - catalyst C), and then to syngas ($H_2/CO = 0.67$) at 260°C. These two pretreatments simulate pretreatment conditions employed in slurry reactors (reduction in hydrogen), followed by F-T synthesis at 260°C. Again, the initial weight loss of about 3%, is due to loss of moisture during heating in helium from room temperature to the reduction temperature. During the reduction in hydrogen, the weight loss was very rapid during the first 20 minutes, and then continued to increase gradually reaching approximately 10% (catalyst C at 120 minutes) and 13% (catalyst B at 240 minutes). Theoretical weight losses for reduction of Fe_2O_3 to Fe_3O_4 , and Fe, are approximately 3.3% and 22%, respectively. Experimental weight losses at the end of hydrogen reduction imply that both catalysts, at this reduction stage, were not completely reduced to metallic iron. Upon the catalysts exposure to syngas, the weight remaining of catalyst B began to increase rapidly (about 2.5% in 100 minutes), and then more slowly, while the catalyst C continued to loose weight initially (about 1% in 100 minutes), but eventually its weight also started to increase slowly with time. The sharp increase in weight remaining of the catalyst B after exposure to syngas suggests that carburization and carbon deposition were the predominant reactions. In the case of catalyst C, reduction of magnetite was the dominant reaction during the first 100 minutes in syngas, whereas the carbide formation and the carbon deposition were dominant reactions afterwards.

Iron Phases in Pretreated and Used Catalyst C from Slurry Reactor Tests

XRD and MES results of pretreated and used catalyst C (batch-4) samples from stirred tank slurry reactor in tests are summarized in Table VI-1.2 and Figures VI-1.7 to VI-1.9.

Figure VI-1.6 Reduction behavior and weight changes of catalysts B and C in TGA unit. Reduction conditions: catalyst B in H₂ at 250°C for 4 h then switched to syngas at 260°C; catalyst C in H₂ at 240°C for 2 h then switched to syngas at 260°C for 6 h.

Iron phases, determined by XRD, after hydrogen reductions at different temperatures and durations are shown in Figure VI-1.7. After the reduction at 240°C for 2 hours (run SB-2145) the catalyst was reduced to magnetite (Fe_3O_4) (Figure VI-1.7A). After the reductions at 250°C for 4 hours (SB-3425), and at 280°C for 8 hours (SA-0376) both magnetite and metallic iron were found in the reduced sample (Figures VI-1.7B and VI-1.7C). MES results in Table VI-1.2 indicate that the extent of reduction increases with increase in the reduction temperature and duration.

Figure VI-1.8 illustrates XRD patterns of catalyst C withdrawn from the reactor immediately after different pretreatments (TOS = 0 h). The catalyst C which was not pretreated (run SB-2486) does not have crystallinity (amorphous XRD pattern). The catalyst pretreated in CO at 280°C for 8 hours (SA-0946) contains χ -carbide (Fe_5C_2) and magnetite, whereas the syngas pretreated catalyst (at 280°C for 8 hours) contains magnetite, ϵ' -carbide ($\text{Fe}_{2.2}\text{C}$) and possibly χ -carbide (SA-1626).

Figures VI-1.9 illustrate the changes of bulk iron phases with time on stream (TOS) with catalyst C (after different pretreatments) from different slurry tests. During F-T synthesis in run SB-2486 both magnetite and ϵ' -carbide were found in samples withdrawn from the reactor between TOS = 51 and 315 hours (Figure VI-1.9a). During this time period the catalyst activity decreased with time-on-stream (Section VI-2 of the report).

During run SB-3425 (hydrogen reduction at 250°C for 4 hours) both magnetite (Fe_3O_4) and ϵ' -carbide ($\text{Fe}_{2.2}\text{C}$) were found in samples withdrawn from the reactor (Figure VI-1.9B, TOS = 111 to 384 h). The MES results of these samples show that the fraction ϵ' - $\text{Fe}_{2.2}\text{C}$ phase increased from 37 to 48%, while the fraction of superparamagnetic iron phase(s) (Spm) decreased from 63 to 41% between 111 and 384 h on stream. At 384 on stream magnetite was also detected by MES analysis. Catalyst activity decreased with time during this test, even though the fraction of iron carbide increased with time.

Table VI-1.2 X-ray Diffraction and MES Results of Pretreated and Used Samples (Catalyst C:100 Fe/3 Cu/4 K/16 SiO₂, batch-4)

Run Number	Pretreatment Conditions	Time on Stream (TOS), h	Phases Identified by Mössbauer	Phases Identified by XRD
SB-2145	H ₂ , 240°C, 2 h	0	69 (Spm), and 31% (Fe ₃ O ₄)	Fe ₃ O ₄
		67	48 (Spm), 24% (Fe ₃ O ₄), 14% (ε'-Fe ₂₂ C) and 14% (Fe ₅ C ₂)	Fe ₃ O ₄ , and ε'-Fe ₂₂ C
		145	63 (Spm) and 37% (ε'-Fe ₂₂ C)	Fe ₃ O ₄ , and ε'-Fe ₂₂ C
		213	65 (Spm) and 35% (ε'-Fe ₂₂ C)	Fe ₃ O ₄ , and ε'-Fe ₂₂ C
		401	55 (Spm) and 45% (ε'-Fe ₂₂ C)	Fe ₃ O ₄ , and ε'-Fe ₂₂ C
		402 (EOR)	54 (Spm), 3% (Fe ₃ O ₄), 39% (ε'-Fe ₂₂ C) and 4% (Fe ₅ C ₂)	Fe ₃ O ₄ , and ε'-Fe ₂₂ C
SB-3425	H ₂ , 250°C, 4 h	0	76%(Spm) and 22% (α-Fe)	Fe ₃ O ₄ and α-Fe
		111	63% (Spm) and 37% (ε'-Fe ₂₂ C)	Fe ₃ O ₄ , and ε'-Fe ₂₂ C
		233	52% (Spm) and 48% (ε'-Fe ₂₂ C)	Fe ₃ O ₄ , and ε'-Fe ₂₂ C
		330	53% (Spm) and 47% (ε'-Fe ₂₂ C)	Fe ₃ O ₄ , and ε'-Fe ₂₂ C
		384	41% (Spm), 11% (Fe ₃ O ₄) and 48% (ε'-Fe ₂₂ C)	Fe ₃ O ₄ , and ε'-Fe ₂₂ C
SA-0376	H ₂ , 280°C, 8 h	0	69%(Spm) and 31% (α-Fe)	Fe ₃ O ₄ and α-Fe
		134	48% (Spm), 42% (ε'-Fe ₂₂ C) and 10% (Fe ₅ C ₂)	ε'-Fe ₂₂ C
		230	54% (Spm), 25% (ε'-Fe ₂₂ C) and 21% (Fe ₅ C ₂)	Fe ₃ O ₄ , and ε'-Fe ₂₂ C
		350	34% (Spm), 7% (Fe ₃ O ₄), 50% (ε'-Fe ₂₂ C) and 9% (Fe ₅ C ₂)	Fe ₃ O ₄ , and ε'-Fe ₂₂ C
SB-2486	No Pretreatment	0		-
		51		Fe ₃ O ₄ , and ε'-Fe ₂₂ C
		100		Fe ₃ O ₄ , and ε'-Fe ₂₂ C
		147		Fe ₃ O ₄ , and ε'-Fe ₂₂ C
		260		Fe ₃ O ₄ , and ε'-Fe ₂₂ C
		315		Fe ₃ O ₄ , and ε'-Fe ₂₂ C
SA-0946	CO, 280°C, 8 h	0	58% (Spm) and 42% (Fe ₅ C ₂)	Fe ₃ O ₄ , and Fe ₅ C ₂
		113	54% (Spm) and 46% (Fe ₅ C ₂)	Fe ₃ O ₄ , and Fe ₅ C ₂
		229	55% (Spm) and 45% (Fe ₅ C ₂)	Fe ₃ O ₄ , and Fe ₅ C ₂
		354	45% (Spm) and 55% (Fe ₅ C ₂)	Fe ₃ O ₄ , and Fe ₅ C ₂
		427	41% (Spm) and 59% (Fe ₅ C ₂)	Fe ₃ O ₄ , and Fe ₅ C ₂
		563	37% (Spm), 24% (Fe ₃ O ₄), 27% (ε'-Fe ₂₂ C) and 12% (Fe ₅ C ₂)	Fe ₃ O ₄ , and Fe ₅ C ₂
SA-1626	H ₂ /CO, 280°C, 8 h	0		Fe ₃ O ₄ , and ε'-Fe ₂₂ C
		137		Fe ₃ O ₄ , and ε'-Fe ₂₂ C
		258		Fe ₃ O ₄ , and ε'-Fe ₂₂ C
		403		Fe ₃ O ₄ , and ε'-Fe ₂₂ C

EOR stands for end of the run sample which was exposed to air; TOS = 0 h means reduced sample.

FTS process conditions for the slurry tests with catalyst C (100 Fe/3 Cu/4 K/16 SiO₂, batch-4) were: T = 260°C, P = 1.48 - 2.17 MPa,

H₂/CO = 0.67, SV = 1.4 - 2.6 NL/g-cat/h.

Figure VI-1.7 XRD patterns of catalyst C (100 Fe/3 Cu/4 K/16 SiO₂, batch-4) after pretreatment with hydrogen at different conditions in a slurry reactor.

Figure VI-1.8 XRD patterns of catalyst C (100 Fe/3 Cu/4 K/16 SiO₂, batch-4) after different pretreatments in a slurry reactor.

Figure VI-1.9a Changes in bulk iron phases with time on stream in a slurry reactor (catalyst C, run SB-2486, No pretreatment).

Figure VI-1.9b Changes in bulk iron phases with time on stream in a slurry reactor (catalyst C, run SB-3425, reduced in H_2 , at 250°C for 4 h).

Similar results were obtained in two other tests with hydrogen reduced catalysts (runs SB-3425 and SA-0376). In both of these two tests magnetite and ϵ' -carbide were identified by XRD analysis, whereas MES analysis revealed the presence of ϵ' -carbide in both tests, but magnetite was detected only in the samples withdrawn from the reactor near the end of the test (Table VI-1.2). In run SA-0376, a fraction of iron was in the form of χ -carbide (9-21%). In both tests the catalyst deactivated with time, whereas the fraction of iron carbide(s) present remained essentially constant.

Figure VI-1.10 illustrates changes in bulk iron phases with time-on-stream during run SA-0946 (CO pretreatment at 280°C for 8 h) and run SA-1626 (syngas pretreatment at 280°C for 8 h). During F-T synthesis in run SA-0946 both χ -carbide and, to a smaller extent, magnetite were identified by XRD (TOS = 113 to 563 h). MES analysis of these samples showed the increase in the fraction of χ -carbide from 46% at 134 h to 59% at 427 h, during which time period the catalyst activity was stable (Section VI-2). However, near the end of the run (TOS = 563) the fraction of magnetite was 24%, and the fraction of iron carbides (χ -carbide and ϵ' -carbide) was only 39%. Catalyst deactivated during the last 120 h on stream, upon exposure of the catalyst to CO rich syngas ($H_2/CO = 0.6$).

During run SA-1626 (Figure VI-1.10b) both magnetite and iron carbides were found in used catalyst samples (TOS = 127-403 hours), and the catalyst deactivated slowly with time.

Figure VI-1.10a Changes in bulk iron phases with time on stream in a slurry reactor (catalyst C, run SA-0946, reduced in CO, at 280°C for 8 h).

Figure VI-1.10b Changes in bulk iron phases with time on stream in a slurry reactor (catalyst C, run SA-1626, reduced in syngas, at 280°C for 8 h).

VI-2 Reaction Studies - Pretreatment Effect Research

Seven different pretreatment procedures were employed in stirred tank slurry reactor tests. Test identifications and pretreatment conditions are listed in Table VI-2.1. Tests SB-2145 and SA-1665 were completed under task 4 (Reproducibility of Catalyst Preparation), but selected results from these two tests are included here for comparison purposes. Our standard (baseline) reduction conditions for the catalyst C were used in these two tests (i.e. hydrogen reduction at 240°C for 2 hours). The purpose of run SB-1486 was to check reproducibility of results following the CO pretreatment, i.e. to repeat pretreatment conditions used in test SA-0946, and obtain results on catalysts activity and selectivity under the same process conditions.

Table VI-2.1 Pretreatment Conditions and Test Designations

Catalyst: 100 Fe/3 Cu/4 K/16 SiO₂

Test (ID)	Temp. (°C)	Reductant	Duration (h)	Pressure (MPa)	Flowrate (cm ³ /min)
SA-1665	240	H ₂	2	0.78	7500
SB-2145	240	H ₂	2	0.78	7500
SB-3425	250	H ₂	4	0.78	7500
SA-0376	280	H ₂	8	0.78	950
SA-0946	280	CO	8	0.78	750
SB-1486	280	CO	8	0.78	750
SA-1626	280	H ₂ /CO = 0.67	8	0.78	750
SA-2186	280	CO/He=1/10	8	1.48	5500
SB-2486	No pretreatment				

Catalyst loading and particle size in, all new tests, were similar to those employed in previous tests of catalyst C (i.e. 10-20 g of catalyst <270 mesh in size in Durasyn 164 oil,

✓
slurry concentration between 3.4 and 6.7 wt%). In run SB-2486 (no pretreatment) the slurry was heated in helium at 0.78 MPa to the desired reaction temperature (260°C) over a period of 3.5 h, and then exposed to the synthesis gas at 260°C, 1.48 MPa (200 psig), syngas molar feed ratio of $H_2/CO = 0.67$ and space velocity of 2.3 NI/g-cat/h.

VI-2.1 Hydrogen Reductions

Changes in syngas conversion with time-on-stream and process conditions after hydrogen reductions at different conditions are shown in Figure VI-2.1a. The important observation is that the hydrogen reduced catalyst quickly reaches its steady state activity (within 4-10 h from exposure to synthesis gas). The catalyst was very stable in run SA-1665 (standard reduction procedure) but some deactivation was observed in all other tests.

Catalyst activity, measured in terms of the apparent reaction rate constant, for these four tests is shown in Figure VI-2.1b. The use of apparent rate constant enables one to compare activity of catalysts tested at different reaction pressures, gas space velocities and/or feed compositions, but at a constant reaction temperature. Catalyst reduced at 250°C for 4 h had the highest initial activity (360 mmol/g-Fe/h/MPa), whereas initial activities in runs SA-0376, SB-2145 and SA-1665 were similar (230-260 mmol/g-Fe/h/MPa). The iron phases in reduced catalysts, determined by XRD (see Section VI-1, Figure VI-1.7), were: α -Fe and magnetite (Fe_3O_4), in runs SA-0376 (reduction at 280°C for 8 h) and SB-3425 (reduction at 250°C for 4 h), and magnetite only in run SB-2145 (reduction at 240°C for 2 h). It is important to note that the catalyst reduced to magnetite only (runs SB-2145 and SA-1665) had higher activity than the catalyst which was almost completely reduced to metallic iron (run SA-0376). This demonstrates that the use of more severe reduction conditions does not necessarily result in higher activity. Previous studies in our laboratory with iron based catalysts without silicon oxide (Bukur et al. 1989; 1995a), have shown that the use of more severe reduction conditions may result in low catalyst activity. Catalyst activity in run SA-1665 was nearly constant up to 400 h on stream, whereas catalysts in runs SB-3425 and SA-0376 started to deactivate after about 100 h and 260 h on stream, respectively.

