Pretreatment Effect and Process Evaluation Studies of Precipitated Iron Fischer-Tropsch Catalysts

D. B. Bukur, X. Lang , M. Koranne and L. Nowicki
Department of Chemical Engineering
Texas A&M University
College Station, TX 77843-3122

Paper prepared for DOE Contractors' Review Meeting
Pittsburgh, PA, September 27-29, 1993

Contract DE-AC22-89PC89868
Duration: September 27, 1989 - September 26, 1993

INTRODUCTION

The objective of this contract is to develop catalysts with enhanced slurry phase activity and higher selectivity to fuel range products, through a better understanding and systematic studies of the effects of pretreatment procedures, promoters and binders (silica) on catalyst performance. The two main research tasks for this contract are Pretreatment Effect Research and Development of Improved Iron/Silica Catalysts. A brief description of progress in each of these areas is given below.

PRETREATMENT EFFECT RESEARCH

Prior studies in our laboratory (Bukur et al., 1987, 1988, 1989a) with a precipitated iron catalyst with nominal composition 100 Fe/3 Cu/0.2 K (in parts per weight) have shown that pretreatment conditions (nature of reductant, activation temperature, duration and pressure) have significant effect on catalyst activity, stability and selectivity during Fischer-Tropsch synthesis (FTS). During the present contract we have completed studies with three precipitated iron catalysts with nominal compositions 100 Fe/0.3 Cu/0.8 K, 100 Fe/5 Cu/4.2 K/25 SiO_2 (Ruhrchemie catalyst), and 100 Fe/5 Cu/4.2 K/ 16 SiO_2. Preliminary results from our studies with the first two of these catalysts have been reported at previous DOE Contractors' Meetings (Bukur et al., 1990c, 1991, 1992).

Pretreatment Studies with 100 Fe/0.3 Cu/0.8 K Catalyst

Catalyst Characterization Studies

The catalyst was characterized by a variety of physico-chemical methods (BET surface area and pore size distribution, X-Ray Diffraction, Mössbauer Effect Spectroscopy, and Transmission Electron Microscopy) before and after different pretreatments, and after Fischer-Tropsch synthesis in a fixed bed reactor at 250°C, 1.48 MPa (200 psig), 2 Nl/g-cat/h, $H_2/CO = 0.67$ for 140 - 200 h.

Results of BET measurements of pretreated catalyst samples are summarized in Table 1. The BET surface area of the catalyst decreased from 190 m^2/g to 130 m^2/g after calcination in air at 300°C for 5 hours, and further to 21-47 m^2/g after pretreatments in hydrogen, carbon monoxide or syngas. The pore volume decreased upon pretreatments in H_2 or CO, but remained unchanged after syngas pretreatment. The pore size distribution of as-prepared and pretreated catalyst was essentially monomodal, and shifted to larger pore diameters after H_2 or CO pretreatments. However, the syngas pretreated catalyst had a bimodal pore size distribution with maxima at 4 and 45 nm. Transmission electron micrographs of samples before and after different pretreatments reveal that particles are largely spherical. An increase in particle size was observed after H_2 reductions both by TEM and XRD analysis. The particle size increased with reduction temperature (e.g. 19 nm after H_2 reduction at 220°C, and 33 nm after reduction at 280°C).

X-ray diffraction (XRD) and Mössbauer effect spectroscopy (MES) were used to identify bulk iron phases in pretreated and used (after FT synthesis) catalyst samples. Calcined catalyst is in the form of α-Fe_2O_3 (~ 16 nm in diameter), which is converted to either metallic iron (α-Fe) or a mixture of α-Fe and Fe_3O_4 (magnetite) after H_2 reductions. During FT synthesis the α-Fe is carburized to iron carbides (χ- Fe_5C_2 or ε' - $Fe_{2.2}C$) or oxidized to magnetite. The gas environment is predominantly reducing at the top of the reactor (since the syngas is introduced at the top), and more oxidizing at the bottom of the reactor due to formation of water and carbon dioxide. Thus, the catalyst samples from the top part of the reactor contain relatively more iron carbides or metallic iron, whereas magnetite is found preferentially in samples from the bottom part of the reactor. Also, relative amounts of χ- Fe_5C_2 carbide are greater in the top part of the reactor than in the bottom part, whereas the opposite trend is observed for ε' - $Fe_{2.2}C$ carbide (Table 2).

After CO or syngas pretreatments, χ- Fe_5C_2 carbide (Hägg carbide) is the dominant phase. During FT synthesis this carbide is partially or completely converted to ε' - $Fe_{2.2}C$ carbide, Fe_3O_4, and/or $FeCO_3$ (siderite). Again it was found that the iron carbides are dominant in samples from the top part of the reactor (reducing atmosphere), whereas Fe_3O_4 or $FeCO_3$ are dominant iron phases in samples from the bottom part.

Temporal release of reduction products (water or carbon dioxide) was monitored continuously during H_2 and CO pretreatments by gas chromatography and mass spectroscopy (Figure 1). It was found that the reduction is very rapid initially (first 5 to 10 minutes), and then continues at a much lower rate. The reduction products were detected in the effluent gas after 8 hours of reduction at 280°C. This has been interpreted as a two step reduction process. The first (fast) step is the reduction of Fe_2O_3 to Fe_3O_4, which is followed by reduction of Fe_3O_4 to either metallic iron (H_2 reduction) or to an iron carbide (CO pretreatment). The second step is a slow one, and the reduction is not complete (H_2 reduction). The amount of CO_2 released during the CO pretreatment was greater than the stoichiometric amount needed for complete oxygen removal and complete carburization of iron in the catalyst. It is assumed that this is due to formation of carbonaceous deposits by Boudouard reaction.

Reaction Studies

The pretreatment conditions employed are listed in Table 3. After the pretreatment, the catalyst was tested in a fixed bed reactor at 200 psig (1.48 MPa), 250°C, 2 (Nl/g-cat/h) with syngas with H_2:CO molar ratio of 2:3. Test duration was between 130 and 200 h. Detailed description of our experimental apparatus, product analysis system and operating procedures can be found elsewhere (Bukur et al. 1989a; 1990 a, b).

Catalyst activity and stability, at the process conditions, as a function of time-on-stream (TOS) is shown in Figure 2. The activity is represented by (H_2+CO) conversion (defined as mole of syngas consumed per mole of syngas fed). The catalyst exhibited similar activity behavior after pretreatments with carbon monoxide (280°C for 8 h) or syngas (both $H_2/CO = 0.7$ at 280°C for 8 h and $H_2/CO = 2.0$ at 310°C for 6 h). Initial (H_2+CO) conversion was between 85 and 93%. However, the catalyst deactivated with time-on-stream, following a similar time-dependent behavior in all three cases. The (H_2+CO) conversion decreased to about 55 % at 150 h on stream.

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

Catalyst activity after reduction with hydrogen was clearly dependent on the reduction conditions employed (temperature, duration and flowrate). After reduction at 250°C, flowrate 4000 cc/min (which corresponds to a linear gas velocity of 150 cm/s) for 2 h, the initial (H_2+CO) conversion was 77 %; whereas after reduction at higher temperature of 280°C, flowrate 175 cc/min (which corresponds to a gas space velocity of 3.0 Nl/g-cat/h) for 8 h the (H_2+CO) conversion was only about 50 %. During the FT synthesis, the (H_2+CO) conversion increased steadily with time reaching 85 and 58 %, respectively. Such time-dependent behavior is in contrast to that observed following CO or syngas pretreatment.