Figure VI-2.1 Synthesis gas conversion (a) and apparent reaction rate constant (b) as a function of time for STSR tests of catalyst C reduced with hydrogen at different temperatures.

Methane and C_1+C_2 gaseous hydrocarbon selectivities in run SA-0376 were similar to those obtained in run SB-3425 (Figure VI-2.2), and slightly higher than those in runs SA-1665 and SB-2145 (standard reduction procedure). This is consistent with results obtained previously in our laboratory, with other iron Fischer-Tropsch catalysts (Bukur et al. 1989; 1995a), which showed that the use of more severe reduction conditions often results in higher gaseous hydrocarbon selectivities.

Total olefin and 2-olefin contents were not affected by differences in reduction conditions employed (Figure VI-2.3). Total olefin content in all three tests decreased from about 85% at C_3 to about 55% at C_{15} , whereas the 2-olefin content increased with increase in carbon number, e.g. it is about 5% for C_4-C_8 hydrocarbons and about 30% at C_{15} .

Lumped hydrocarbon product distributions and product yields obtained in four tests in which hydrogen reductions were employed are summarized in Table VI-2.2, together with results from Mobil's and Rheinpreussen's bubble column slurry reactor tests of precipitated Fe-Cu-K catalysts. Hydrocarbon product distribution in run SA-1665 was similar to that obtained in Mobil's run CT-256-13 (Kuo, 1985). Catalyst productivity (expressed as gHC/g-Fe/h) in this test at reaction pressure of 1.48 MPa was similar to that obtained in Mobil's run, but it was significantly higher during testing at 2.17 MPa. In the other three tests the average molecular weight of hydrocarbon products produced was lower than that in run SA-1665. Catalyst productivity was either higher (run SB-3425) or lower (runs SB-2145 and SA-0376) than that obtained in run SA-1665. Yield of oxygenates was relatively low in all four tests, except in run SA-0376 at 324 hours on stream (testing at 2.17 MPa).

VI-2.2 Effect of Reductant Type

In comparison to hydrogen reductions, the time needed to reach a steady state activity was longer when other reductants were used, i.e. about 20 h for the syngas pretreated (SA-1626) or unreduced catalyst (SB-2486), and about 80 h for the CO pretreated catalyst (run SA-0946). Since the process conditions, including the gas space velocity, were the same in runs SB-2486, SA-1626, and SA-0946, the values of syngas conversion can be used as a measure

Figure VI-2.2 Methane selectivity (a) and (C₁+C₂) hydrocarbon selectivity (b) as a function of time for time for STSR tests of catalyst C reduced with hydrogen at different temperatures.

Figure VI-2.3 Olefin content (a) and 2-olefin content (b) dependence on carbon number for catalyst C reduced with hydrogen at different temperatures.

Table VI-2.2 Effect of Pretreatment Procedure on Catalyst Performance in Slurry Reactor Tests

Run ID Pretreatment	SA-1665 H ₂ , 240°C		SB-2145 H ₂ , 240°C	SB-3425 H ₂ , 250°C	SA-0376 H ₂ , 280°C		Mobil ^a CT-256-13 Kuo (1985)	Rheinpreussen ^a Kölbel et al. (1955)
Test conditions								
Temperature, °C	260	260	260	260	260	260	257	268
Pressure, MPa	1.48	2.17	1.48	1.48	1.48	2.17	1.48	1.20
Space velocity, NI/g-Fe/h	2.3	3.4	2.4	3.0	2.3	3.4	2.3	3.1
Feed H ₂ /CO ratio	0.67	0.67	0.67	0.67	0.67	0.67	0.73	0.67
Time on stream, h	220	361	310	264	156	324	475	
CO conversion, %	83.6	80.1	69.1	76.9	81.0	74.3	90	91
(H ₂ +CO) conversion, %	78.5	75.8	64.4	71.9	75.9	69.5	82	89
(H ₂ /CO) usage ratio	0.56	0.58	0.55	0.56	0.56	0.56	0.59	0.63
Hydrocarbon selectivities, wt%								
CH ₄	3.2	3.0	4.1	4.4	4.9	4.8	2.7	3.2 ^b
C ₂ -C ₄	12.2	13.7	15.0	15.5	16.8	18.3	11.1	31.3
C ₅ -C ₁₁	12.8	12.7	20.9	20.4	18.8	26.5	18.1	53.6
C ₁₂ +	71.9	70.5	60.0	59.7	59.5	50.4	68.1	11.9
C ₁ +C ₂	6.6	6.8	8.3	8.2	9.5	9.6	5.6	6.8
Yields								
Nm ³ /kg-Fe/h	1.8	2.6	1.5	2.2	1.7	2.4	1.9	2.8
g HC/Nm ³ (H ₂ +CO)	205	205	194	196	192	187	206	178
g C ₃ +/Nm ³ (H ₂ +CO)	191	191	178	179	174	169	195	166
g Oxy/Nm ³ (H ₂ +CO)	2.8	3.1	10.7	9.6	6.2	18.2		
g HC/g-Fe/h	0.38	0.53	0.29	0.43	0.34	0.44	0.39	0.49

^a Slurry bubble column reactor test.^b CH₄ + C₂H₆

of relative catalyst F-T activity (Figure VI-2.4a). Initial activity of the unreduced catalyst (SB-2486) was the lowest, but at approximately 20 h on stream it was the same as that of the CO pretreated catalyst (SA-0946). After 20 h on stream the conversion (activity) of unreduced catalyst started to decline, whereas that of the CO pretreated catalyst continued to increase up to 80 h, and then became stable at about 76%. Initially, the conversion of the syngas pretreated catalyst was higher than that of the unreduced and the CO pretreated catalyst, and it reached its steady state value of ~70% at about 20 h. The steady state activity of the syngas pretreated catalyst was lower than that of the CO pretreated catalyst. Although, the syngas conversion of the hydrogen reduced catalyst (SB-2145) up to 80 h on stream was higher than those obtained in the other tests, this does not imply the highest catalyst activity, since the gas space velocity in run SB-2145 (1.4 NI/g-cat/h) was significantly lower than in the other three tests (2.3 NI/g-cat/h).

Activity comparison, in terms of the apparent reaction rate constant for first order reaction in hydrogen, is given in Figure VI-2.4b. Initially, the CO and syngas activated catalysts had the highest activity ($k = 280 \text{ mmol/g-Fe/h/MPa}$), whereas the catalyst reduced with hydrogen at 280°C for 8 h and the catalyst which was not pretreated were the least active ($k = 240 \text{ mmol/g-Fe/h/MPa}$). Activity of the CO and syngas catalysts increased with time during the first 100 h on stream, whereas the activity in run SA-0376 remained fairly stable and the activity in run SB-2486 started to decline after passing through a maximum at about 50 h (this follows the same trend as the syngas conversion in Figure VI-2.4a). Catalyst activity in run SA-0946 remained high and stable up to 400 h on stream (at different gas space velocity and/or reaction pressure), whereas the catalysts in the other three tests deactivated with time on stream.

Methane and C_1+C_2 selectivities (Figure VI-2.5) of hydrogen reduced and unpretreated catalyst increased during the first 100 h of synthesis and then became stable, whereas methane selectivities of the syngas and CO activated catalysts exhibited the opposite trend, i.e. they decreased with time. Initially (during the first 20 h on stream) methane selectivities increased

Figure VI-2.4 Effect of reductant type on (a) synthesis gas conversion and (b) apparent reaction rate constant in STSR tests with catalyst C.

Figure VI-2.5 Effect of reductant type on (a) methane selectivity and (b) (C₁+C₂) hydrocarbon selectivity in STSR tests with catalyst C.

in the following order: No pretreatment (2 mol%) < hydrogen reduced catalysts (~3 mol%) < CO activated catalyst (3.6-4%) < syngas activated catalyst (5.8 - 6%). After 300 h on stream methane selectivity increased in the following order: CO activated catalyst $\approx$ no pretreatment (~2.5 mol%) < hydrogen reduced catalysts (3.6-3.8 mol%) < syngas activated catalyst (4 mol%). During testing at 2.17 MPa methane selectivity of the CO activated catalyst (SA-0946) was low (2.2 - 2.8 mol%). This is similar to values obtained in run SA-1665 (standard hydrogen reduction at 240°C for 2 hours). However, the activity of the catalyst in run SA-1665 at 400 h on stream was significantly lower than that of the CO pretreated catalyst ($k = 220$ mmol/g-Fe/h/MPa in run SA-1665 vs. $k = 360$ mmol/g-Fe/h/MPa in run SA-0946).

Total olefin and 2-olefin contents obtained during early periods (84-146 hours) in tests after different pretreatments are shown in Figure VI-2.6. Total olefin content was the highest in run SA-0946 (CO pretreatment at 280°C) and the lowest in run SA-0376 (hydrogen reduction at 280°C). Total olefin content in all tests decreased with increase in carbon number (for C_3+ hydrocarbons) and in run SA-0946 the propene content was about 88%, and that of C_{15} hydrocarbons was 70%, whereas in run SA-0376 the total olefin content decreased from 86% to 55% over the same carbon number range (Figure VI-6.6a). Very high olefin content (including 76% ethylene selectivity) was also obtained in run SB-2486 (no pretreatment). The 2-olefin content increased with increase in carbon number in all four tests. The lowest 2-olefin selectivity was obtained in a test with the catalyst which was not pretreated, and the highest 2-olefin selectivity was obtained with the syngas pretreated catalyst (Figure VI-2.6b).

Lumped hydrocarbon product distributions and product yields obtained in tests SA-0946 (CO pretreatment), SA-1626 (syngas pretreatment), SB-2486 (no pretreatment) and SA-2186 (TAMU pretreatment, see section VI-2.3) are summarized in Table VI-2.3, together with results from Mobil's and Rheinpreussen's bubble column slurry reactor tests of precipitated Fe-Cu-K catalysts. Low methane and gaseous hydrocarbon selectivities (C_1+C_2 and C_2-C_4 hydrocarbons) were obtained in runs SA-0946, SA-2186 and SB-2486 at reaction pressures of 1.48 and 2.17 MPa. Catalyst productivity (expressed as gHC/g-Fe/h) at reaction pressure of

Figure VI-2.6 Effect of reductant type on (a) olefin content and (b) 2-olefin content in STSR tests with catalyst C.

Table VI-2.3 Effect of Pretreatment Procedure on Catalyst Performance in Slurry Reactor Tests

Run ID Pretreatment	SA-0946 CO, 280°C		SA-1676 H ₂ /CO, 280°C		SB-2486 no pretr.	SA-2186 TAMU pretr.		Mobil ^a CT-256-13 Kuo (1985)	Rheinpreussen ^a Kölbel et al. (1955)
Test conditions									
Temperature, °C	260	260	260	260	260	260	260	257	268
Pressure, MPa	1.48	2.17	1.48	2.17	1.48	1.48	2.17	1.48	1.20
Space velocity, NL/g-Fe/h	3.0	4.4	3.0	4.4	2.4	3.9	5.8	2.3	3.1
Feed H ₂ /CO ratio	0.67	0.67	0.67	0.67	0.67	0.67	0.67	0.73	0.67
Time on stream, h	216	419	216	396	245	145	314	475	
CO conversion, %	85.0	84.6	76.6	59.4	66.9	81.3	83.6	90	91
(H ₂ +CO) conversion, %	79.9	80.1	72.1	56.3	62.4	76.6	79.0	82	89
(H ₂ /CO) usage ratio	0.57	0.58	0.57	0.58	0.55	0.57	0.57	0.59	0.63
Hydrocarbon selectivities, wt%									
CH ₄	3.6	2.6	4.9	5.1	3.2	3.9	3.0	2.7	3.2 ^b
C ₂ -C ₄	15.5	12.9	15.9	17.5	11.7	15.9	14.1	11.1	31.3
C ₅ -C ₁₁	18.9	19.2	16.7	24.2	19.3	19.7	16.2	18.1	53.6
C ₁₂ ⁺	62.0	65.3	62.6	53.2	65.8	60.6	66.6	68.1	11.9
C ₁ +C ₂	8.1	6.2	9.6	9.9	6.2	8.3	7.0	5.6	6.8
Yields									
Nm ³ /kg-Fe/h	2.4	3.5	2.2	2.5	1.5	3.0	4.5	1.9	2.8
g HC/Nm ³ (H ₂ +CO)	202	202	196	191	197	192	190	206	178
g C ₃ ⁺ /Nm ³ (H ₂ +CO)	186	189	177	172	185	176	177	195	166
g Oxy/Nm ³ (H ₂ +CO)	7.7	7.7	9.4	13.3	11.8	6.4	7.9		
g HC/g-Fe/h	0.49	0.71	0.43	0.47	0.29	0.58	0.86	0.39	0.49

^a Slurry bubble column reactor test.^b CH₄ + C₂H₆

1.48 MPa in runs SA-0946 and SA-2186 was equal to or higher than that obtained in Mobil's and Rheinpreussen's bubble column reactor tests, and was markedly higher in both runs during testing at 2.17 MPa. The highest catalyst productivity, 0.86 g hydrocarbons produced/g-Fe/h, was achieved using the TAMU pretreatment procedure, while maintaining the desired selectivity. This is the best performance to date, in our laboratory or anywhere else, for catalysts developed for high wax production ("high alpha" catalysts). The performance of the CO activated catalyst was also superior relative to other catalysts developed for high wax production : catalyst productivity of 0.71 gHC/g-Fe/h, and hydrocarbon selectivity within the DOE's performance targets (low methane and C₁+C₂ selectivities).

VI-2.3 Run SA-2186 with 100 Fe/3 Cu/4 K/16 SiO₂ Catalyst (Batch-4)

Twelve grams of the catalyst (< 270 mesh in size) was loaded for the test, together with 313 g Durasyn 164 oil as the initial slurry medium. A new pretreatment procedure (referred to as TAMU pretreatment) was employed. Pretreatment conditions were provided in Table VI-2.1.

Following the reduction, the catalyst was tested at 260°C, 1.48 MPa, syngas molar feed ratio of 0.67 (H₂/CO = 0.67) and gas space velocity of 2.3 NI/g-cat/h. Catalyst activity, measured by (H₂+CO) conversion and the apparent reaction rate constant is shown in Figures VI-2.7a and VI-2.7b, respectively. The syngas conversion increased rapidly with time during the first 20 hours of testing and then stabilized at about 76-78%. The usage ratio (not shown) decreased from 0.62 to 0.58 at 20 h and then remained stable at these conditions. The apparent reaction rate constant followed the same trend as the syngas conversion, and was fairly constant between 20 and 200 hours on stream (about 400 mmol/g-Fe/h/MPa). At 209 h on stream, the reaction pressure and gas space velocity were increased to 2.17 MPa and 3.4 NI/g-cat/h (5.8 NI/g-Fe/h). After 20 hours at these conditions, the syngas conversion was about 76%, and then increased with time reaching 83% at about 500 h on stream. The apparent reaction constant also increased with time during testing at 2.17 MPa, and reached 450 mmol/g-Fe/h/MPa at 500 hours.