After reduction at 250°C, 4000 cc/min for 2h the catalyst was completely reduced to metallic iron and was very active in the subsequent synthesis. After reduction at higher temperature (280°C, 175 cc/min for 8h) the reduction was incomplete (mostly magnetite) and the catalyst activity was much lower. Surface area of the calcined catalyst was 130 m^2/g, after H_2 reduction at 250°C and 280°C, it drops to only 21 m^2/g in both cases, which indicates that sintering of Fe_2O_3 particles to Fe or Fe_3O_4, though very severe, is similar at two temperatures. Therefore, the difference in catalyst activity is mainly related to the initial degree of iron reduction. Completely reduced catalyst is more active for FT synthesis. Used catalyst samples contain two types of iron carbides (χ and ϵ'), and superparamagnetic oxides/hydroxides (probably magnetite, based on XRD results). The more active catalyst (H_2 reduction at 250°C) also has some α-Fe (Table 2), whereas the less active catalyst does not contain metallic iron.

Another explanation for the observed differences in catalyst activity has been proposed by Sault (1991), on the basis of surface composition measurements by Auger Electron Spectroscopy. This study was conducted at Sandia National Laboratory using a catalyst synthesized in our Laboratory with nominal composition 100 Fe/3 Cu/0.2 K. In this study it was found that H_2 reductions are accompanied by sulfur migration to the surface of the catalyst. The sulfur arises from bulk sulfate impurities present in the metal nitrates used to prepare the catalyst. Sulfur coverage increases with both activation time and temperature, due to an increase in the rate of sulfur diffusion with temperature. Since sulfur is known to act as a poison for FT synthesis, the catalyst reduced at higher temperature and/or longer duration is expected to have lower FT activity, which is indeed observed in our studies with both 100 Fe/3 Cu/0.2 K and 100 Fe/0.3 Cu/0.8 K catalysts.

Hydrocarbon product distribution and the fraction of olefins in hydrocarbons for each of the five pretreatment procedures are given in Table 3. Hydrocarbon selectivity remained relatively stable in tests in which hydrogen reductions were employed. After CO or syngas pretreatment, hydrocarbon selectivity usually shifted towards lower molecular weight hydrocarbons, especially methane, as the catalyst deactivated with time. For example, methane selectivity gradually increased from 4.3 to 5.0 wt % between 70 to 150 h on stream in test FB-0352 (i.e. the increase of about 16 %). Low methane and gaseous hydrocarbon selectivities, and high C_{12+} selectivities were obtained when CO and/or syngas pretreatments were employed. CO pretreated catalyst had the lowest methane selectivity. On the other hand, hydrogen reduced catalyst produced more methane and other low molecular weight products. The highest methane selectivity, about 9 %, was obtained following reduction with H_2 at 250°C.

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

Pretreatment Studies with Ruhrchemie Catalyst

Catalyst Characterization Studies

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

The as-received catalyst had the BET surface area of 295 m^2/g and the pore volume of 0.58 cm^3/g, both of which remained unchanged (within experimental errors) after calcination in air at 300°C for 5 hours (Table 5). After different pretreatments with H_2, CO or syngas both the BET surface area and the pore volume of the catalyst decreased, while the average pore diameter increased. The surface area of the pretreated catalysts ranged from 100 to 180 m^2/g, whereas the pore volume varied from 0.31 to 0.49 cm^3/g. The decrease in the surface area and the pore volume is attributed to a partial collapse of the porous iron oxide/hydroxide network, which is stabilized by the presence of silica. In the absence of silica the surface areas of pretreated precipitated iron catalysts are between 10 and 40 m^2/g (Bukur et al., 1989b, also see Table 1). The pore size distribution of as-received and pretreated catalyst was rather broad with a maximum at about 20 nm, which shifted slightly to higher values after H_2 or CO pretreatments. The catalyst, before and after pretreatments, also had micropores less than 1.5 nm (the lower limit of detection) in diameter.

Transmission electron micrographs of calcined sample and samples after pretreatments with either H_2 at 220°C or CO at 280°C reveal that particles are small and spherical (~ 3.5 nm). An increase in particle size was observed after H_2 reductions by X-ray line broadening method. The particle size increased with reduction temperature (e.g. 5 nm after H_2 reduction at 220°C, and 10 nm after reduction at 280°C for 8 hours).

The extent of bulk iron reduction following H_2 and CO pretreatments was studied by isothermal reduction. The isothermal reduction profiles (Figure 3) indicate that the reduction occurs in two steps: Facile reduction of Fe_2O_3 to Fe_3O_4, followed by slow reduction of Fe_3O_4 to either metallic iron (H_2 reduction) or an iron carbide (CO pretreatment). The first step is completed in about 15-30 minutes, whereas the second step is not complete even after 8-10 hours . The amount of CO_2 released during the CO pretreatment at 280°C was greater than the stoichiometric amount needed for complete oxygen removal and complete carburization of iron in the catalyst. It is assumed that this is due to formation of carbonaceous deposits by Boudouard reaction.

X-ray diffraction (XRD) and Mössbauer effect spectroscopy (MES) were used to identify bulk iron phases in pretreated and used (after FT synthesis) catalyst samples. After H_2 reductions the bulk iron is in the form of either Fe_3O_4 (magnetite) - reduction at 220°C, or a mixture of Fe_3O_4 and α-Fe (reductions at 280°C). During FT synthesis the iron carbides (χ- Fe_5C_2 or ε' - $Fe_{2.2}C$) are formed by carburization of α-Fe and/or Fe_3O_4. The used catalysts contain iron carbides and magnetite (Table 6).

After CO or syngas pretreatments, the χ- Fe_5C_2 carbide and superparamagnetic oxides are the only phases present (Table 6). The latter is probably in the form of small magnetite particles, which needs to be confirmed by MES measurements at low temperatures. During FT synthesis this carbide is partially converted to magnetite. Iron carbide content is higher in samples from the top part of the reactor (reducing atmosphere), whereas magnetite and superparamagnetic oxides are the dominant iron phases in samples from the bottom part (more oxidizing atmosphere).

Reaction Studies

Six different pretreatment procedures were employed in the fixed bed reactor (FBR) tests, and another two in a stirred tank slurry reactor (STSR) tests. Test identifications and pretreatment conditions are listed in Table 7. After the pretreatment, the catalyst was tested at baseline process conditions: 250°C, 1.48 MPa (200 psig), 2.0 Nl/g-cat/h (3.8 Nl/g-Fe/h) with syngas H_2:CO ratio of 2:3 (0.67) in both fixed bed and slurry phase reactors. Results from the fixed bed reactor tests only are discussed in this paper.