Figure VI-2.7 Synthesis gas conversion (a) and apparent reaction rate constant (b) as a function of time for STSR test of catalyst C after TAMU pretreatment procedure.

After 20 h on stream, methane selectivity (Figure VI-2.8a) varied between 2.9 and 3.3 mol%, and C₁+C₂ hydrocarbon selectivity was between 6.6 and 7.8 mol% (Figure VI-2.8b). Gaseous hydrocarbon selectivities were gradually decreasing during testing at 2.17 MPa. At 500 h on stream, the methane and C₁+C₂ selectivities were 2.5 and 6.4 mol%, respectively.

The catalyst productivity at 260°C, 2.17 MPa, syngas molar feed ratio of 0.67 (H₂/CO = 0.67) and gas space velocity of 3.4 NI/g-cat/h was 0.86 (g hydrocarbons produced/g-Fe/h). As noted above, this is the highest catalyst productivity obtained in our laboratory, and is significantly higher than that obtained in the two most successful bubble column slurry reactor operations at comparable conversions and low methane selectivities (Mobil's work, and Kölbel's Rheinpreussen demonstration plant unit). Two main reasons for higher catalyst space-time-yield (productivity) obtained in the present study relative to the previous ones are: (1) the use of higher reaction pressure, and (2) higher intrinsic activity of our catalyst.

Concluding Remarks on the Pretreatment Effect Research

A very rapid achievement of steady state activity (Figure VI-2.1) of the hydrogen reduced catalysts (SB-3425, SA-0376 and SB-2145) indicates either that magnetite and α -Fe are active for FTS or that they are rapidly converted to an active carbide phase. However, the conversion of magnetite to zero-valent iron is a slow step in reduction of iron oxide, and it is unlikely that it can occur to an appreciable extent after 2 h of exposure to syngas at 260°C. For example, the unreduced iron requires about 20 h of exposure to reach its steady state activity (SB-2486). Activity of the unreduced catalyst (largely Fe³⁺ iron) is low initially, and it increases during the first 25 h of synthesis, due to formation of magnetite and/or ϵ' -carbide, indicating that one or both of these phases are active for FTS. Activity of the CO reduced catalyst is rather low initially (χ -carbide), and increases gradually with time. This behavior is not consistent with a hypothesis that iron carbide is the active phase for the FTS. If the latter hypothesis was correct, one would expect the initial activity of the partially carbided catalyst to be markedly greater than that of the catalyst in the form of magnetite (run SB-3425). Also, the

Figure VI-2.8 Methane selectivity (a) and (C₁+C₂) hydrocarbon selectivity (b) as a function of time for time for STSR tests of catalyst C after TAMU pretreatment procedure.

catalyst in test SA-0946 had a long induction period, and its activity at ~20 h on stream was similar to that of the unreduced catalyst. Initial activity of the syngas activated catalyst (mixture of iron carbides and magnetite) was high, but it also went through an induction period lasting approximately 25 h. It is possible that the active surface sites of the CO and syngas pretreated catalysts were partially blocked with excess carbon formed during the pretreatment, and that this had caused lower than expected activity. Steady state activities, of catalysts pretreated by CO and syngas were higher than those of the hydrogen and unreduced catalysts. Magnetite was virtually absent in the CO and syngas pretreated catalysts, whereas both hydrogen and unreduced catalyst contained both magnetite and ϵ' -carbide (Section VI-1, Table VI-1.2). These observations are consistent with the hypothesis that both magnetite and iron carbides are active for FTS, and that iron carbides have higher FTS activity than magnetite.

Methane selectivities of the CO and syngas pretreated catalysts decreased with time, whereas those of the hydrogen reduced and unreduced catalysts increased with time (Figures VI-2.2a and VI-2.5a). These data suggest that methane selectivity is low on catalysts containing iron oxides, and is higher on carbided catalysts. A possible reason for markedly higher methane selectivity on carbided catalysts during early periods of synthesis, is that part of methane is produced by reaction between hydrogen and surface carbon formed during the pretreatment.

Significant improvements in the catalyst activity were obtained through the use of different pretreatment procedures. Our standard reduction procedure with the catalyst C (hydrogen reduction at 240°C for 2 hours) resulted in the initial activity, expressed in terms of the apparent reaction rate constant, of about 250 mmol/g-Fe/h/MPa. The activity decreased with time and at about 400 h the apparent rate reached the value of 220 mmol/g-Fe/h/MPa (run SA-1665) or 140 mmol/g-Fe/h (run SB-2145). The initial activity of the catalyst reduced with hydrogen at 250°C for 4 hours (run SB-3425) was about 350 mmol/g-Fe/h/MPa, which represents a 40% increase relative to the standard reduction procedure. However, the catalyst

activity decreased with time and at about 300 h the apparent rate constant was 250 mmol/g-Fe/h/MPa (similar to the value obtained in run SA-1665). ✓

The CO pretreatment (SA-0946), syngas pretreatment (SA-1626) and TAMU pretreatment (SA-2186) also resulted in improved catalyst activity, relative to the standard reduction procedure. The initial values of the apparent reaction rate constant, after these pretreatments, were 300-400 mmol/g-Fe/h/MPa, corresponding to 20-60% increase in activity relative to the standard procedure. Activity of the CO and TAMU pretreated catalysts increased with time, and at 400 hours the values of the apparent reaction rate constants were 360 and 430 mmol/g-Fe/h, respectively. As the result of the improvement in the catalyst activity, while maintaining low methane and gaseous hydrocarbon selectivities, the catalyst productivities in these two tests were markedly higher than those obtained in Mobil's and Rheinpreussen's slurry bubble column reactor tests. The catalyst productivity in Rheinpreussen test was 0.49 gHC/g-Fe/h, and those obtained in runs SA-0946 and SA-2186 were 0.71 and 0.86 gHC/g-Fe/h, respectively (Table VI-2.3). This represents 45-75% improvement in catalyst productivity relative to that achieved in Rheinpreussen's demonstration plant unit, and sets new standards of performance for "high alpha" iron catalysts. We believe that the performance of our catalyst B (100 Fe/5 Cu/6 K/24 SiO₂) can be also improved through the use of better pretreatment procedures.

VI-3 References

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VII Calcination Effect Research

Calcination involves heating the dried powder in the temperature range 300-600°C in various atmospheres, usually air. Several processes occur: sintering, solid state reaction, loss of porosity. In most catalyst systems calcination is beneficial since it establishes the correct "state" of the catalyst that is most responsive to activation.

Very little systematic study of the effect of calcination on precipitated F-T catalysts has appeared (Anderson, 1956, 1984), yet this is a promising area for controlling essential properties. It is known that heat treatment of co-precipitated Fe_2O_3 -CuO samples gives mixed phases, e.g. CuFe_2O_4 , that may result in superior dispersions with reductive activation. Calcination results in sintering and loss of surface area. Calcined catalysts have better attrition properties, which is important for the slurry F-T process. Changes in the pore volume and pore size distribution may have significant effect on intraparticle diffusion and consequently on hydrocarbon product distribution. However, there have been no studies to investigate these effects.

In a related study (Hadjigeorgiou and Richardson, 1986) it was reported that Ni/ThO₂ catalysts, used in the F-T synthesis of light hydrocarbons, showed an activity enhancement of up to a factor of ten when the hydrogel was calcined rapidly on a hot-plate (flash calcined) compared with conventional oven heating. This was attributed to rapid reactions in the gel that led to "decoration" of reduced nickel particles by ThO₂ (Richardson et al., 1989). It is possible that this effect may enhance activity of precipitated 100 Fe/x Cu/y K/z SiO₂ catalysts during calcination. The large-scale analogy to the hot-plate is a "spray-roasting" which may be employed in the catalyst scale-up, if this procedure proves to be effective.

The effect of calcination temperature (300-500°C) and flash calcination on physical properties of catalysts B and C is described in section VII-1, whereas results from F-T synthesis tests in fixed bed and stirred tank slurry reactors are described in section VII-2.

VII-1 Catalyst Characterization Studies

Calcinations at temperatures 300-500°C were done in a downflow fixed bed reactor unit. The air flow rate during calcination was set at approximately 50 cm³/g-cat/min and the catalyst bed temperature was increased to a desired calcination temperature at a rate of 2°C/min. After reaching the final temperature these conditions were maintained for 5 hours. After that the system was allowed to cool down to room temperature with air flowing through the catalyst bed. Calcination at 700°C was done in a high temperature furnace. The furnace was preheated to 700°C first, and the catalyst was spread over a preheated crucible to form a thin layer. During one hour calcination the air flow was fed into the furnace, passing over a thin layer of catalyst. This procedure is referred to as flash calcination.

Calcined catalysts were characterized by BET surface area, pore volume and pore size distributions. The pretreated and used catalysts from slurry and/or fixed bed runs were characterized by XRD and MES.

BET Surface Area and Pore Volume Results

BET surface area and pore volume results of catalysts B (100 Fe/5 Cu/6 K/24 SiO₂, batch-3) and C (100 Fe/3 Cu/4 K/16 SiO₂, batch-4) calcined at different temperatures are summarized in Table VII-1.1. The surface areas of catalyst C and B calcined at 300°C for 5 h (baseline conditions) were about 290 m²/g, and decreased gradually to about 100 m²/g with the increase in calcination temperature from 300 to 700°C. The BET surface areas of both catalysts are similar after calcinations at the same conditions (temperature and duration). The surface area of catalysts B and C, is also affected by the duration of calcination, and it decreases with increase in calcination time (results at 500°C at different durations of calcination).

Table VII-1.1 Effect of Calcination Conditions on the Textural Properties of Catalysts B and C

Catalyst	Calcination Temperature, °C / Duration, h	BET Surface Area, m ² /g		Pore Volume, cm ³ /g
		Single Point	BET Plot	
100 Fe/3 Cu/4 K/16 SiO ₂ S3416-4	300 / 5	310	306	0.45
	400 / 5	263	268	0.42
	500 / 0.5	233	-	-
	500 / 1	231	216	0.4
	500 / 5	183	188	0.36
	700 / 0.5	118	-	-
	700 / 1	108	106	0.30
	300 / 5	258	284	0.51
100 Fe/5 Cu/6 K/24 SiO ₂ S5624-3	400 / 5	271	253	0.48
	500 / 1	227	212	0.46
	500 / 5	219	193	0.43
	700 / 0.5	115	108	0.33
	700 / 1	100	96	0.33

Pore volumes of catalysts C and B (calcined at 300°C) were 0.45 and 0.50 cm³/g, respectively, and the corresponding values after calcination at 700°C were 0.30 and 0.33 cm³/g, respectively. Total pore volume of catalyst B is slightly larger than that of catalyst C at all calcination temperatures. The pore volumes of these two catalysts are also affected to some extent by the duration of calcination. The decrease in surface area and pore volume with increasing calcination temperature is due to sintering.

Pore Size Distributions

Figure VII-1.1 illustrates the pore size distribution of catalysts C and B after calcination at different temperatures ranging from 300 to 700°C. The catalysts exhibit bimodal pore size distributions at all calcination temperatures. The pore size (diameter) varied from about 2 to 20 nm for both catalysts, but the pore size shifted to larger values with increase in calcination temperature. Catalysts calcined at 700°C for 1 hour, had a more narrow pore size distribution, with a large fraction of pores being about 10 nm in diameter.

Iron Phases in Reduced and Used Catalysts

Catalysts B and C calcined at temperatures 300-500°C did not exhibit crystallinity, i.e. they are either amorphous or the crystallites are too small to be detected by XRD. Catalysts B and C calcined at 700°C for 1 h were crystalline, and exhibit the XRD pattern of hematite (α -Fe₂O₃). Results of XRD and MES analysis of reduced and used catalysts from fixed bed and stirred tank slurry reactor tests are summarized in Table VII-1.2.

Used catalysts B and C, calcined at 300-500°C, from fixed bed reactor tests contained only ϵ' -Fe_{2.2}C (samples from both top and bottom portions of the reactor). In two tests with catalysts calcined at 700°C (FA-3495 and FB-0236) magnetite and ϵ' -carbide were identified in samples from the bottom portion of the reactor (oxidizing atmosphere) by both XRD and MES analysis, whereas only ϵ' -carbide was identified in samples from the top portion of the reactor (reducing atmosphere).

Figure VII-1.1a Effect of calcination temperature on the pore size distribution of catalyst C (100 Fe/3 Cu/4 K/16 SiO₂, batch-4).

Figure VII-1.1b Effect of calcination temperature on the pore size distribution of catalyst B (100 Fe/5 Cu/6 K/24 SiO₂, batch-3).

Table VII-1.2

Iron Phases in Catalysts B and C from Fixed Bed and Slurry Reactor Tests

Run Number	Catalyst	Time on Stream (TOS), h	Iron Phases Identified by Mössbauer	Iron Phases Identified by XRD
FA-1605	100 Fe/3 Cu/4 K/16 SiO ₂ (S3416-4, calcined at 300°C, 5 h)	120 top 120 bot	49% (Spm) and 51% (ϵ' -Fe ₂₂ C) 50% (Spm) and 50% (ϵ' -Fe ₂₂ C)	ϵ' -Fe ₂₂ C ϵ' -Fe ₂₂ C
FA-3305	100 Fe/3 Cu/4 K/16 SiO ₂ (S3416-4, calcined at 400°C, 5 h)	120 top 120 bot	55% (Spm) and 45% (ϵ' -Fe ₂₂ C) 52% (Spm) and 48% (ϵ' -Fe ₂₂ C)	ϵ' -Fe ₂₂ C ϵ' -Fe ₂₂ C
FA-3095	100 Fe/3 Cu/4 K/16 SiO ₂ (S3416-4, calcined at 500°C, 5 h)	120 top 120 bot	58% (Spm) and 42% (ϵ' -Fe ₂₂ C) 59% (Spm) and 41% (ϵ' -Fe ₂₂ C)	ϵ' -Fe ₂₂ C ϵ' -Fe ₂₂ C
FA-3495	100 Fe/3 Cu/4 K/16 SiO ₂ (S3416-4, calcined at 700°C, 1 h)	116 top 116 bot	45% (Spm) and 55% (ϵ' -Fe ₂₂ C) 42% (Spm), 18% (Fe ₃ O ₄) and 40% (ϵ' -Fe ₂₂ C)	ϵ' -Fe ₂₂ C Fe ₃ O ₄ and ϵ' -Fe ₂₂ C
SB-0676	100 Fe/3 Cu/4 K/16 SiO ₂ (S3416-4, calcined at 700°C, 1 h)	0 120 221 305	73% (Spm), and 27% (Fe ₃ O ₄) 39% (Spm), 26% (Fe ₃ O ₄) and 35% (ϵ' -Fe ₂₂ C) 26% (Spm), 19% (Fe ₃ O ₄) and 55% (ϵ' -Fe ₂₂ C) 26% (Spm), 22% (Fe ₃ O ₄) and 52% (ϵ' -Fe ₂₂ C)	Fe ₃ O ₄ Fe ₃ O ₄ and ϵ' -Fe ₂₂ C Fe ₃ O ₄ and ϵ' -Fe ₂₂ C Fe ₃ O ₄ and ϵ' -Fe ₂₂ C
FB-1715	100 Fe/5 Cu/6 K/24 SiO ₂ (S5624-3, calcined at 300°C, 5 h)	119	40% (Spm) and 60% (ϵ' -Fe ₂₂ C) 42% (Spm) and 58% (ϵ' -Fe ₂₂ C)	ϵ' -Fe ₂₂ C ϵ' -Fe ₂₂ C
FB-2975	100 Fe/5 Cu/6 K/24 SiO ₂ (S5624-3, calcined at 400°C, 5 h)	142 top 142 bot	54% (Spm) and 46% (ϵ' -Fe ₂₂ C) 53% (Spm) and 47% (ϵ' -Fe ₂₂ C)	ϵ' -Fe ₂₂ C ϵ' -Fe ₂₂ C
FA-2925	100 Fe/5 Cu/6 K/24 SiO ₂ (S5624-3, calcined at 500°C, 5 h)	140 top 140 bot	60% (Spm) and 40% (ϵ' -Fe ₂₂ C) 56% (Spm) and 44% (ϵ' -Fe ₂₂ C)	ϵ' -Fe ₂₂ C ϵ' -Fe ₂₂ C
FB-0236	100 Fe/5 Cu/6 K/24 SiO ₂ (S5624-3, calcined at 700°C, 1 h)	120 top 120 bot	39% (Spm) and 61% (ϵ' -Fe ₂₂ C) 34% (Spm), 9% (Fe ₃ O ₄) and 57% (ϵ' -Fe ₂₂ C)	ϵ' -Fe ₂₂ C Fe ₃ O ₄ and ϵ' -Fe ₂₂ C
SB-1276	100 Fe/5 Cu/6 K/24 SiO ₂ (S5624-3, calcined at 700°C, 1 h)	0 138 239 311 384	59% (Spm), 27% (Fe ₃ O ₄), and 14% (α -Fe) 44% (Spm), 30% (Fe ₃ O ₄) and 26% (ϵ' -Fe ₂₂ C) 39% (Spm), 26% (Fe ₃ O ₄) and 35% (ϵ' -Fe ₂₂ C) 33% (Spm), 24% (Fe ₃ O ₄) and 43% (ϵ' -Fe ₂₂ C) 27% (Spm), 23% (Fe ₃ O ₄) and 50% (ϵ' -Fe ₂₂ C)	Fe ₃ O ₄ and α -Fe Fe ₃ O ₄ and ϵ' -Fe ₂₂ C Fe ₃ O ₄ and ϵ' -Fe ₂₂ C Fe ₃ O ₄ and ϵ' -Fe ₂₂ C Fe ₃ O ₄ and ϵ' -Fe ₂₂ C

TOS = 0 h means reduced sample.

FTS process conditions for slurry tests with catalyst C (100 Fe/3 Cu/4 K/16 SiO₂) were: T = 260°C, P = 1.48 - 2.17 MPa, H₂/CO = 0.67, SV = 1.4 - 1.8 NI/g-cat/h.

FTS process conditions for slurry tests with catalyst B (100 Fe/5 Cu/6 K/24 SiO₂) were: T = 260°C, P = 1.48 - 2.17 MPa, H₂/CO = 0.67, SV = 1.2 - 2.2 NI/g-cat/h.

FTS process conditions for fixed bed tests with catalysts C and B were: T = 250°C, P = 1.48 MPa, H₂/CO = 0.67, SV = 2.0 NI/g-cat/h.

After the reduction at 240°C for 2 h (run SB-0676, TOS = 0 h) catalyst C, calcined at 700°C for 1 h, was not reduced to metallic iron and only magnetite (Fe_3O_4) was identified by both XRD and MES analysis. In samples withdrawn from the slurry reactor at TOS = 120-305 h, both magnetite and pseudo-hexagonal iron carbide ($\epsilon\text{'-Fe}_{2.2}\text{C}$) were found. The catalyst activity in run SB-0676 declined slowly with time on stream (see Figure VII-2.8b).

Figure VII-1.2 illustrates the XRD patterns of catalyst samples withdrawn from slurry test SB-1276 with catalyst B calcined at 700°C for 1 h, and reduced at 250°C in H_2 for 4 h. Magnetite (Fe_3O_4) and metallic iron ($\alpha\text{-Fe}$) were found in the sample withdrawn immediately after the hydrogen reduction (TOS = 0 h) as shown in Figure VII-1.2A. Both magnetite (Fe_3O_4) and pseudo-hexagonal iron carbide ($\epsilon\text{'-Fe}_{2.2}\text{C}$) were found in the samples withdrawn during F-T synthesis (Figure VII-1.2B to VII-1.2E). These results are in qualitative agreement with the MES analysis (Table VII-1.2). From the MES results of used catalyst samples from run SB-1276 it appears that the fraction of iron phase(s) exhibiting superparamagnetic behavior decreases from 44% (at TOS = 138 h) to 27% (at TOS = 384 h), and the fraction of iron in the form of magnetite decreases from 30 to 23% during the same time period. Also, the fraction of pseudo-hexagonal iron carbide increased from 26 to 50% as the time on stream increased from 138 to 384 h (Table VII-1.2). Catalyst activity was continually decreasing with time during run SB-1267 (see Figure VII-2.5b).

Figure VII-1.2 Changes in bulk iron phases with time on stream during run SB-1276 with catalyst B (100 Fe/5 Cu/6 K/24 SiO_2 , batch-3) calcined at 700°C for 1 h and reduced at 250°C in H_2 for 4 h: (A) TOS = 0 h; (B) TOS = 138 h; (C) TOS = 239 h; (D) TOS = 311 h; (E) TOS = 384 h.

VII-2 Reaction Studies

In this section we report results on the effect of calcination temperature on performance of catalysts B (from batch-3) and C (from batch-4) during F-T synthesis. Both catalysts were calcined in air at 400°C, 500°C and 700°C, to study the effect of calcination temperature relative to our standard (baseline) calcination temperature of 300°C for 5 hours.

Six fixed bed tests were completed and results from these tests are compared with those obtained in tests carried out with catalysts calcined at 300°C. Test identification and calcination conditions are listed in Table VII-2.1. Two tests with catalysts B and C calcined at 700°C for 1 h were conducted in a STSR to determine whether the trends found in fixed bed reactor tests remain the same during F-T synthesis in slurry phase. Results from these two tests are compared with tests SA-1665 (catalyst C) and SB-1295 (catalyst B) made with catalysts calcined at 300°C. Slurry tests identifications are also listed in Table VII-2.1.

VII-2.1 Fixed Bed Reactor Tests

About 3 g of the catalyst sized to 30/60 mesh (250-600 μm) was diluted 1:7 (reactor B) or 1:9 (reactor A) by volume with glass beads of the same size range and charged into the reactor. The catalyst was reduced with hydrogen at atmospheric pressure, gas flow rate of 7500 cm^3/min either at 250°C for 4 hours (catalyst B) or at 240°C for 2 hours (catalyst C), and then tested at 250°C, 1.48 MPa (200 psig), 2 NL/g-cat/h using syngas with H_2/CO molar ratio of 0.67. Test durations were 120-140 h, including 30 hour conditioning period to reach the reaction temperature of 250°C.

Table VII-2.1. Calcination Temperatures and Test Designations

Test ID	Catalyst used	Calcination temperature, (°C)
FB-1715	100 Fe/5 Cu/6 K/24 SiO ₂	300
FB-2975		400
FA-2925		500
FB-0236		700
SB-1295		300
SB-1276		700
FA-1605	100 Fe/3 Cu/4 K/16 SiO ₂	300
FA-3095		400
FA-3905		500
FA-3495		700
SA-1665		300
SB-0676		700

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

Fixed Bed Reactor Tests of Catalyst B (100 Fe/5 Cu/6 K/24 SiO₂)

Changes in synthesis gas conversion with time-on-stream are shown in Figure VII-2.1. Before the feed interruption at about 70 h on stream, the catalyst calcined at 400°C (run FA-2975) had the highest conversion (~70%). Upon resumption of this test, the conversion increased gradually with time and approached 60% at 140 hours. The catalyst B calcined at 500°C (run FB-2925) had the same activity and deactivation trends as the catalyst calcined at

Figure VII-2.1 · Synthesis gas conversion as a function of time for fixed bed reactor tests of catalyst B calcined at different temperatures.

300°C (run FB-1715). Initially, conversions in run FB-0236 with the catalyst calcined at 700°C for 1 h were lower than in other tests, which was partly due to fluctuations in reactor temperature. However, after about 80 h on stream, the syngas conversions in this run were similar to those obtained with catalysts calcined at lower temperatures (300 to 500°C). The usage ratios in all four tests were similar (0.58-0.60) and stable with time.

Gaseous hydrocarbon selectivities as a function of time on stream for all four tests are shown in Figure VII-2.2. Catalysts calcined at 400°C (before interruption of the feed flow) and at 700°C produced more methane than the ones calcined at 300°C or 500°C (Figure VII-2.2a). Gaseous hydrocarbon selectivity (C_2 - C_4 hydrocarbons) of the catalyst calcined at 700°C (run FB-0236) was higher than that obtained in other tests (Figure VII-2.2b).

Fixed Bed Reactor Tests of Catalyst C (100 Fe/3 Cu/4 K/16 SiO₂)

As shown in Figure VII-2.3, the initial syngas conversion of the catalysts calcined at 400°C (run FA-3305) and 500°C (run FA-3095), were the same as that of the catalyst calcined at 300°C (run FA-1605). However, the catalysts calcined at 400°C and 500°C deactivated faster than the catalyst calcined at 300°C, and at 100 h on stream the conversions in these two tests were about 8% less than those obtained in run FA-1605. The synthesis gas conversion in run FA-3495 with the catalyst calcined at 700°C was significantly lower than that obtained with catalysts calcined at 300-500°C. The usage ratios in all four tests were about the same, 0.57-0.60 indicating similar WGS activity.

Gaseous hydrocarbon selectivities in all four tests were similar. For example, methane selectivity was generally between 5% and 6%, (Figure VII-2.4a), and C_2 - C_4 selectivities were between 21% and 25% (Figure VII-2.4b).

Figure VII-2.2 Methane selectivity (a) and (C₂-C₄) hydrocarbon selectivity (b) as a function of time for fixed bed reactor tests of catalyst B calcined at different temperatures.

Figure VII-2.3 Synthesis gas conversion as a function of time for fixed bed reactor tests of catalyst C calcined at different temperatures.

Figure VII-2.4 Methane selectivity (a) and (C₂-C₄) hydrocarbon selectivity (b) as a function of time for fixed bed reactor tests of catalyst B calcined at different temperatures.

VII-2. 2 Stirred Tank Slurry Reactor Tests

For slurry reactor tests 14 to 16 g of catalyst B and C (particle size less than 53 μm) calcined at 700°C for one hour was charged to a reactor, and Durasyn 164 oil was used as the initial slurry liquid. The initial concentration of slurry was 4.8-5.4 wt%. The catalyst was reduced with hydrogen, at 7500 cm^3/min , 0.8 MPa and 250°C for 4 hours (catalyst B), or 240°C for 2 hours (catalyst C). The same reduction conditions were used for catalysts B and C calcined at 300°C.

Slurry Reactor Tests of Catalyst B

After the pretreatment, the catalysts were tested at 260°C, 1.48 MPa, synthesis gas molar feed ratio of 0.67 and gas space velocity of 2.2 NL/g-cat/h for 48 h, and then at 1.8 NL/g-cat/h for the next 138 hours. The syngas conversion in run SB-1276 with the catalyst calcined at 700°C was significantly lower than that obtained in the test of the catalyst calcined at 300°C (SB-1295) under the same process conditions (Figure VII-2.5a). For example at 260°C, 1.48 MPa, gas space velocity of 1.8 NL/g-cat/h the syngas conversion was about 70% for the catalyst calcined at 300°C, whereas the syngas conversion with the catalyst calcined at 700°C was 57%. To get higher conversions with the catalyst calcined at 700°C, higher reaction pressure (2.17 MPa) and lower gas space velocity (1.2 NL/g-cat/h) were used.

Comparison of catalyst activity in terms of the apparent reaction rate constant is shown in Figure VII-2.5b. The catalyst deactivated with time in both tests, but during the first 150 hours on stream the rate of deactivation was much higher on the catalyst calcined at 300°C (run SB-1295). The deactivation rate of the catalyst calcined at 700°C (run SB-1276)

Figure VII-2.5 Synthesis gas conversion (a) and apparent reaction rate constant (b) as a function of time for STSR tests of catalyst B calcined at different temperatures.

was nearly constant regardless of the test conditions, and its activity was lower than that of the catalyst calcined at 300°C.

The catalyst calcined at 700°C had also lower WGS activity than the catalyst calcined at 300°C. The H_2/CO usage ratio obtained for this catalyst was about 0.56 in run SB-1295, whereas in run SB-1276 it was 0.60 (see Table VII-2.2).

The catalyst calcined at 700°C had relatively high initial methane selectivity (Figure VII-2.6a). However, after 60-70 hours on stream, the methane selectivity started to decrease, and after about 200 hours it was nearly the same as methane selectivity obtained with the catalyst calcined at 300°C (about 4 mol%). The same trend was observed for C_1+C_2 selectivity (Figure VII-2.6b).

Olefin selectivity for the catalyst B in tests SB-1295 and SB-1276 is shown in Figure VII-2.7. The olefin content obtained with the catalyst calcined at 700°C is almost independent of carbon number (for C_5+ hydrocarbons). Ethene selectivity in run SB-1276 was high (~72%), and the maximum olefin content (~82%) was obtained for propene. The olefin content was approximately 70 % for C_8+ hydrocarbons. The olefin content in run SB-1295 (catalyst calcined at 300°C) decreased from 82% (propene) to about 50% (at C_{15}). 2-olefin content obtained in run SB-1276 was lower than that in run SB-1295 with the catalyst calcined at 300°C. The catalyst calcined at 700°C had markedly higher selectivity to alpha olefins for $C_{10}+$ hydrocarbons.

Lumped hydrocarbon distribution, activity parameters and product yields obtained in runs SB-1295 and SB-1276 at 120-160 hours on stream are shown in Table VII-2.2. The catalyst calcined at 700°C had higher selectivity to lower molecular weight hydrocarbons than the catalyst calcined at 300°C, and produced much more oxygenates (30 g/Nm³ in run SB-1276 vs. 6.9 g/Nm³ in run SB-1295).

Figure VII-2.6 Methane selectivity (a) and (C₁+C₂) hydrocarbon selectivity (b) as a function of time for STSR tests of catalyst B calcined at different temperatures.

Figure VII-2.7 Olefin content (a) and 2-olefin content (b) dependence on carbon number for catalyst B calcined at different temperatures.