During the steady state FT synthesis, the catalyst was most active after it was reduced according to the manufacturer's procedure, i.e. H_2 at 220°C, superficial gas velocity of 150 cm/s (corresponding to 4,000 cc/min) for 1 h. The syngas (H_2+CO) conversion was about 72-73% (Figure 4). After reduction at higher temperature of 280°C for 1h, but maintaining the same H_2 flowrate, the syngas conversion was significantly lower, 63 % . When the catalyst was reduced at 280°C using a much lower H_2 flowrate (correspondiing to a gas space velocity of 3.0 Nl/g-cat/h) for 8 h and 24 h, respectively, the syngas conversion decreased further. After 8 h reduction the initial syngas conversion (1 h at the process conditions) was only 47 %; it then continued to increase with time, reaching 62 % at 154 h on stream. After 24 h reduction the initial syngas conversion was somewhat higher, 54 %, and it increased with time to stabilize at about 58 %. Thus, the steady state activities after 8 h and 24 h H_2 reductions at 280°C were similar. The corresponding values of the apparent reaction rate constant are listed in Table 8, and they follow the same trend as syngas conversions. All four H_2 reduction procedures led to either a stable or gradually increasing activity during the synthesis.

Activity of the catalyst reduced at 220°C was about 20% higher than that of the catalyst reduced at 280°C for 24 hours. This is believed to be due to higher surface area (smaller crystallite size) of the catalyst reduced at low temperature, and differences in catalyst composition (bulk iron phases, as well as on the surface of the catalyst) during the FT synthesis.

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

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

The effect of pretreatment conditions on hydrocarbon product distributions is illustrated in Table 8. The catalyst selectivity remained relatively stable between 70 and 170 h on stream. The CO activated catalyst had the lowest methane selectivity (~5.6 %). The catalyst reduced with H_2 at 220°C for 1 h also had relatively low methane selectivity (6.2 %), and had the lowest selectivity to C_2-C_4 hydrocarbons (17.4 %). These two pretreatment procedures resulted in high $C_{12}+$ selectivities, about 55.6% (H_2 at 220°C) and 52.2 % (CO activation). Hydrocarbon selectivities were similar following three procedures using hydrogen reduction at 280°C with different flowrates and/or durations. In all three cases, methane selectivity was high (8.8 to 10.4 %), whereas the $C_{12}+$ selectivity was low, only 32 to 36 %. The syngas pretreatment gave an intermediate behavior: 7 % methane selectivity and 43 % $C_{12}+$ selectivity.

Pretreatment Studies with 100 Fe/5 Cu/4.2 K/ 16 SiO_2 Catalyst

This catalyst is one of the silicon oxide containing catalysts prepared in our laboratory which has shown desirable properties (activity, selectivity and stability) during a screening test in a fixed bed reactor. Three pretreatment procedures were used to study their effect on subsequent catalyst performance in a stirred tank slurry reactor. Test designations and pretreatment conditions are listed in Table 9.

The synthesis gas conversions following the pretreatment are shown in Figure 5 for the three tests. Results from testing at the baseline conditions (260°C, 1.48 MPa, 1.5 Nl/g-cat/h. $H_2/CO= 0.67$) and at higher pressure (2.17 MPa, i.e. 300 psig) are shown in this figure. It can be seen that after H_2 reduction (SB-2832) the initial (H_2+CO) conversion was high (84 % at 17 h on stream). The syngas conversion gradually decreased with time to 77 % at 263 h, for a loss in conversion of about 0.68% per day. During testing at 2.17 MPa and 2.2 Nl/g-cat/h (same absolute pressure to gas space velocity ratio, which results in the same contact time as at the baseline conditions), the syngas conversion continued to decrease gradually with time. For example, at 284 h and 480 h on stream, the syngas conversion was 74 and 69 %, respectively.

In test SA-3172 (syngas pretreatment) the (H_2+CO) conversion was 84 - 87 % during the first 55 h on stream. At this time the Autoclave reactor head temperature was decreased from 260 to 210°C in an attempt to control the unusually high methane selectivity (about 9.5 wt%). Following this the syngas conversion decreased and stabilized at about 30 % (70 - 105 h on stream). After changing the reaction pressure and gas space velocity to 2.17 MPa and 2.1 Nl/g-cat/h, respectively, the syngas conversion first increased to 83 % at 115 h, then gradually decreased and leveled to about 79 % at 194 h. Upon returning to the baseline conditions at 200 h on stream, the (H_2+CO) conversion stabilized at 78 %. The latter value is comparable to those obtained between 80 -100 h on stream. Regeneration with H_2 at 250°C, 1.48 MPa, 2000 cc/min for 4 h resulted in a temporary increase of conversion followed by a decline to 74% at 336 h on stream.

Catalyst activity immediately after CO pretreatment in test SB-3362 was low (not shown in Figure 5) because of the loss of slurry liquid, and the reaction was temporarily interrupted. The catalyst activity increased quickly after a sufficient amount of liquid was added and synthesis gas flow resumed at 39 h. The (H_2+CO) conversion was fairly stable (71 - 74 %) between 70 and 230 h on stream. During testing at 2.17 MPa and 2.2 Nl/g-cat/h (the same P/SV ratio as at the baseline conditions), the syngas conversion was lower, about 65 - 67 %. Upon returning to the baseline conditions (407-488 h) the (H_2+CO) conversion increased to 70 %. The latter value is comparable to those obtained between 70 and 230 h on stream. The catalyst activity was fairly stable during the test after the initial upset, and the loss of conversion was only 0.24 % per day. However, the catalyst was not properly activated because of the loss of the liquid medium, and interruption of synthesis during the early part of the testing may have had a detrimental effect on catalyst activity.

The reactor productivity increased in all three tests during testing at higher pressure (Table 10). An increase in reaction pressure of 46.5% (from 1.48 to 2.17 MPa) accompanied by simultaneous equivalent increase in gas space velocity (from 1.5 to 2.2 Nl/g-cat/h) resulted in increase of the space-time-yield (STY) ranging from 32% (H_2 reduced catalyst) to 47% (syngas pretreated catalyst). Obviously, these results provide a strong incentive for carrying FT synthesis at higher reaction pressures and gas space velocities. This, however, may result in faster catalyst deactivation and thus shorter catalyst lifetime.

Hydrocarbon selectivities as a function of TOS for each of the pretreatment procedures are shown in Figure 6. In these figures, cumulative values are shown for lumped product distributions of selected product groups: methane, C_1-C_4, and C_1-C_{11}. Distances between numerical values for these groups show mass percentage of: methane, C_2-C_4 (light gases), C_5-C_{11} (gasoline) and C_{12+} (diesel and wax) hydrocarbon products. There were no significant changes in hydrocarbon product distributions during testing at the baseline conditions in all three tests. An increase in reaction pressure, from 1.48 to 2.17 MPa, either had no effect on hydrocarbon product distribution (SB-2832) or resulted in slight decrease of low molecular products (Runs SA-3172 and SB-3362) and the corresponding increase of C_{12+} products. The effect of pressure was the most pronounced in run SB-3362 (CO pretreatment), in which methane selectivity decreased from 3.5 to 2.9 wt% whereas C_{12+} increased from 59.5 to 63.7 %. In runs SB-2832 and SA-3172, the catalyst was also regenerated with H_2 during the test. In run SB-2832 hydrocarbon selectivity did not change after regeneration with H_2 at 240°C for 1 h (at 666 h on stream). However, hydrocarbon selectivity shifted significantly toward gaseous hydrocarbons in run SA-3172 after regeneration with H_2 at 250C for 4 h (at 223 h on stream), as shown in Figure 6b. Regeneration conditions were more severe in the latter case, which is probably the reason for the observed change in hydrocarbon selectivity.