Table VII-2.2 Effect of Calcination Temperature on the Performance of Catalysts B and C in Slurry Reactor Tests

Test designation Catalyst	SB-1295 100 Fe/5 Cu/6 K/24 SiO ₂ ^a	SB-1276	SA-1665 100 Fe/3 Cu/4 K/16 SiO ₂ ^b	SB-0626
Calcination temperature, °C	300	700	300	700
Test conditions				
Temperature, °C	260	260	260	260
Pressure, MPa	1.48	1.48	1.48	2.17
Space velocity, NI/g-cat/h	1.8	1.8	1.4	1.4
Feed H ₂ /CO ratio	0.67	0.67	0.67	0.67
Time on stream, h	122	159	112	485
CO conversion, %	74.3	59.1	84.1	70.9
(H ₂ +CO) conversion, %	69.6	56.6	79.0	67.4
STY, mmol (H ₂ +CO)/g-cat/h	57	43	49	61
k, mmol/g-Fe/h/MPa ^c	259	181	238	176
(H ₂ /CO) usage ratio	0.56	0.60	0.57	0.58
K _p = P _{CO2} ·P _{H2} /P _{CO} ·P _{H2O}	39	33	23	55
% CO converted to CO ₂	48.9	49.4	48.9	48.2
Hydrocarbon selectivity, wt%				
CH ₄	4.4	6.1	3.2	3.2
C ₂ -C ₄	15.6	20.1	12.3	15.2
C ₅ -C ₁₁	21.8	36.7	12.0	15.7
C ₁₂ -C ₁₈	18.4	24.2		
C ₁₂ ⁺	59.2	37.0	72.5	66.0
C ₁ +C ₂	8.3	11.2	6.6	7.2
Yield, g/Nm³(H₂+CO) Converted				
Hydrocarbons	205	186	204	201
Oxygenates	6.9	30	2.4	4.2
Catalyst productivity, g HC/g-cat/h	0.26	0.18	0.22	0.27

^a Iron content of this catalyst (0.554 g-Fe/g-cat)^b Iron content of this catalyst (0.597 g-Fe/g-cat)^c Apparent rate constant for a first order reaction in hydrogen

Slurry Reactor Tests of Catalyst C

The catalysts were tested initially at 260°C, 1.48 MPa, synthesis gas molar feed ratio of 0.67 and gas space velocity 1.4 NI/g-cat/h, and then the pressure was increased to 2.17 MPa, and the gas space velocity was increased to either 2.0 NI/g-cat/h in run SA-1665 or to 1.8 NI/g-cat/h in run SB-0626. The syngas conversions on the catalyst calcined at 700°C (run SB-0626) were lower than those obtained in run SA-1665 with the catalyst calcined at 300°C (Figure VII-2.8a).

The apparent reaction rate constants for these two tests are shown in Figure VII-2.8b. The initial value of k in run SA-1665 was about 250 mmol/g-Fe/h/MPa and then it decreased to 240 mmol/g-Fe/h/MPa at 270 hours. The activity of the catalyst C calcined at 700°C also decreased with time, and its deactivation rate was fairly constant. The reaction rate constant decreased from initial value of 150 mmol/g-Fe/h/MPa to 117 mmol/g-Fe/h/MPa at 380 hours. The WGS activity of the catalyst C was not affected by calcination temperature, and varied between 0.56 and 0.57 in both tests (Table VII-2.2).

Initially, the catalyst calcined at 700°C (SB-0626) had higher methane and C_1+C_2 selectivity than the catalyst calcined at 300°C (SA-1665) (Figure VII-2.9). For example, at about 100 h on stream the methane selectivities were 4 mol% and 2.8 mol% for the catalysts calcined at 700°C and 300°C, respectively. However, methane and C_1+C_2 hydrocarbon selectivity of the catalyst calcined at 700°C decreased with time, and became more similar to those obtained in run SA-1665. For example, at 250 hours the methane selectivities were 3.5 mol% and 2.8 mol% for the catalyst calcined at 700°C and 300°C, respectively.

Figure VII-2.8 Synthesis gas conversion (a) and apparent reaction rate constant (b) as a function of time for STSR tests of catalyst C calcined at different temperatures.

Figure VII-2.9 Methane selectivity (a) and (C₁+C₂) hydrocarbon selectivity (b) as a function of time for STSR tests of catalyst C calcined at different temperatures.

Total olefin and 2-olefin contents of catalyst C calcined at two different temperatures are shown in Figure VII-2.10. As in the case of catalyst B, the olefin content of the catalyst calcined at 700°C is almost independent of carbon number for C₅+ hydrocarbons, and its 2-olefin content is lower than that obtained with the catalyst calcined at 300°C (SA-1665).

Lumped hydrocarbon distribution at different times on stream is shown in Table VII-2.2. Catalyst calcined at 700°C had higher selectivity to lower molecular weight products, and its gasoline fraction is 27-31% of total hydrocarbon products. Also, the catalyst calcined at 700°C had much higher yield of oxygenates than the catalyst calcined at 300°C.

Figure VII-2.10 Olefin content (a) and 2-olefin content (b) dependence on carbon number for catalyst C calcined at different temperatures.

Concluding Remarks on the Calcination Effect Research

We have conducted six fixed bed reactor tests, and two slurry reactor tests under this task. Both catalyst B (100 Fe/5 Cu/6 K/24 SiO₂) and C (100 Fe/3 Cu/4 K/16 SiO₂) were tested in fixed bed reactors after calcinations at 400°C and 500°C for 5 h, and after flash calcination at 700°C for 1 h, and in a stirred tank slurry reactor after flash calcination at 700°C for 1 h.

In fixed bed reactor tests, activities, as well as gaseous hydrocarbon selectivities, of catalysts B and C calcined at 400°C and 500°C, were similar to those of catalysts calcined at 300°C. Catalysts calcined at 700°C for 1 h had lower activity, than the catalysts calcined at temperatures of 300-500°C. Gaseous hydrocarbon selectivity of catalyst C, was not strongly affected by the use of different calcination temperatures, whereas the catalyst B calcined at 700°C had higher gaseous hydrocarbon selectivity than the catalysts calcined at lower temperatures.

The main findings from slurry reactor tests are: (1) The activity of catalysts B and C calcined at 700°C is lower than that of these two catalysts calcined at 300°C; (2) Gaseous hydrocarbon selectivities are higher on catalysts calcined at 700°C; (3) Alpha olefin selectivity of C₁₀+ hydrocarbons was markedly higher on catalysts calcined at 700°C; and (4) Oxygenate yields were about four times higher on the catalysts B and C calcined at 700°C, than on the catalysts calcined at 300°C.

VII-3 References

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VIII Catalyst Characterization

The goals of this task are to: (a) provide basic characterization of all catalyst prepared (atomic absorption analysis, surface area, X-ray diffraction); (b) determine bulk iron phases after the pretreatment and during Fischer-Tropsch synthesis in fixed bed and/or slurry reactors by XRD and Mössbauer effect spectroscopy (at University of Kentucky); and (c) study reduction behavior of iron F-T catalysts by isothermal and temperature programmed reduction (TPR). These studies may lead to activity-structure relationships, and better understanding of the factors which influence catalyst activity, selectivity and longevity.

Results obtained under this task are described in Chapters III-VII and Chapter IX of this report, in sections titled Catalyst Characterization Studies.

IX Testing of Alternative Catalysts

Although catalysts B and C have desirable activity and selectivity characteristics, they may not have a sufficient mechanical strength and attrition properties required for utilization in commercial bubble column slurry reactors. This task has been undertaken with the objective to test catalysts with potentially improved mechanical and attrition properties. Four supported catalysts were synthesized (see Appendix 1 for details) by conventional impregnation of two commercial supports (silica - Davison grade 952; and alumina - Vista B). Nominal compositions (on mass basis) of synthesized catalysts are: (1) 100 Fe/5 Cu/6 K/139 SiO₂ (2) 100 Fe/10 Cu/6 K/134 SiO₂, (3) 100 Fe/5 Cu/6 K/139 Al₂O₃ and (4) 100 Fe/10 Cu/6 K/134 Al₂O₃. The corresponding weight % of iron (as metal) in the prepared catalysts is about 33.8%.

Reduction behavior of the four supported catalysts was studied by both temperature programmed and isothermal reduction in hydrogen, and by isothermal reduction in CO at 280°C. Also, two precipitated promoted iron catalysts, containing aluminum oxide as a binder, were characterized by isothermal reduction in the TGA unit with hydrogen at 240°C and 280°C. Nominal compositions of these two catalysts are: 100 Fe/5 Cu/4.2 K/20 Al₂O₃ and 100 Fe/5 Cu/4.2 K/31.6 Al₂O₃. These catalysts were synthesized earlier in our laboratory during DOE contract DE-AC22-85PC80011 using the procedure described in Appendix 1. Composition of these two catalysts is similar to our catalysts C and B, except that aluminum oxide was used as a binder instead of silicon oxide. Results from catalyst characterization studies are described in section IX-1, whereas results from three slurry reactor tests of catalysts 100 Fe/5 Cu/4.2 K/20 Al₂O₃ (run SA-0097), 100 Fe/5 Cu/6 K/139 SiO₂ (SB-0627) and 100 Fe/5 Cu/9 K/139 Al₂O₃ (SB-2337) are described in section IX-2.

IX-1 Catalyst Characterization Studies

Elemental Analysis and BET Surface Area Measurements

Elemental compositions of the four catalysts prepared by impregnation of the two supports, determined by Huffman Laboratories, Inc., are listed in Table IX-1.1. In general, amounts of promoters (Cu and K), relative to metallic iron, are in good agreement with their intended (nominal) amounts. However, experimentally determined amounts of silica and alumina are in all cases less than the expected amounts, which is due to experimental errors (incomplete dissolution of these two oxides and errors in their quantification).

The BET surface areas of calcined supports (air at 500°C for 5 h) were 308 m²/g (Davison silica support) and 195 m²/g (Vista B alumina support), whereas the corresponding pore volumes were 0.7 cm³/g and 0.45 cm³/g (Table IX-1.1).

The surface areas of impregnated supports (after calcination at 300°C for 5 h) determined by single point BET method in the Pulse Chemisorb 2705 unit are also summarized in Table IX-1.1. The BET surface area of silica supported catalysts (100 Fe/5 Cu/6 K/139 SiO₂ and 100 Fe/10 Cu/6 K/134 SiO₂) is about 94-103 m²/g, and that of alumina supported catalysts (100 Fe/5 Cu/6 K/139 Al₂O₃ and 100 Fe/5 Cu/6 K/134 Al₂O₃) is 94-136 m²/g. Comparing the BET surface areas of supports before and after the impregnation it is observed that the surface areas of both supports (252 m²/g for silica and 213 m²/g for alumina) is reduced markedly (to about 94-136 m²/g) after the addition of iron, copper, and potassium. The decrease in surface area of the supports is attributed to the pore filling and/or pore blocking of mesopores during the impregnation step.

Temperature Programmed Reduction (TPR)

Results from TPR measurements (peak positions and degree of reduction) of the four supported catalysts are summarized in Table IX-1.2.

Figure IX-1.1 illustrates TPR profiles of 100 Fe/x Cu/ 6 K/y SiO₂ catalysts (where x= 5 or 10; y = 134 or 139) prepared by impregnation of the Davison silica support. The peak positions for the catalyst having smaller amount of copper promoter (5 pbw of Cu per 100

Table IX-1.1 Elemental Analysis and Textural Properties of Supports and Supported Catalysts

Catalyst or Support	Composition by AAS# 100 Fe/x Cu/y K/z SiO ₂	Surface area*, m ² /g		Pore Volume, cm ³ /g
		Single Point	BET Plot	
Silica (Davison, grade 952)**	-	252	308	0.70
Alumina (Vista B)**	-	213	195	0.45
100 Fe/5 Cu/6 K/139 SiO ₂	100 / 5 / 5.6 / 125	100		
100 Fe/10 Cu/6 K/134 SiO ₂	100 / 8.9 / 5.7 / 122	94		
100 Fe/5 Cu/6 K/139 Al ₂ O ₃	100 / 4.8 / 5.7 / 119	136		
100 Fe/10 Cu/6 K/134 Al ₂ O ₃	100 / 8.3 / 5.4 / 97	94		

* Samples were degassed at 200°C in He flow (50 cm³/min) for 2.5 hours.

** Calcined in air at 500°C for 5 h.

measurements conducted at Huffman Laboratories, Inc.

Figure IX-1.1

Effect of copper addition on the TPR behavior of silica supported iron catalysts:

(a) 100 Fe/5 Cu/6 K/139 SiO₂; and (b) 100 Fe/10 Cu/6 K/134 SiO₂.

Figure IX-1.2

Effect of copper addition on the TPR behavior of alumina supported iron catalysts:

(a) 100 Fe/5 Cu/6 K/139 Al₂O₃; and (b) 100 Fe/10 Cu/6 K/134 Al₂O₃.

Table IX-1.2 TPR Results for Supported Fischer-Tropsch Catalysts

Sample	Reduction Temperature Range, °C	Peak Position, °C		Degree of Reduction, (%) (#)	
		First Stage	Second Stg.	First stage	Total*
100 Fe/5 Cu/6 K/139 SiO ₂	RT to 800	344	544	21	85
100 Fe/10 Cu/6 K/134 SiO ₂	RT to 800	358	560	27	102
100 Fe/5 Cu/6 K/139 Al ₂ O ₃	RT to 900	339	602	20	73
100 Fe/10 Cu/6 K/134 Al ₂ O ₃	RT to 900	284	612	26	103

* The %degree of reduction are for the temperature range of RT to 800°C.

Sample wt = 20 mg, reducing gas = 5%H₂/95%N₂, flow rate = 40 cm³/min, ramp = 20°C/min, temperature range = room temperature to 800 - 900°C.

pbw of Fe) are lower (344°C and 544°C) than the corresponding values (358°C and 560°C) observed for the catalyst having 10 pbw of copper per 100 pbw of Fe, which is not consistent with the role of copper as promoter which facilitates iron reduction. However, the degree of reduction for both the first and second stage of the reduction increased with the increasing amount of copper promoter. The degree of reduction values for the first stage of iron oxide reduction are 21% and 27%, respectively for the catalysts having 5 and 10 parts of copper. Also, the total degree of reduction values (at the end of TPR) for these two catalysts are 85% and 102%, respectively. These results are consistent with the expected effect of copper promotion on the reduction of iron oxides.

TPR profiles of 100 Fe/x Cu/ 6 K/y Al₂O₃ catalysts (where x= 5 or 10; y = 134 or 139) are shown in Figure IX-1.2. The peak positions for the first stage of reduction are 284°C and 339°C for the catalysts having 10 and 5 parts of copper, respectively. These results are consistent with the expected effect of copper promotion on the reduction of iron oxide. However, the peak positions (602°C and 612°C) for the second stage of reduction are not consistent with the expected promotional effect of copper. The degree of reduction values (Table IX-1.2) for the first stage of reduction are 20% and 26% for the catalysts having 5 and 10 parts of copper, respectively, whereas the expected degree of reduction corresponding to complete conversion of iron oxide (Fe₂O₃) into magnetite (Fe₃O₄) for these two catalysts is 10.8% and 10.5%, respectively. These results indicate that some of the magnetite is reduced to metallic iron during the first stage of the reduction. Total degree of reduction values for these two catalysts are 73% and 103%, respectively. These results clearly show that the addition of copper promotes the reduction of iron.

Isothermal Reduction

Results from isothermal reduction experiments in thermogravimetric analysis (TGA) unit are summarized in Table IX-1.3, and Figures IX-1.3 to IX-1.5.