The effect of pretreatment procedure on hydrocarbon selectivity is shown in Table 10. In this table the average values from mass balances at the baseline conditions (up to 240 h on stream) and at higher reaction pressure are used for comparison. The catalyst had low methane and high C_{12+} selectivity after either CO or H_2 pretreatment. The average hydrocarbon product distribution at the baseline conditions after CO pretreatment was: CH_4 = 3.5 wt%, (C_2-C_4) = 15.8 %, (C_5-C_{11}) = 21.2 % and C_{12+} = 59.5 %; whereas after H_2 reduction it was: CH_4 = 4.6 wt%, (C_2-C_4) = 15.5 %, (C_5-C_{11}) = 22.0 % and C_{12+} = 57.9 %. Hydrocarbon selectivities were similar after these two pretreatment procedures. On the other hand, in run SA-3172, following syngas pretreatment, the catalyst produced significantly more methane and light gases. In this test the average hydrocarbon product distribution at the baseline conditions was: CH_4 = 10.4 wt%, (C_2-C_4) = 18.2 %, (C_5-C_{11}) = 19.8 % and C_{12+} = 51.6 %. This is completely unexpected, based on our previous studies with several precipitated iron catalysts. The syngas pretreated catalysts normally do not produce high yields of methane and gaseous hydrocarbons (e.g. see Bukur et al., 1989a, and results for 100 Fe/0.3 Cu/0.8 K and Ruhrchemie catalysts).

IRON/SILICA CATALYSTS

Performance of silica containing iron Fischer-Tropsch catalysts of nominal composition 100 Fe/5 Cu/4.2 K/x SiO_2 (x=0,8,24 and 100) was evaluated in our laboratory (Bukur et al., 1989b; 1989 c; 1990b). It was found that these catalysts are suitable for production of transportation fuels by minimizing methane and gaseous hydrocarbon selectivities. The objective of current contract is to determine optimal concentrations of promoters (CuO, K_2O) and SiO_2 binder to achieve the specified catalyst performance (Table 11).

Results from STSR tests of some of the best silica containing precipitated iron catalysts synthesized in our laboratory are shown in Figures 7 and 8. Variations in (H_2+CO) conversion with TOS for three catalysts (designated A,B and C) are shown in Figure 7. Process conditions in all tests were: 260°C,1.48 MPa,H_2/CO=0.66-0.70, whereas gas space velocity varied between 2.2 and 3.4 Nl/g-Fe/h . In two of the tests (Catalysts A and C) process conditions were varied during the test, however results from these periods are not shown. Three types of catalyst behaviour were observed in these tests. Catalyst A had initially high conversion (~ 88%), but its activity decreased gradually with TOS. During the test of Catalyst B, the (H_2+CO) conversion was initially about 81% decreasing to 76% at 150 h on stream. Between 160 and 240 h the catalyst was tested at 265°C (results not shown in Figure 7), and it continued to deactivate. Upon returning to the baseline conditions, the activity became stable as evidenced by nearly constant value of (H_2+CO) conversion (66-68%) between 240 and 530 h on stream. In the test of catalyst C gas space velocity was decreased twice to obtain higher conversions . At a constant gas space velocity (3.4 and 3.0 Nl/g-Fe/h) the activity increased slightly with time up to about 390 h. During the last portion of the test (400-500 h) at gas space velocity of 2.3 Nl/g-Fe/h the catalyst exhibited some deactivation. Deactivation rates of catalysts A,B and C were estimated to be: 1.7,1.2 and 1.1 % per day, respectively. These estimates are rather conservative, and are based on the initial catalyst activity (Bukur et al., 1991).

Performance of all three catalysts was somewhat below specified target values shown in Table 11. For example, the (H_2+CO) conversions were between 68 and 88% and catalyst productivities varied between 1.5 and 2.5 Nm^3 (H2+CO) converted/kg-Fe/h, whereas the corresponding target values are 88% and 2.5, respectively. It should be noted that these measures do not necessarily reflect the intrinsic catalyst activity. For a given catalyst these two measures (conversion and catalyst productivity) depend on the reactor type (e.g. fixed bed, STSR or bubble column slurry reactor-BCSR) and process conditions employed.

Selectivities of methane and (C1+C2) hydrocarbons obtained in tests of these three catalysts are shown in Figure 8. In tests of Catalysts A and B selectivities of methane and (C1+C2) hydrocarbons increased gradually with TOS, whereas in the test of catalyst B these two selectivities passed through a maximum at about 150 h. Methane selectivity of all three catalysts was less than 3%,whereas (C1+C2) selectivity was less than 7% throughout the entire test. The latter value is within the specified target performance.

Performance of our catalyst B is compared with that of other catalysts tested in our laboratory and elsewhere, and the relevant results are presented in Table 12. As can be seen performance of our catalyst B was very similar to that of the best Mobil's catalyst in the wax mode of operation (Kuo,1985). The latter catalyst was tested in a bubble column slurry reactor (BCSR), the behaviour of which approaches that of a plug flow reactor. Our catalyst B was significantly more active than the Mobil's catalyst used in run CT-256. We have chosen an apparent first order reaction rate constant evaluated at a common temperature of 260°C, as a measure of catalyst activity. STSR was modeled as a perfectly mixed flow reactor, whereas the rate constant from a BCSR was estimated using a model which assumes that the gas phase is in plug flow and the liquid is unmixed (Bukur, 1983). The catalyst B was also more active than Ruhrchemie,UCI and UOP (Abrevaya et al.,1991) catalysts, and it produced less methane and gaseous hydrocarbons than these catalysts.

In summary, two of iron FTS catalysts synthesized in our laboratory (catalysts B and C) have met specified performance targets for hydrocarbon selectivity and catalyst stability. Syngas conversion and catalyst productivity targets have not been met by a small margin only. The latter targets are very difficult to achieve in a stirred tank slurry reactor. However, simple calculations show that both catalysts would exceed these targets in a BSCR.

Acknowledgements

The work on development of iron/silica catalysts was supported in part by the Texas Advanced Technology Program under Grant No. 999903-222. We are grateful to the U.S. DOE/PETC for financial support of our studies of Fischer-Tropsch synthesis over iron catalysts. Mössbauer Effect Spectroscopy measurements and data analysis were made at the University of Kentucky (Consortium for Fossil Fuel Liquefaction Science).

Literature Cited

Abrevaya, H., Frame, R. R. and Targos, W. M. "Technology Development for Iron-Fischer Tropsch Catalysts," Liquefaction Contractors' Review Meeting Proc., pp 219-235, Pittsburgh, Pennsylvania, September 3-5, 1991.

Bukur, D. B., "Some Comments on Models for Fischer-Tropsch Reaction in Slurry Bubble Column Reactors," Chem. Eng. Sci. 38, 441-446 (1983).

Bukur, D. B., et al., "Activation and Promotion Studies in Fixed Bed Reactors with Precipitated Iron Fischer-Tropsch Catalyst" in Proceedings of Seventh Indirect Liquefaction Contractors' Review Meeting, Vol I, pp.41-68, Pittsburgh, Pennsylvania, December 7-9, 1987.

Bukur, D. B., Lang, X., Patel, S. A., Zimmerman, W. H., Rosynek, M. P. and Withers, H. P., "Development and Process Evaluation of Improved Fischer-Tropsch Slurry Catalysts," Indirect Liquefaction Contractors' Review Meeting Proceedings, pp. 453-482, Pittsburgh, Pennsylvania, November 15-17, 1988.

Bukur, D. B., Lang, X., Rossin, J. A., Zimmerman, W. H., M. P., Yeh, E. B., and Li, C. "Activation Studies with a Promoted Precipitated Iron Fischer-Tropsch Catalyst," Ind. Eng. Chem. Research, 28, 1130-1140 (1989a).

Bukur, D.B., Mukesh, D., Patel, S.A., Rosynek, M.P., Zimmerman, W.H., "Development and Process Evaluation of Improved Fischer-Tropsch Slurry Catalysts", Final

Report prepared for Air Products and Chemicals, Inc., under DOE Contract No. DE-AC22-85PC8011, 1989b: Texas A & M University, College Station, TX.

Bukur, D. B., Rosynek, M. P., Patel, S. A., Mukesh, D. and Withers, H. P., "Promoter and Binder/Support Effects on the Activity and Selectivity of Iron/Fischer-Tropsch Catalysts," Indirect Liquefaction Contractors' Review Meeting Proc, pp. 157-192, Pittsburgh, PA, November 13-15, 1989c.

Bukur, D. B., Mukesh, D. and Patel, S. A., "Promoter Effects on Precipitated Iron Catalysts for Fischer-Tropsch Synthesis," Ind. Eng. Chem. Research, 29, 194-204 (1990a).

Bukur, D. B., Lang, X., Mukesh, D., Zimmerman, W. H., Rosynek, M. P., and Li, C. "Binder/Support Effect on the Activity and Selectivity of Iron Catalysts in the Fischer-Tropsch Synthesis," Ind. Eng. Chem. Research, 29, 1588-1599 (1990b).

Bukur, D. B. Ledakowics, S. and Manne, R., "Fischer-Tropsch Synthesis over Iron/Silica Catalysts," in Proc. of Indirect Liquefaction Contractors' Review Meeting, pp. 221-244, Pittsburgh, PA, November 6-8, 1990c.

Bukur, D. B., Nowicki, L., Manne, R. K. and Lang X., "Development of Improved Fischer-Tropsch Catalysts-Part II," Liquefaction Contractors' Review Meeting Proc., pp.236-253, Pittsburgh, Pennsylvania, September 3-5, 1991.

Bukur, D. B., Nowicki, L., Lang X. and Skala, D., "Development of Improved Fischer-Tropsch Catalysts-Part III," Liquefaction Contractors' Review Meeting Proc., pp.493-516. Pittsburgh, Pennsylvania, September 22-24, 1992.

Kölbel, H., and Ralek, M. "The Fischer-Tropsch Synthesis in the Liquid Phase," Catal. Rev.-Sci. Eng. 21, 225-274 (1980).

Kuo, J. C. W., "Two Stage Process for Conversion of Synthesis Gas to High Quality Transportation Fuels," Final Report by Mobil R&D Co. for DOE Contract No. DE-AC22-83PC600019 (1985).

Sault, A. G., "An Auger Electron Spetroscopy Study of the Activation of Iron Fischer-Tropsch catalsyst", Indirect Liquefaction Contractors' Review Meeting. Proc., pp.324-336, Pittsburgh, September 3-5, 1991.

Table 1 Summary of BET Results of Pretreated 100 Fe/0.3 Cu/0.8 K Catalyst Samples.

RUN NO.	PRETREATMENT CONDITIONS	SURFACE AREA (m^2/g)	PORE VOLUME (cc/g)	PORE DIAMETER[a] (nm)
As prepared	None	190	0.33	7
Calcined	Air, 300°C, 5 h	130	0.36	11
FA-2451	H_2, 220°C, 1h, 3550 cc/min	48	0.25	21
FA-2491	H_2, 250°C, 2h, 3550 cc/min	21	0.20	38
FA-2751	H_2, 280°C, 8h, 85 cc/min	21	0.28	54
FA-2531	CO, 280°C, 8h, 85 cc/min	44	0.25	23
FA-2501	H_2/CO=0.67, 280°C, 8h, 85 cc/min	34	0.30	35
FA-2551	H_2/CO=2, 310°C, 6h, 1200 cc/min	47	0.36	31

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

Table 2 Summary of MES Results of 100 Fe/0.3 Cu/0.8 K Catalyst Sample

PRETREATMENT CONDITIONS	RELATIVE AMOUNTS OF PHASES (%)	
	REDUCED CATALYST	AFTER FT SYNTHES
H_2, 250°C, 2 h 3550 cc/min	100 (α-Fe)	Top: 13 (Spm); 64 (χ-C) 21 (α-Fe) Bott: 8 (Spm); 14 (M); 7 (χ-C); 71 (ε'-C)
H_2, 280°C, 8 h 85 cc/min	α-Fe; M (XRD)	Top: 7 (Spm); 36 (χ-C); 57 (ε'-C) Bott. 5 (χ-C). 95 (ε'-C)
CO, 280°C, 8 h 85 cc/min	13 (Spm); 87 (χ-C)	Avg: 2 (Spm); 50 (M); 43 (ε'-C); 5 (S)
H_2/CO=0.7, 280°C, 8 h, 85 cc/min	16 (Spm); 84 (χ-C)	Top: 6 (Spm); 94(χ-C) Bott: 9 (Spm); 59 (M); 32(ε'-C)
H_2/CO=2, 310°C, 6 h, 1200 cc/min	5 (Spm), 95 (χ-C)	Top: 35 (Spm); 65 (χ-C Bott: 100 (S)

Spm=Superparamagnetic iron oxide/hydroxide; M=Magnetite; χ-C=χ-Carbide; ε'-C=ε'-Carbide; S=Siderite