Degree of reduction of 100 Fe/5 Cu/4.2 K/20 Al₂O₃ catalyst (Figure IX-1.3a) increased rapidly during the first 70 minutes of reduction, and then slowly at both reduction

Table IX-1.3 Summary of isothermal reduction experiments with alternative F-T catalysts in the TGA unit

Catalyst	Reduction Temperature, °C	% Degree of Reduction
100 Fe/5 Cu/4.2 K/20 Al ₂ O ₃	240 280	59 69
100 Fe/5 Cu/4.2 K/31.6 Al ₂ O ₃	240 280	28 42
100 Fe/5 Cu/4.2 K/100 SiO ₂	280 240	38 33
100 Fe/5 Cu/6 K/139 SiO ₂	280	43
100 Fe/10 Cu/6 K/134 SiO ₂	280	79
100 Fe/5 Cu/6 K/139 Al ₂ O ₃	280	35
100 Fe/10 Cu/6 K/134 Al ₂ O ₃	280	51

Reduction conditions: Reducing gas = H₂ (100 cm³/min), ramping in He = 5°C/min, sample wt = ~ 20 mg, and total reduction time = ~ 8 h. The sample was dried at 280°C in He (100 cm³/min) for 30 minutes.

Figure IX-1.3 Effect of alumina content and reduction temperature on the reduction behavior of promoted Fischer-Tropsch catalysts in hydrogen: (a) 100 Fe/5 Cu/4.2 K/20 Al₂O₃; (b) 100 Fe/5 Cu/4.2 K/31.6 Al₂O₃.

temperatures (240°C and 280°C). The degree of reduction values (Table IX-1.3) at the end of 8 h reduction period are about 59% and 69%, for the reduction temperatures of 240°C and 280°C, respectively.

Degree of reduction of 100 Fe/5 Cu/4.2 K/31.6 Al₂O₃ catalyst (Figure IX-1.3b) increased rapidly during the first 100 minutes of reduction, and then continued to increase slowly at both reduction temperatures (240°C and 280°C). At the end of the reduction period the degree of reduction values are about 28% and 42%, at the reduction temperatures of 240°C and 280°C, respectively. These results show that the reduction is inhibited by the addition of aluminum oxide, which is indicative of interactions between the iron and the alumina.

Degree of reduction of 100 Fe/5 Cu/6 K/139 SiO₂ catalyst increased gradually during the first 220 minutes of reduction, and then very slowly (Figure IX-1.4). After 8 h of reduction with hydrogen at 280°C the final degree of reduction is about 43%. The degree of reduction of 100 Fe/10 Cu/6 K/134 SiO₂ catalyst increased rapidly during the first 50 minutes of reduction (to about 70%), and then very slowly reaching 79% after 8 hours of reduction in hydrogen at 280°C. These results clearly show that the reduction of iron in silica supported catalysts increases with the increasing amount of Cu promoter.

The alumina supported catalysts (100 Fe/5 Cu/6 K/139 Al₂O₃ and 100 Fe/10 Cu/6 K/134 Al₂O₃) exhibited the same type of behavior as the two silica supported catalysts (Figure IX-1.5). At the end of 8 h reduction period at 280°C, the degrees of reduction were about 35% and 51%, for the catalysts containing 5 and 10 parts pbw of Cu per 100 pbw of Fe. These results again show that the addition of copper promotes the reduction of iron oxide. Also, it appears that the interactions between iron and alumina support are stronger than on the silica support, resulting in lower reducibility of iron on alumina.

Reduction behavior of the silica and alumina supported catalysts in CO at 280°C is shown in Figures IX-1.6 and IX-1.7, respectively. The two silica supported catalysts lost about 2% of the initial weight during heating in helium from room temperature to 280°C, due

Figure IX-1.4 Effect of copper promotion on the degree of reduction of silica supported iron catalysts in hydrogen at 280°C.

Figure IX-1.5 Effect of copper promotion on the degree of reduction of alumina supported iron catalysts in hydrogen at 280°C.

to removal of the adsorbed moisture. The weight loss was fairly rapid during the first 100 minutes of exposure to CO. After 200 minutes, both catalysts started to gain weight. Interestingly, the weight loss of both catalysts is almost the same during the entire reduction period. As shown above (Figure IX-1.4) the degree of reduction in hydrogen (at 280°C) of the catalyst having 10 parts of copper was significantly higher than that of the catalyst having 5 parts of copper. Hence, the relatively low weight loss of the catalyst having 10 parts of copper during CO reduction suggests that carburization (formation of iron carbides) and carbon deposition are dominant processes from the very beginning of the catalyst exposure to CO.

Alumina supported catalysts had lost about 6% of the initial weight during heating in helium from room temperature to 280°C, due to removal of adsorbed moisture. The weight loss was rapid during the first 60 minutes of exposure to CO. After 200 minutes of reduction, the weight remaining began to increase slowly with time. The weight loss during the first 60 minutes of reduction was slightly higher for the catalyst having 5 parts of copper compared to the catalyst having 10 parts of copper. Again, this suggests that carburization and/or carbon deposition are dominant processes on the catalyst having higher copper content.

The observed changes in weight for all four catalysts during the CO reduction are the net result of three competing reactions: (a) reduction of iron oxides; (b) carbon deposition ($2\text{CO} \rightarrow \text{CO}_2 + \text{C}$); and (c) carbide formation (i.e. carburization). For all four catalysts, the theoretical weight loss corresponding to formation of χ -carbide ($\text{Fe}_2\text{O}_3 \rightarrow \chi\text{-Fe}_5\text{C}_2$) is about 14%, whereas the theoretical weight loss for formation of magnetite ($\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4$) is about 2.4%. After 100 minutes of CO reduction, the experimental weight loss was about 5-7% on all four catalysts, suggesting that oxide reduction and carburization are the dominant reactions, and that carburization is incomplete. During the later stages of reduction a gradual

Figure IX-1.6 Effect of copper promotion on the reduction behavior of silica supported iron catalysts in CO at 280°C.

Figure IX-1.7 Effect of copper promotion on the reduction behavior of alumina supported iron catalysts in CO at 280°C.

increase in weight was observed with all four catalysts. This suggests that the carbon deposition is the dominant reaction, even though the carburization was not completed.

XRD Measurements

Results of XRD analysis of used catalysts from three slurry reactor tests are summarized in Table IX-1.4. As an illustration, the XRD patterns of catalysts withdrawn from the slurry reactor run SA-0097 with 100 Fe/5 Cu/4.2 K/20 Al₂O₃ catalyst are shown in Figure IX-1.8.

Magnetite (Fe₃O₄) and α -Fe were the major phases (Figure IX-1.8A) in the sample withdrawn immediately after the hydrogen reduction at 250°C for 4 hours (TOS = 0 h). During Fischer-Tropsch synthesis both magnetite and ϵ '-carbide (Fe_{2.2}C) were identified in samples withdrawn from the reactor between 4 and 308 hours on stream (Figure IX-1.8B to IX-1.8E). XRD patterns of samples withdrawn after 4 h (1-B) and 308 h (1-E) on stream are similar. The catalyst activity during this test decreased slowly with time (see section IX-2 of this chapter).

Used catalysts from runs SB-0627 (silica supported catalyst) and SB-2337 (alumina supported catalyst) contained magnetite and ϵ '-carbide (and possibly χ -carbide, as well). The increase in crystallinity of iron phases (i.e. increase in crystallite size) with time on stream was observed in catalyst samples from both runs. Catalysts deactivated with time in both tests (Section IX-2).

Table IX-1.4 Iron Phases in Used Catalyst Samples by X-ray Diffraction

Run Number	Catalyst	Time on Stream (TOS), h	Phases Identified by XRD
SA-0097	100 Fe/5 Cu/4.2 K/20 Al ₂ O ₃	0	Fe ₃ O ₄ and α -Fe
		4	Fe ₃ O ₄ and ϵ' -Fe ₂₂ C
		24	Fe ₃ O ₄ and ϵ' -Fe ₂₂ C
		162	Fe ₃ O ₄ and ϵ' -Fe ₂₂ C
		308	Fe ₃ O ₄ and ϵ' -Fe ₂₂ C
SB-2337	100 Fe/5 Cu/9 K/139 Al ₂ O ₃	76	Fe ₃ O ₄ and ϵ' -Fe ₂₂ C
		144	Fe ₃ O ₄ and ϵ' -Fe ₂₂ C
		237	Fe ₃ O ₄ and ϵ' -Fe ₂₂ C
SB-0627	100 Fe/5 Cu/6 K/139 SiO ₂	150	Fe ₃ O ₄ , and ϵ' -Fe ₂₂ C
		306	Fe ₃ O ₄ , ϵ' -Fe ₂₂ C and χ -Fe ₅ C ₂ (?)

F-T process conditions in run SA-0097 were: T = 260°C, P = 1.48 - 2.17 MPa, H₂/CO = 0.67, SV = 1.4 - 2.1 NI/g-cat/h.

F-T process conditions in run SB-2337 were: T = 260°C, P = 1.48 MPa, H₂/CO = 0.67, SV = 1.3 NI/g-cat/h.

F-T process conditions in run SB-0627 were: T = 260°C, P = 1.48 - 2.17 MPa, H₂/CO = 0.67, SV = 1.4 - 2.0 NI/g-cat/h.

Figure IX-1.8 Changes in bulk iron phases with time on stream during run SA-0097 with the 100 Fe/5 Cu/4.2 K/20 Al_2O_3 catalyst.

IX-2 Reaction Studies

Three slurry reactor tests were conducted, and the reduction and process conditions employed in these tests are shown in Table IX-2.1. About 11-15 g of catalyst was used in these tests resulting in 3.8-5.1 wt% slurry. Durasyn 164-oil was used as the start-up liquid in all three tests. In run SA-0097 the catalyst which passed through a 270 mesh sieve (particles less than 63 micron in diameter) was loaded into the reactor, whereas in runs SB-0627 and SB-2337 the catalyst particle size was 45-63 microns (270-325 mesh).

Table IX-2.1 Reduction and Process Conditions in STSR Tests of Alternative Catalysts

Catalyst	Run ID	Reduction Conditions	Process Conditions ^a		
			TOS (h)	P (MPa)	SV (NL/g/h)
100 Fe/5 Cu/4.2 K/20 Al ₂ O ₃ Iron content: 0.57 g-Fe/g-cat	SA-0097	H ₂ , 250°C, 0.8 MPa, 4 h, 7500 cm ³ /min	0-162	1.48	1.4
			162-309	2.17	2.1
100 Fe/5 Cu/6 K/139 SiO ₂ Iron content: 0.34 g-Fe/g-cat	SB-0627	CO/He = 1/8, 0.8 MPa 8 h, 7000 cm ³ /min	0-150	1.48	1.4
			150-306	2.17	2.0
100 Fe/5 Cu/9 K/139 Al ₂ O ₃ Iron content: 0.33 g-Fe/g-cat	SB-2337	CO/He = 1/5, 0.8 MPa 8 h, 4000 cm ³ /min	0-237	1.48	1.3

^a Other process conditions: T = 260°C, H₂/CO = 0/67.

The alumina containing catalyst (100 Fe/5 Cu/4.2 K/20 Al₂O₃) was pretreated using our standard reduction procedure for catalyst B, since its composition is similar to that of the catalyst B, except that aluminum oxide is used as binder instead of silicon oxide. The alumina and silica supported catalyst were reduced with CO, diluted with helium, at 280°C for 8 hours, since both catalysts responded well to CO pretreatment in the TGA unit (Section IX-1).

Catalyst Activity and Stability

Changes in synthesis gas conversion and H_2/CO usage ratio with time-on-stream at different process conditions for all three tests are shown in Figure IX-2.1. Results from run SA-1665 with catalyst C (100 Fe/3 Cu/4 K/16 SiO_2) are also shown for comparison.

The baseline catalyst C had the highest conversion (about 80%) and was very stable with time during testing at both 1.48 MPa and 2.17 MPa (Figure IX-2.1a). The alumina containing catalyst (SA-0097) had lower syngas conversion of about 60%, and was fairly stable during testing at 1.48 MPa (up to 162 h), but began to deactivate during testing at 2.17 MPa. The silica supported catalyst (SB-0627) was significantly more active than the alumina supported catalyst (SB-2337), but both catalysts deactivated fairly rapidly with time. For example the syngas conversion in run SB-0627 decreased from about 70% at 30 hours on stream to about 40% at 300 hours, whereas in run SB-2337 the maximum value of conversion was about 47% (at 32 h) and only 19% at 236 h.

The water-gas-shift (WGS) activity of the catalyst C was high (Figure IX-2.1b), as evidenced by low value of the usage ratio (about 0.57), whereas the silica supported catalyst (SB-0627) had relatively low WGS activity, particularly during testing at 2.17 MPa (usage ratio between 0.8 and 1). The WGS activity of the two alumina containing catalysts was relatively high (usage ratio of 0.60-0.64).

Changes in catalyst activity, expressed in terms of the apparent reaction rate constant for the first order reaction with respect to hydrogen, are shown in Figure IX-2.2. In addition to results obtained in three tests with alternative catalysts results from two tests with baseline catalysts B (run SB-1295) and C (run SA-1665) are also shown for comparison. Initially, the catalyst B and the silica supported catalyst (SB-0627) were the most active ($k = 350-380$ mmol/g-Fe/h/MPa), but both catalysts deactivated with time on stream. The apparent reaction rate constant in run SB-1295 (Catalyst B) reached a constant value of about 225 mmol/g-Fe/h/MPa at about 150 h on stream, whereas the silica supported catalyst (SB-0627) continued to deactivate with time and at 300 h its apparent reaction rate constant was 150

Figure IX-2.1 Synthesis gas conversion (a) and H₂/CO usage ratio (b) as a function of time for STSR tests of alternative catalysts and the baseline catalyst C.

Figure IX-2.2 Apparent reaction rate constant as a function of time for STSR tests of alternative catalysts and the baseline catalysts B and C.

mmol/g-Fe/h/MPa. Catalyst C (SA-1665) was the most stable and its apparent reaction rate constant decreased from the initial value of about 250 mmol/g-Fe/h/MPa to about 225 mmol/g-Fe/h/MPa at 350 hours. The alumina containing catalyst (SA-0097) was markedly less active than the silica containing catalysts B and C, and its apparent reaction rate constant was between 125 and 175 mmol/g-Fe/h/MPa. The alumina supported catalyst was the least active and its apparent reaction rate constant was between 60 and 175 mmol/g-Fe/h/MPa.

Gaseous Hydrocarbon Selectivities

Silica supported catalyst (SB-0627) had the highest methane (7-8 mol%) and C_1+C_2 selectivities (Figures IX-2.3a and IX-2.3b). Alumina containing catalyst (SA-0097) had methane selectivity between 5 and 6 mol%, which is high in comparison to our baseline catalysts C (2-3 mol%) and B (3-4 mol%, not shown in Figure IX-2.3a). Methane selectivity of the alumina supported catalyst was the lowest of the three alternative catalysts (about 3.5-3.8 mol%) which is consistent with its high potassium content (9 pbw of K per 100 pbw of Fe). However, the activity of this catalyst was very low and its deactivation rate was high (Figure IX-2.2). C_1+C_2 selectivities of the three alternative catalysts were high in comparison to the baseline catalyst C (Figure IX-2.3b).

Figure IX-2.3 Methane selectivity (a) and (C₁+C₂) hydrocarbon selectivity (b) as a function of time for STSR tests of alternative catalysts and the baseline catalyst C.