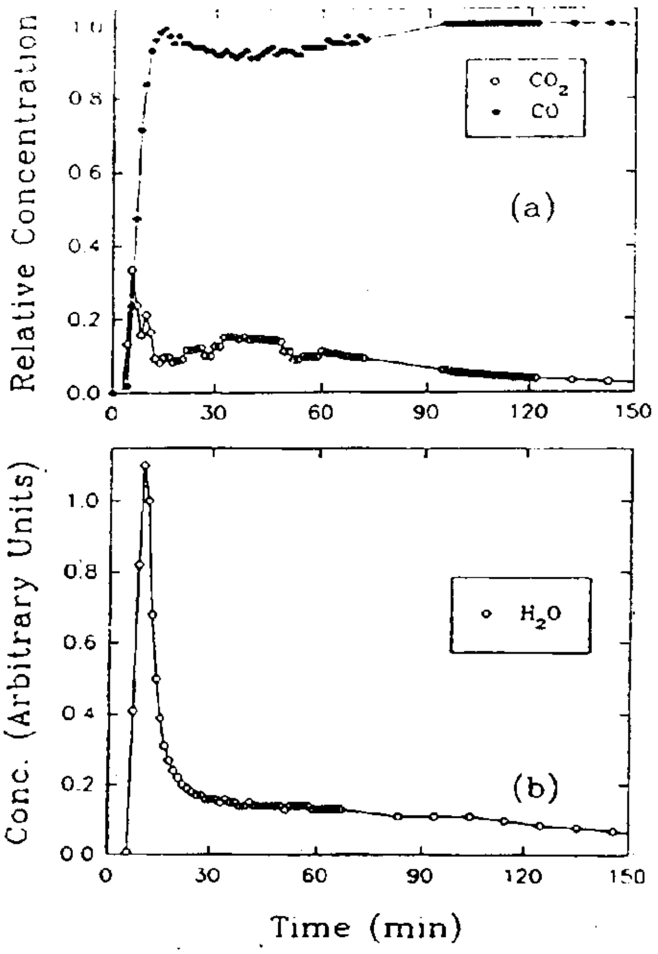

Figure 1. Isothermal reduction profiles of 100 Fe/0.3 Cu/0.8 K catalyst at 280°C as a function of duration of reduction: a) CO reduction; b) H_2 reduction.

Table 3 Pretreatment Conditions and Test Designations
Catalyst: 100 Fe/0.3 Cu/0.8 K

Test (ID)	Temp. (°C)	Reductant	Duration (h)	Pressure (MPa)	Flowrate (cm^3/min)
FB-0403	250	H_2	2	0.1	4,000
FB-3221	280	H_2	8	0.1	175
FB-0352	280	H_2/CO=0.7	8	0.1	150
FB-0942	310	H_2/CO=2.0	6	0.1	1,200
FB-0021	280	CO	8	0.1	175
SA-0791	250	H_2	2	0.8	7,500
SB-2262*	280	H_2/CO=0.7	12	0.8	343

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

* Different catalyst batch used in this test

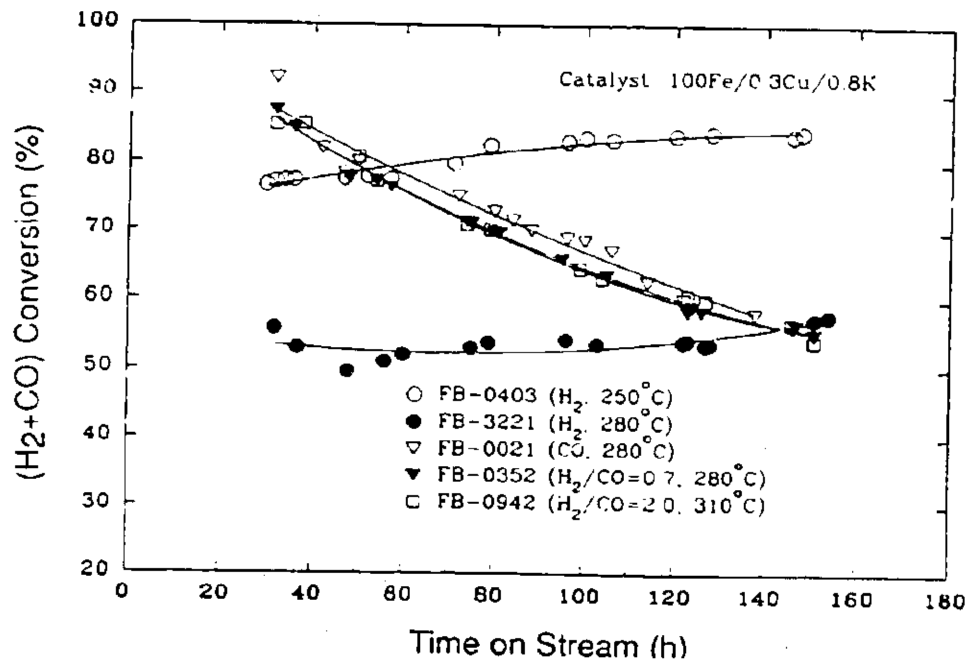

Figure 2. Effect of pretreatment conditions on conversion and catalyst stability

Table 4 Summary of Results for Pretreatment Effect Study with 100 Fe/0.3 Cu/0.8 K Catalyst

Test designation	FB-0403		FB-3221		FB-0352		FB-0942		FB-0021	
Time-on-stream, h	67	116	72	149	72	144	62	134	68	92
CO conversion, %	86.4	89.5	56.0	61.0	76.8	59.7	72.8	57.5	73.0	70.1
(H_2+CO) conversion, %	81.4	84.3	54.1	58.2	70.7	55.7	70.7	56.6	70.0	67.6
STY, mmol/g-cat/h	73	75	48	52	63	50	63	50	63	60
k, mmol/g-Fe/h/MPa[a]	218	229	134	142	177	134	190	142	180	171
(H_2/CO) usage ratio	0.61	0.61	0.60	0.60	0.59	0.59	0.64	0.64	0.61	0.61
(H_2/CO) exit ratio	1.30	1.54	0.74	0.80	1.18	0.86	0.79	0.74	0.82	0.81
$K_p = P_{CO_2}P_{H_2}/P_{CO}P_{H_2O}$	77.0	78.1	46.1	48.0	20.0	17.8	5.60	4.10	18.0	15.0
mmol CH_4/g-Fe/h	2.44	2.44	1.23	1.35	1.11	1.00	1.21	1.00	1.00	0.89
Hydrocarbon selectivity (wt%)										
CH_4	9.1	8.4	6.8	6.8	4.3	5.0	4.4	4.8	3.1	3.7
C_2-C_4	26.5	24.4	23.0	22.4	18.6	20.6	18.8	19.5	18.1	18.2
C_5-C_{11}	41.3	41.7	37.8	30.2	23.1	24.0	24.6	24.0	23.5	22.5
C_{12+}	23.1	25.5	32.4	40.6	54.0	50.4	52.2	51.7	55.3	55.5
Chain growth parameter, α_{1-10}	0.73	0.75	0.72	0.70	0.72	0.73	0.75	0.73	0.77	0.75
Olefin content (wt%)										
C_2-C_4	75.2	73.2	77.3	76.3	79.8	78.0	81.3	80.2	81.3	81.5
C_5-C_{11}	73.0	72.7	70.9	71.8	85.2	84.6	65.1	85.6	80.6	82.1

Process conditions 250°C, 1.48 MPa (200 psig), 2.0 Nl/g-cat/h, H_2/CO=0.67

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

Table 5 Summary of BET Results of Pretreated Ruhrchemie Catalyst Samples.