Concluding Remarks on Alternative Catalysts

Three catalysts 100 Fe/5 Cu/4.2 K/20 Al₂O₃ (run SA-0097), 100 Fe/5 Cu/6 K/139 SiO₂ (SB-0627) and 100 Fe/5 Cu/9 K/139 Al₂O₃ (SB-2337) were evaluated in slurry reactor tests under this task. The alumina containing catalyst 100 Fe/5 Cu/4.2 K/20 Al₂O₃ was chosen, because of its similarity with our baseline catalysts B and C (similar promoter, Cu and K, and binder amounts, except that aluminum oxide was used as the binder instead of silicon oxide). The alumina and silica supported catalysts were chosen because they are expected to have high mechanical strength and high attrition resistance during testing in slurry reactors.

The alumina containing catalyst (SA-0097) was markedly less active and had higher methane and gaseous hydrocarbon selectivities than the baseline catalysts. The silica supported catalyst (100 Fe/5 Cu/6 K/139 SiO₂) deactivated fairly rapidly with time, and had markedly higher gaseous hydrocarbon selectivities than the baseline catalysts B and C. The alumina supported catalyst (100 Fe/5 Cu/6 K/139 Al₂O₃) was the least active, and deactivated rapidly with time-on-stream. Gaseous hydrocarbon selectivities were higher than those obtained in tests with the baseline catalysts B and C, but were lower than those obtained in tests of the other two alternative catalysts. The reasons for fairly rapid loss in activity in tests with the alumina and silica supported catalysts are not understood at the present time. In general the performance of the three alternative catalysts was inferior in comparison to our baseline catalysts.

X Characterization of Product Distribution and Data Analysis

The objective of this task is to perform detailed gas chromatographic analysis of selected liquid and wax products collected during the STSR tests (Tasks 3-7 and 9), and provide information on the effects of time on stream (catalyst aging), process conditions, pretreatment conditions and/or catalyst promoters on product distribution.

Results obtained under this task are described in Chapters III-VII and Chapter IX of this report, in sections titled Reaction Studies. The information provided includes the following: lumped hydrocarbon product distribution, product yields (hydrocarbons and oxygenates), carbon number distribution (in the form of Anderson-Schulz-Flory plots), and total olefin and 2-olefin content as a function of carbon number.

XI CONCLUSIONS

The overall objectives of this contract were to: (1) demonstrate repeatability of performance and preparation procedure of two high activity, high alpha iron F-T catalysts synthesized at TAMU during the DOE Contract DE-AC22-89PC89868; and (2) seek potential improvements in the catalyst performance through variations in process conditions, pretreatment procedures and/or modifications in preparation steps (e.g. means of introduction of promoters and calcination conditions). The major conclusions are:

1. Repeatability of performance of two catalysts designated B (100 Fe/5 Cu/6 K/24 SiO₂ containing 55.4 wt% of iron) and C (100 Fe/3 Cu/4 K/16 SiO₂ containing 59.7 wt% of iron) synthesized during the previous DOE Contract DE-AC22-89PC89868 was successfully demonstrated. The catalyst B was more stable in the original test (SB-1931) than in the two recent tests (SB-3354 and SB-0665), whereas the opposite trend was observed in tests with the catalyst C (runs SB-0261, SB-0045 and SA-0705). Hydrocarbon product distributions and olefin selectivities in multiple tests with the same catalyst were reproducible.
2. Performance of catalysts B and C is comparable to, or exceeds, that obtained in the two most successful bubble column slurry reactor (BCSR) tests conducted by Mobil and Rheinpreussen. In Mobil's run CT-256-13 at synthesis gas conversion of 82%, methane and C₁+C₂ selectivities were 2.7 and 5.6 wt%, respectively, whereas the catalyst productivity was about 0.26 g HC/g-cat/h (Test conditions: 257°C, 1.48 MPa, 2.3 NI/g-Fe/h, H₂/CO = 0.73). In Rheinpreussen's demonstration plant unit the C₁+C₂ selectivity was 6.8% at the synthesis gas conversion of 89%, and the catalyst productivity was about 0.33 g HC/g-cat/h (Test conditions: 268°C, 1.48 MPa, 3.1 NI/g-Fe/h, H₂/CO = 0.67).

In run SB-3354 with catalyst B (TOS = 97 h) the following results were obtained at 260°C, 1.48 MPa, 3.2 NI/g-Fe/h, H₂/CO = 0.67: Methane and C₁+C₂ selectivities were 3.2

and 5.3 wt%, respectively, and the catalyst productivity was 0.26 g HC/g-cat/h at the synthesis gas conversion of 71.5%.

The performance of catalyst C in run SB-0045 at the reaction pressure of 1.48 MPa and 215 hours on stream, was very similar to that obtained in Mobil's run CT-256-13. However, the productivity of catalyst C was improved at reaction pressure of 2.17 MPa and gas space velocity of 3.4 NI/g-Fe/h (TOS = 336 h). Methane and C₁+C₂ selectivities were 2.6 and 5.4 wt%, respectively, and the catalyst productivity was 0.36 g HC/g-cat/h at the synthesis gas conversion of about 80%. The latter productivity is higher than productivity's obtained in Mobil's and Rheinpreussen's bubble column slurry reactor tests, primarily due to the use of higher reaction pressure and higher gas space velocity in the present study.

3. The use of higher reaction pressure and proportionally higher gas space velocity, to maintain constant gas residence time in the reactor, was successfully demonstrated in several tests with catalyst C (runs SB-0045, SA-0075, SA-1665, SA-0946 and SA-2186). Slurry F-T reactors have normally operated at pressures less than 1.5 MPa, whereas the coal gasifiers which generate the synthesis gas operate at pressures between 2 and 3 MPa. The use of higher operating pressures and higher gas space velocity increases reactor productivity and improves the process economics. Space-time-yields were increased up to 48% by increasing reaction pressure from 1.48 MPa to 2.17 MPa, while maintaining the gas contact time and synthesis gas conversion at a constant value. No adverse effects of operation at higher pressure on catalyst activity were observed in several of these tests (up to 250 hours of testing at 2.17 MPa).

4. Repeatability of performance of catalysts B and C was demonstrated in multiple tests with catalysts from different preparation batches. Three STSR tests were conducted with catalyst B, and four tests with catalyst C. In general, catalysts from different preparation batches (100-400 g of catalyst batches) had similar performance (activity and selectivity) and

reproducibility of catalyst preparation procedure on a laboratory scale has been successfully demonstrated.

5. The addition of CaO promoter to baseline catalysts B and C (catalysts with nominal compositions $100 \text{ Fe}/3 \text{ Cu}/4 \text{ K}/x \text{ Ca}/16 \text{ SiO}_2$ and $100 \text{ Fe}/5 \text{ Cu}/5 \text{ K}/x \text{ Ca}/24 \text{ SiO}_2$, where $x = 2$ or 6) was not found to be beneficial for their performance. The addition of larger amount of CaO ($x = 6$) resulted in markedly lower catalyst activity, whereas selectivity of the two catalysts with $x = 6$, was similar to that of the corresponding baseline catalysts (fixed bed reactor tests). The two catalysts with $x = 2$ were also tested in slurry reactors.

At reaction pressure of 1.48 MPa, selectivity of gaseous hydrocarbons on CaO containing catalysts was higher than that of the corresponding baseline catalysts. However, at reaction pressure of 2.17 MPa the gaseous hydrocarbon selectivity decreased on the CaO containing catalysts, and was nearly the same as that of the baseline catalysts at 1.48 MPa. The CaO promoted catalysts may be suitable for operation at higher reaction pressures.

6. The effect of use of two different sources of potassium on the performance of catalysts B and C was studied in fixed bed and slurry bed reactors. In our standard catalyst preparation procedure silicon oxide is introduced by addition of a dilute potassium silicate (K_2SiO_3) solution to the iron/copper precipitate. This procedure introduces potassium in the excess of the desired amount. Potassium is completely removed by washing of the precipitate. Addition of the desired amount of potassium promoter is accomplished via "incipient wetness" method, using KHCO_3 dissolved in water. An obvious alternative to the above procedure is to utilize potassium from K_2SiO_3 as the source of potassium, i.e. discontinue with washing when the residual amount of potassium equals the desired amount of promoter. Catalysts B and C were synthesized using potassium silicate as the source of the potassium promoter, and performance of these catalysts was compared with those synthesized using our usual procedure (Section IV-2). On the basis of results obtained in these tests it was concluded that the baseline procedure utilizing impregnation of Fe-Cu-SiO₂ precursor with the aqueous solution of KHCO_3 is the

preferred method of catalyst preparation. The second procedure, which avoids the impregnation step, provides satisfactory results, and may be used as an alternative.

7. Significant improvements in activity of the catalyst C (from batch-4) were obtained through the use of different pretreatment procedures. The initial activity (measured by a value of the apparent reaction rate constant, k) of the catalyst reduced with hydrogen at 250°C for 4 hours (run SB-3425) was about 40% higher than that of hydrogen reduced at 240°C for 2 hours (baseline reduction procedure). However, the catalyst activity decreased with time and at about 300 h its apparent rate constant ($k = 250 \text{ mmol/g-Fe/MPa/h}$) was similar to the value obtained in run SA-1665 employing the baseline reduction procedure.

The CO pretreatment (SA-0946), syngas pretreatment (SA-1626) and TAMU pretreatment (SA-2186) also resulted in improved catalyst activity, relative to the standard reduction procedure. The initial values of the apparent reaction rate constant, after these pretreatments, were 300-400 mmol/g-Fe/MPa/h, corresponding to 20-60% increase in activity relative to the standard procedure. Activity of the CO and TAMU pretreated catalysts increased with time, and at 400 hours the values of the apparent reaction rate constants were 360 and 430 mmol/g-Fe/MPa/h, respectively. As the result of the improvement in the catalyst activity, while maintaining low methane and gaseous hydrocarbon selectivities, the catalyst productivities in these two tests were markedly higher than those obtained in Mobil's and Rheinpreussen's slurry bubble column reactor tests. The catalyst productivity in Rheinpreussen test was 0.49 gHC/g-Fe/h, and those obtained in runs SA-0946 and SA-2186 were 0.71 and 0.86 gHC/g-Fe/h, respectively. This represents 45-75% improvement in catalyst productivity relative to that achieved in Rheinpreussen's demonstration plant unit, and sets new standards of performance for "high alpha" iron catalysts. We believe that the performance of our catalyst B (100 Fe/5 Cu/6 K/24 SiO₂) can be also improved through the use of better pretreatment procedures.

8. The effect of calcination temperature on performance of catalysts B and C during F-T synthesis was investigated in fixed and slurry bed reactors. Both catalyst B (100 Fe/5 Cu/6 K/24 SiO₂) and C (100 Fe/3 Cu/4 K/16 SiO₂) were tested in fixed bed reactors after calcinations at 400°C and 500°C for 5 h, and after flash calcination at 700°C for 1 h, and in a stirred tank slurry reactor after flash calcination at 700°C for 1 h.

The main findings from slurry reactor tests were: (1) The activity of catalysts B and C calcined at 700°C was lower than that of these two catalysts calcined at 300°C (baseline calcination temperature); (2) Gaseous hydrocarbon selectivities were higher on catalysts calcined at 700°C; (3) Alpha olefin selectivity of C₁₀+ hydrocarbons was markedly higher on catalysts calcined at 700°C, which is of potential significance, since alpha olefins are valuable products; and (4) Oxygenates yields were about four times higher on the catalysts B and C calcined at 700°C, than on the catalysts calcined at 300°C.

9. Although catalysts B and C have desirable activity and selectivity characteristics, they may not have a sufficient mechanical strength and attrition properties required for utilization in commercial bubble column slurry reactors. Three catalysts 100 Fe/5 Cu/4.2 K/20 Al₂O₃ (run SA-0097), 100 Fe/5 Cu/6 K/139 SiO₂ (SB-0627) and 100 Fe/5 Cu/9 K/139 Al₂O₃ (SB-2337) were evaluated in slurry reactor tests as potential alternatives to our baseline catalysts B and C. The performance of the three alternative catalysts was inferior in comparison to our baseline catalysts. The alternative catalysts had lower activity, faster deactivation rate, and produced more gaseous hydrocarbon products than the baseline catalysts.

In general, all major objectives of this contract have been achieved. Significant improvements in catalyst productivity were achieved through the use of higher operating pressure (2.17 MPa) and use of different pretreatment procedures. Catalyst productivities achieved in runs SA-0946 and SA-2186, 0.71 and 0.86 gHC/g-Fe/h, respectively, have established new standards of performance for "high alpha" iron catalysts.

XII Acknowledgments

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Appendix 1

Catalysts Preparation Procedure

A1-1 Co - Precipitation Procedure

Desired compositions of copper-promoted iron-based catalysts were prepared by continuous co-precipitation, using an apparatus and a technique similar to that employed by previous investigators (Kölbel and Ralek, 1980; Deckwer et al., 1982). Unlike conventional batch precipitation, this approach ensures that precipitation occurs at a constant, rather than continuously changing, pH, resulting in much more uniform and predictable particle size and pore/structure.

In the present case, an aqueous solution containing $\text{Fe}(\text{NO}_3)_3$ (~ 0.6 M) and a concentration of $\text{Cu}(\text{NO}_3)_2$ that corresponds to the desired Fe/Cu ratio in the final catalyst, and a second solution containing aqueous NH_3 (~ 2.7 M) are maintained in stirred vessels at $84 \pm 2^\circ\text{C}$. The two solutions are separately conveyed by fluid pumps to a stirred tubular reaction vessel that is thermostated at $82 \pm 2^\circ\text{C}$. Precipitation (to form FeOOH and $\text{Cu}(\text{OH})_2$) occurs continuously as the two solutions are pumped upward through the vessel, while an in-line pH electrode is used to monitor the pH of the reactor effluent, which is maintained at 6.0 ± 0.2 . Collection of the slurried precipitate is made in ice-cooled vessels and is continued until one of the two solutions is consumed. The precipitate is then thoroughly washed by vacuum filtration to remove excess NH_3 and NO_3^- , using ~ 10 liters of deionized and distilled water per 100 g (dry weight) of the final catalyst. The washed precipitate is then used for the preparation of final catalysts.

A1-2 Addition of Silicon Oxide

The wet Fe/Cu precipitate is mixed with deionized and distilled water to make a uniform slurry. Dilute potassium silicate solution containing a desired amount of silica (SiO_2) was added to the slurry very slowly. During potassium silicate addition the pH was

maintained at about 9.0. Once the addition of potassium silicate was over and the pH was stabilized, a 10% dilute nitric acid was added drop by drop until the pH reaches ~ 6.0 - 6.5 with constant stirring. Stirring was continued for additional four hours after the addition of nitric acid. Immediately after completing the stirring procedure the resulting silica containing slurry was filtered, washed (to remove the K^+ ions) and vacuum oven dried at 50°C for 48 h and then at 120°C for 24 h.