RUN NO.	PRETREATMENT CONDITIONS	SURFACE AREA (m^2/g)	PORE VOLUME (cc/g)	PORE DIAMETER[a] (Å)
As prepared	None	295	0.58	79
Calcined	Air, 300°C, 5 h	290	0.62	86
FA-2351	H_2, 220°C, 1h, 3550 cc/min	179	0.46	103
FA-2391	H_2, 280°C, 1h, 3160 cc/min	136	0.42	124
FA-1821	H_2, 280°C, 8h, 125 cc/min	160	0.49	122
FA-1801	CO, 280°C, 8h, 125 cc/min	118	0.34	115
FA-2551	H_2/CO=2, 310°C, 6h, 1200 cc/min	99	0.31	125

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

Table 6 Summary of MES Results of Ruhrchemie Catalyst Samples.

PRETREATMENT CONDITIONS	RELATIVE AMOUNTS OF PHASES (%)	
	REDUCED CATALYST	AFTER FT SYNTHESIS
H_2, 220°C, 1h 3550 cc/min	100 (Spm)	Top: Fe_xC, Fe_3O_4 (XRD) Bott: Fe_xC, Fe_3O_4 (XRD)
H_2, 280°C, 1 h 3160 cc/min	87 (Spm); 13(α-Fe)	Top: Fe_xC (XRD) Bott: Fe_xC, Fe_3O_4 (XRD)
H_2, 280°C, 8 h 125 cc/min	86 (Spm); 6 (M); 8 (α-Fe)	Top: Fe_xC (XRD) Bott: Fe_xC (XRD)
CO, 280°C, 12 h 125 cc/min	46 (Spm); 54 (χ-C)	Avg: 27 (Spm); 68 (M); 5 (α-Fe)
H_2/CO=2, 310°C, 6 h, 1200 cc/min	46 (Spm); 54 (χ-C)	Top: 63 (Spm); 37 (χ-C) Bott: 45 (Spm), 38 (M), 17 (χ-C)

Spm=Superparamagnetic iron oxide/hydroxide; M=Magnetite; χ-C=χ-Carbide;
Fe_xC=Iron Carbide(s)

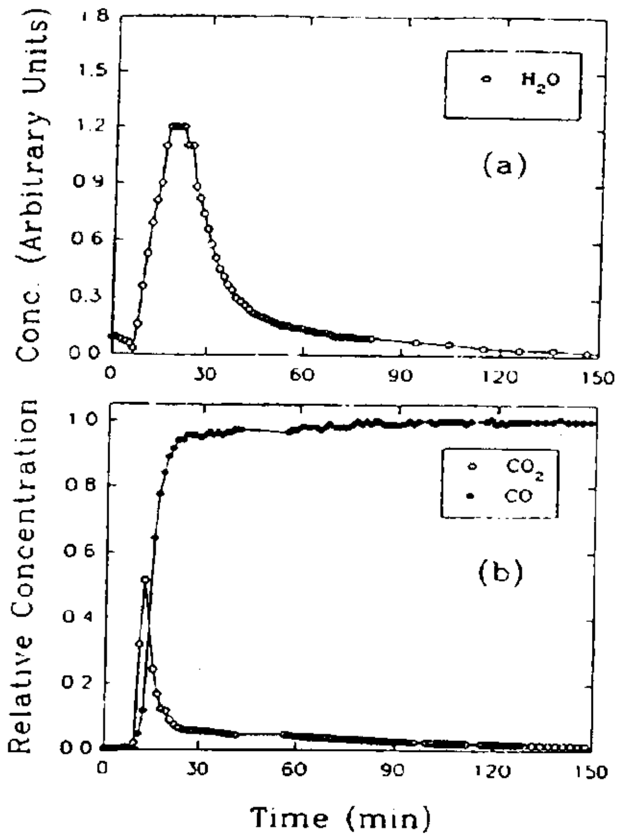

Figure 3. Isothermal reduction profile of Ruhrchemie catalyst at 280°C as a function of duration of reduction: a) H_2 reduction; b) CO reduction.

Table 7 Pretreatment Conditions and Test Designations Ruhrchemie Catalyst.

TEST (ID)	TEMP. (°C)	REDUCTANT	DURATION (h)	PRESSURE (MPa)	FLOWRATE (cm^3/min)
FA-0113	220	H_2	1	0.1	4,000
FB-0183	280	H_2	1	0.1	4,000
FB-1593	280	H_2	8	0.1	175
FB-1733	280	H_2	24	0.1	175
FB-2290	310	H_2/CO=2.0	6	0.1	1,200
FB-1588	280	CO	12	0.1	170
SA-0888	280	CO	16	0.8	1,730
SB-1370	220	H_2	1	0.8	7,500

FA, FB = Fixed bed reactor test. SA, SB = Slurry phase reactor test

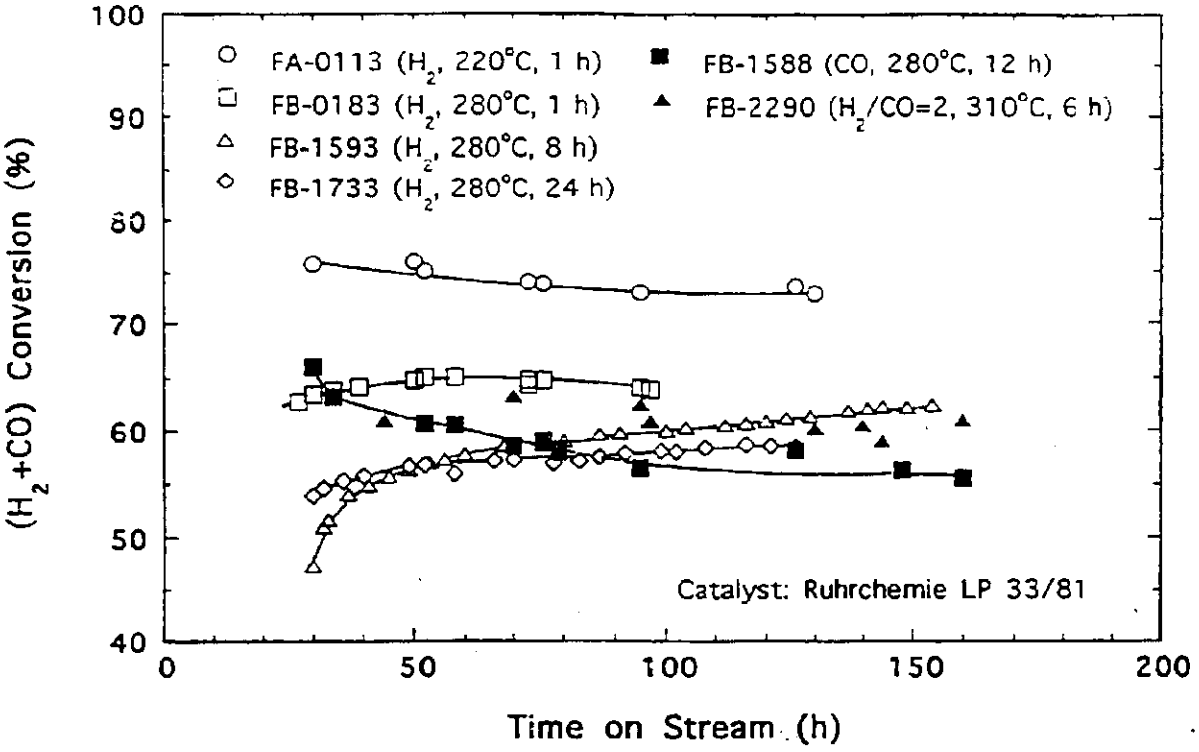

Figure 4. Effect of pretreatment conditions on conversion and catalyst stability

Tabie 8 Summary of Results for Pretreatment Effect Study with Ruhrchemie Catalyst