A1-3 Addition of Aluminum Oxide

The method used to prepare the alumina containing precipitated iron catalysts employed an Fe/Cu precipitate of the desired composition (100 Fe/5 Cu) that had been already vacuum dried. Under an atmosphere of dry nitrogen (to prevent exposure to atmospheric water) an appropriate amount of liquid sec-butoxide was dissolved in a volume of 2-butanol needed to just fill the pores of the precipitate sample (incipient wetness method). The required amount of dried Fe/Cu precipitate was added to the butoxide solution, and the resulting slurry was stirred for 16 hours to ensure complete pore filling by viscous alkoxide solution. Excess alcohol solvent was then removed by heating the mixture in a vacuum oven for 6 h at 60°C. Hydrolytic decomposition of the impregnated aluminum sec-butoxide to form Al_2O_3 was accomplished by exposure of the material for 16 h at 25°C to air that was saturated with water vapor. The alumina-containing catalysts after being thoroughly washed and dried in a vacuum oven for 16 h at 120°C, were impregnated with $KHCO_3$ (see below) and were re-dried to yield the final catalysts.

A1-4 Impregnation by Potassium

Addition of the desired levels of potassium promoter to Fe-Cu-SiO₂ (or Fe-Cu-Al₂O₃) catalyst precursors was made by pore filling technique, using dried precipitate that has been crushed to < 30 mesh. In this method, the required amount of $KHCO_3$ is dissolved in a volume of water that is ~ 5% larger than that needed to just fill all of the pores of the solid.

The solution is then added to a weighed sample of the dried catalyst, resulting in the so-called "incipient wetness" condition. Excess solvent (water) is then removed by vacuum-aided evaporation, with continuous rotational agitation. The final product is dried further in a vacuum oven at 120°C for 16 h. This procedure ensures uniform and complete distribution of the potassium salt throughout the catalyst pore structure.

A1-5 Potassium from Potassium Silicate (K_2SiO_3) Source

In some of the iron based F-T synthesis catalysts the source of potassium was potassium silicate. For the preparation of these catalyst formulations the wet precipitate (cake) was utilized after the addition of potassium silicate to the Fe-Cu precipitate slurry. After the addition of potassium silicate, the potassium content in the slurry is usually higher than the desired potassium content. Excess potassium was removed by decantation of appropriate amounts of water from the slurry, and the remaining water was removed by vacuum aided evaporation. Then the final solids were dried in a vacuum oven at 50°C for 48 h and at 120°C for 24 h.

A1-6 Addition of Calcium Oxide Promoter

Catalysts with nominal composition 100 Fe/3 Cu/4 K/x Ca/16 SiO_2 and 100 Fe/5 Cu/5 K/x Ca/24 SiO_2 (where: $x = 2$ or 6) were prepared by impregnation of the corresponding Fe-Cu- SiO_2 precursors. Dried precursors (prepared as described above in A1-1 and A1-2) were impregnated first with calcium acetate monohydrate (in catalysts with $x = 2$) and then with potassium bicarbonate by incipient wetness method. For catalysts with $x = 6$, the dried precursors were impregnated first with potassium bicarbonate, followed by impregnation with calcium acetate monohydrate.

A1-7 Impregnation of Commercial Supports

We have prepared four supported catalysts (~ 50 g each) by impregnation with aqueous solutions of iron and promoter salts. The supports (silica - Davison grade 952; and alumina - Vista B) were sieved and calcined at 500°C in air for 5 h prior to impregnation. Catalysts containing iron, copper and potassium on silica or alumina were prepared by co-impregnation with aqueous solutions containing desired amounts of ferric nitrate, copper nitrate and potassium bicarbonate in successive steps. The total volume of impregnating solution (which contains the calculated amounts of promoters) was about 95 ml in each catalyst preparation. However, the amount of impregnating solution consumed in each impregnation step was different and varied with the support. For example during the preparation of silica supported catalysts we were able to complete the preparation of catalysts in three impregnation steps, whereas seven impregnation steps were used in preparation of alumina supported catalysts. After each impregnation step the sample was vacuum dried at 100°C for about 2 h. After the final impregnation and drying for 12 h in vacuum, the catalyst was calcined in air at 300°C for 5 h. Various steps in the catalyst preparation are shown in Figure A1-1. Nominal compositions (on mass basis) of synthesized catalysts are: (1) 100 Fe/5 Cu/6 K/139 SiO₂, (2) 100 Fe/10 Cu/6 K/134 SiO₂, (3) 100 Fe/5 Cu/6 K/139 Al₂O₃ and (4) 100 Fe/10 Cu/6 K/134 Al₂O₃. The corresponding weight % of iron (as metal) in the prepared catalysts is approximately 33.8%.

References

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Figure A1-1 Steps in preparation of alumina or silica supported catalysts.

Appendix 2 Catalyst Characterization Equipment and Procedures

A2-1 Elemental Analysis

Catalyst bulk compositions were determined by Atomic Absorption Spectroscopy (AAS) using a Varian SpectrAA-30 spectrophotometer. For AAS analysis, a required amount of catalyst was dissolved in an acid mixture of hydrochloric (HCl) and hydrofluoric acid (HF) followed by dilution with distilled water to 100 ml. Portions of this sample were properly diluted and then the amounts of Cu, K, and Fe were determined by AAS. The composition of silica was determined either directly by the AAS method or by calculation method. In the latter method, the composition of silica in the catalyst was estimated indirectly using the measured amounts of Fe, Cu, and K and by assuming that oxides of these elements were in the form of Fe_2O_3 , CuO , and K_2CO_3 . The weight percent of SiO_2 was calculated from the equation:

$$\begin{aligned} W_{\text{SiO}_2} &= 100\% - W_{\text{Fe}} (M_{\text{Fe}_2\text{O}_3}/2M_{\text{Fe}}) - W_{\text{Cu}} (M_{\text{CuO}}/M_{\text{Cu}}) - W_{\text{K}} (M_{\text{K}_2\text{CO}_3}/2M_{\text{K}}) \\ &= 100\% - 1.43 W_{\text{Fe}} - 1.25 W_{\text{Cu}} - 1.77 W_{\text{K}} \end{aligned}$$

where: w_i is the weight percent of element i determined by AAS, M_i is the molecular (or atomic) weight of species i .

A2-2 BET Surface Area, Pore Volume and Pore Size Distribution Measurements

The BET surface area and pore volume measurements of the catalysts after calcination were obtained by nitrogen physisorption at 77 K using Micromeritics Digisorb 2600 system. The samples (~ 1-2 g) were degassed at 150°C for 12 h prior to each measurement. Surface area only was also determined using Pulse Chemisorb 2705 instrument (Micromeritics Inc.). Catalyst samples were outgassed in a flow of nitrogen (~ 30 cm^3/min) at 200°C for 3 to 12 h prior to each measurement.

A2-3 X-Ray Diffraction Measurements

Powder X-ray diffraction patterns of catalyst samples before pretreatment, after pretreatment, and after Fischer-Tropsch synthesis reaction (used catalysts) were obtained on a Scintag XDS-2000 diffractometer using $\text{CuK}\alpha$ radiation ($\lambda = 1.54 \text{ \AA}$) starting from $2\theta = 28^\circ$ to 68° at a rate of $1^\circ/\text{min}$. The pretreated and used catalyst samples from fixed bed and slurry reactor tests were handled in an inert atmosphere to prevent catalyst oxidation prior to and during XRD measurements.

Handling of Slurry Reactor Samples - No Extraction

A small portion (7-8 g) of a slurry sample withdrawn from the reactor was transferred into a small cylindrical vessel (sampling cylinder) which can be sealed air-tight. The sampling cylinder was transferred to a glove box filled with inert gas (Argon). The slurry samples for XRD analyses were removed in an inert atmosphere and washed with dry and warm Varsol solvent, until the filtrate (Varsol) was clear. After this the solid residue (catalyst plus some wax) is transferred into a sample holder or stored in a sample vial. The sample holder is sealed in the glove box and then placed directly in the X-ray diffractometer. The sample holders are made out of Plexiglas which does not yield any diffraction peaks. The above procedure prevents exposure of catalyst samples to an oxidizing environment.

Extracted Samples for X-ray Analysis

Catalyst samples from slurry reactor tests were separated from wax in an inert atmosphere according to the following procedure. A slurry sample (about 7-8 g), from the sampling cylinder was dispersed in 500 ml of 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 xylene. 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 pure Argon. The extraction apparatus was then taken out of the glove bag and the extraction is carried out first with 200 ml xylene

for 10 h, followed by methyl ethyl ketone (MEK) for another 10 h. The top of the condenser unit was closed so that no air could enter the system during the 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.

Fixed Bed Reactor Samples

At the end of reaction tests the reactor was sealed (air-tight) in an inert gas atmosphere and then transferred to a glove box. Catalyst samples removed from the top, bottom, and /or middle portions of the reactor were analyzed separately, after magnetic separation from glass beads (used as a diluent during FT synthesis) in a glove box. Such a separation was found to increase the intensity of the XRD peaks significantly.

Catalyst Passivation Procedure after Isothermal Reductions

After an isothermal reduction in a thermal gravimetric analyzer the catalyst sample was cooled to a room temperature in helium flow ($100 \text{ cm}^3/\text{min}$). Then a small stream (at a low flow rate) of purified air was introduced into the helium stream. Gradually the air flow was increased very slowly until a final oxygen content was about 20%. The passivation process was marked by the occurrence of small exotherms (typically 2-3 K) in the catalyst bed and subsequent return to room temperature. At the end of passivation the sample was loaded into a specially designed sample holder and analyzed by X-ray diffractometer.

A2-4 Mössbauer Effect Spectroscopy

The Mössbauer measurements were conducted at the University of Kentucky (The Consortium for Fossil Fuel Liquefaction Science) using a constant acceleration spectrometer of standard design. The radioactive source consisted of 50 - 100 mCi of ^{57}Co in a Pd matrix. The samples were in powdered form and were mounted in Plexiglas compression holders to present a thin aspect to the gamma ray beam. Calibration spectra of metallic iron were obtained simultaneously at the other end of the drive. The spectra were analyzed by least-

squares regression of a sum of Lorentzian lines to the experimental data. The hyperfine parameters (the isomer shift, the quadrupole splitting, and the magnetic hyperfine field) were obtained from the estimated line positions. Iron phases were identified by matching the observed values of the hyperfine parameters to those from literature .

A2-5 Temperature Programmed Reduction (TPR) Measurements

Temperature-programmed reduction (TPR) studies were performed using 5% H₂/95 %N₂ as reductant. In a typical TPR experiment about 10 to 20 mg of catalyst was packed in a quartz reactor and purged with helium to remove the moisture from the catalyst sample. Then the catalyst sample was heated in a flow of 5% H₂/95 %N₂ (flow rate of 40 cm³/min) from room temperature to 800-900°C at a heating rate of 20°C/min. Consumption of the 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. In order to quantify the degree of reduction, CuO standard was used for the calibration of the peak areas. All experiments were conducted in Pulse Chemisorb 2705 unit (Micromeritics Inc.) equipped with thermal conductivity detector and temperature programmable furnace for TPR/TPD studies.

A2-6 Isothermal Reductions by Thermogravimetric Analysis

Isothermal reduction in thermogravimetric analysis (TGA) experiments was conducted using approximately 20 mg catalyst samples. The catalyst sample was purged with helium (40 cm³/min) and temperature was ramped at a rate of 5°C/min from room temperature to a desired reduction temperature. Then the helium flow was switched to a reductant (hydrogen, carbon monoxide or synthesis gas) at 40-100 cm³/min, and the temperature was maintained at a constant value for a total period of up to 8 hours. The degree of reduction was calculated from the weight loss vs. time data. Experiments were conducted in a simultaneous TGA/DTA apparatus (TA Instruments, Model SDT 2960).

Appendix 3 Fixed and Slurry Bed Reactors and Product Analysis System

A3-1 Fixed bed reactor

Two fixed bed reactors were for screening tests of F-T catalysts. A simplified flow diagram of one of the existing reactors is shown in Figure A3-1. The reactor is a conventional downflow fixed bed reactor (1.3 cm inside diameter, effective length of 30 cm). Bed temperature is monitored through six thermocouples placed along the reactor. The reactor is heated externally with heating tapes wound around periphery of alumina blocks surrounding the stainless steel reactor. The reduction gas, an inert gas (helium or nitrogen), and/or a premixed synthesis gas passes through a series of oxygen removal, alumina, and activated charcoal traps to remove trace impurities. The gas flow rate is controlled using calibrated mass flow controllers, and the feed was preheated before entering the reactor. After leaving the reactor, the exit gas passes through a high pressure trap, which is maintained at about 90 - 150°C, to condense high molecular weight products. After releasing pressure through a back pressure regulator, the gas passes through a low pressure ice trap to collect any remaining condensibles. The flow rate of the tail gas exiting the system is measured frequently with a soap film flow meter.

During mass balance periods liquid products are allowed to accumulate in high and low pressure mass balance (steady state) traps. At the conclusion of the mass balance period, flow is directed to waste traps placed in parallel with the mass balance traps, and liquid products from the mass balance traps are collected and weighed. After startup, and following any change in process conditions, the reactor is allowed to operate undisturbed for 20 - 40 hours in order to achieve steady conditions before the next mass balance is performed. High molecular weight hydrocarbons (wax), collected in the high pressure trap, and liquid products, collected in the ice trap, are analyzed by gas chromatography.

Figure A3-1 Schematic diagram of fixed bed reactor system used for catalyst testing.

A3-2 Stirred Tank Slurry Reactor

A schematic representation of a 1 liter stirred tank slurry-phase reactor (Autoclave Engineers, Inc.) is shown in Figure A3-2. 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, a 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 line. The slurry level in the reactor is controlled by withdrawing accumulated slurry oil at the end of each mass balance period through a porous metal filter. 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. Slurry samples can be also withdrawn from the reactor through a dipleg tube for subsequent catalyst characterization.

During system startup, or during an unsteady period, the reactor effluent passes through the unsteady state trap. 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 state traps. 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

Figure A3-2 Schematic of stirred tank slurry reactor system.

equilibrate for at least 14 to 16 hours before obtaining material balances over an additional 8-12 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. All products collected in the steady state traps are analyzed by gas chromatography after physical separation into an aqueous and organic phase. Exit gas composition is determined by an on-line gas chromatograph, and wax from the reactor is analyzed on a capillary column (see below).

A3-3 Product Analysis

A versatile analytical and computerized data handling system consisting of four GC's linked to a data acquisition system is used for product analysis (Figure A3-3). In the gas effluent from the reactor unreacted H_2 , CO and product CO_2 and C_1 - C_5 hydrocarbon gases are analyzed on the Carle AGC-400 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 C_1 - C_6 alcohols, C_2 - C_4 aldehydes, C_3 - C_6 ketones and carboxylic acids. The water content is determined by Karl-Fischer titrator. The organic fraction is analyzed in a Varian 3400 GC for C_4 - C_{30} hydrocarbons, C_4 - C_{11} alcohols, C_3 - C_6 ketones, and C_2 - C_6 aldehydes. The wax fraction is dissolved in CS_2 or other organic solvents and is analyzed on the Varian 3400 for hydrocarbons up to C_{30} .

Several integrators are used to collect and integrate the data from all the GC's. The results are then transferred to a PC for further analysis and reduction. Mass balance program uses pull up templates to prompt the operator to enter the needed information. 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

Figure A3-3 Analysis of Fischer-Tropsch synthesis products with automated data acquisition and reduction system.

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 mass balance program also calculates Schulz-Flory chain growth parameters and produces Schulz-Flory plots.