Test designation	FA-0113		FB-0183	FB-1593		FB-1733		FB-2290		FB-1588	
Time-on-stream, h	68	117	71	72	144	71	116	73	157	71	167
CO conversion, %	74.9	73.8	66.4	61.2	64.9	58.7	60.7	61.1	57.9	55.4	51.6
(H_2+CO) conversion, %	71.9	71.5	64.7	59.2	62.5	57.3	58.7	63.3	60.9	58.6	54.4
STY, mmol/g-cat/h	64.0	64.1	58.2	53.0	55.9	51.0	52.1	56.8	55.0	52.0	49.1
k, mmol/g-Fe/h/MPa[a]	241	243	215	192	205	187	190	225	216	201	187
(H_2/CO) usage ratio	0.61	0.61	0.67	0.64	0.63	0.66	0.64	0.75	0.78	0.75	0.78
(H_2/CO) exit ratio	0.95	0.82	0.79	0.78	0.81	0.75	0.78	0.60	0.57	0.60	0.60
$K_p = P_{CO_2}P_{H_2}/P_{CO}P_{H_2O}$	12.7	9.9	12.5	13.0	16.0	11.1	11.0	2.28	1.71	2.20	2.00
mmol CH_4/g-Fe/h	1.99	2.01	2.98	2.43	2.69	2.33	2.36	2.04	1.94	1.41	1.33
Hydrocarbon selectivity, wt%											
CH4	6.1	6.4	10.4	9.4	10.0	9.0	8.6	7.0	6.9	5.6	5.6
C2-C4	16.8	18.0	24.2	22.5	23.2	25.3	23.0	22.7	23.3	22.7	22.8
C5-C11	19.8	21.7	32.8	29.6	31.7	32.9	31.6	22.4	31.7	18.6	20.2
C12+	57.3	53.9	32.6	38.5	35.1	32.8	36.8	47.9	38.1	53.1	51.4
Chain growth parameter, $\alpha_{1\sim10}$[b]	0.59	0.61	0.68	0.69	0.70	0.69	0.69	0.65	0.64	0.65	0.67
Olefin content, wt%											
C2-C4	64.3	66.1	64.7	63.8	63.3	65.6	65.5	75.9	76.8	77.6	80.8
C5-C11	66.7	68.6	68.1	68.6	68.7	69.4	69.5	80.4	62.0	77.2	77.1

Process conditions: 250°C, 1.48 MPa (200 psig), 2.0 Nl/g-cat/h, H_2/CO=0.67

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

[b]: Parameter estimated from products with carbon number in the range C_1-C_{10}.

Table 9 Pretreatment Conditions and Test Designations

Catalyst: 100 Fe/5 Cu/4.2 K/16 SiO_2

Test (ID)	Temp. (^oC)	Reductant	Duration (h)	Pressure (MPa)	Flowrate (cm^3/min)
SB-2832	240	H_2	2	0.8	7,500
SA-3172	280	$H_2/CO=0.7$	5.5	0.8	280
SB-3362	280	CO	8	0.8	750

SA, SB = Slurry phase reactor test;

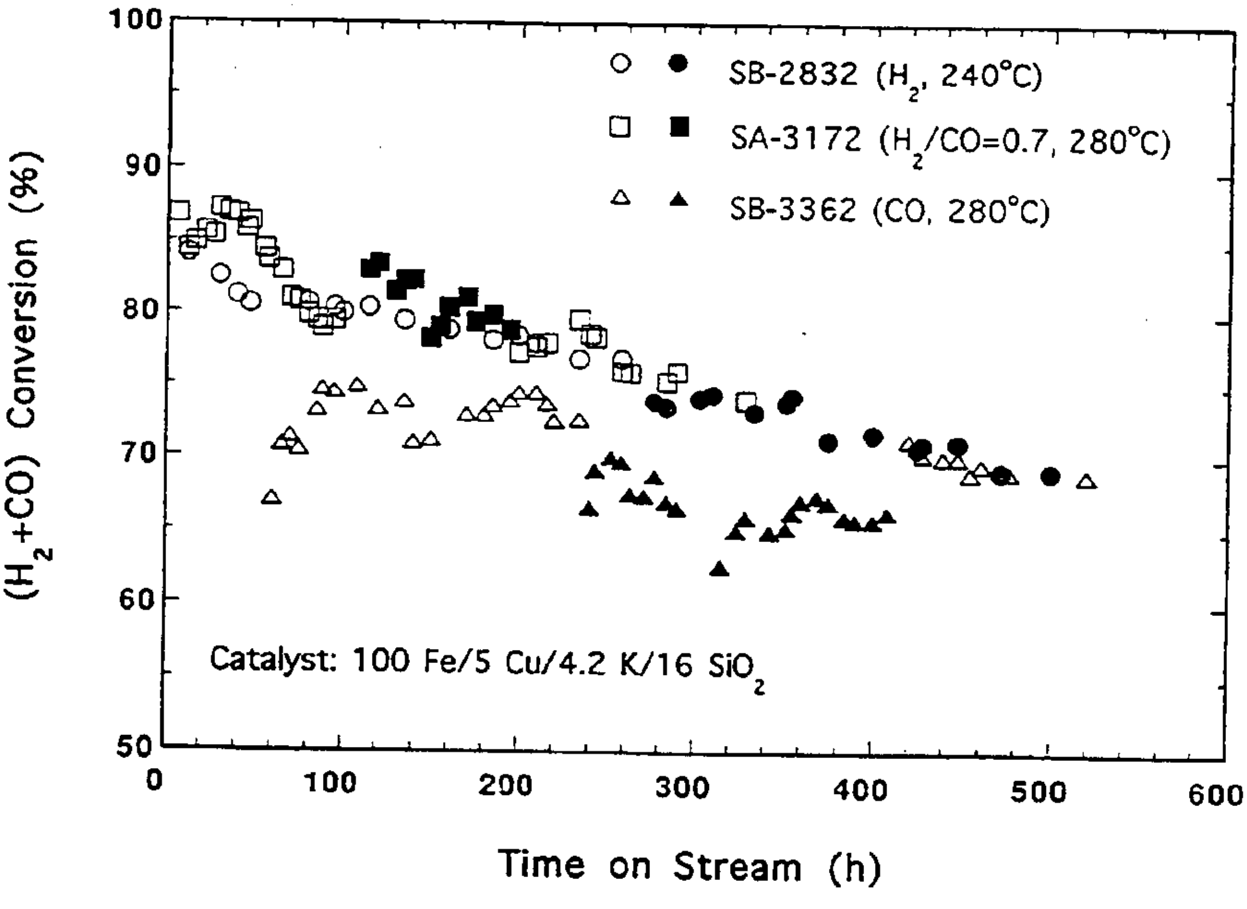

Figure 5. Effect of pretreatment conditions on conversion and catalyst stability

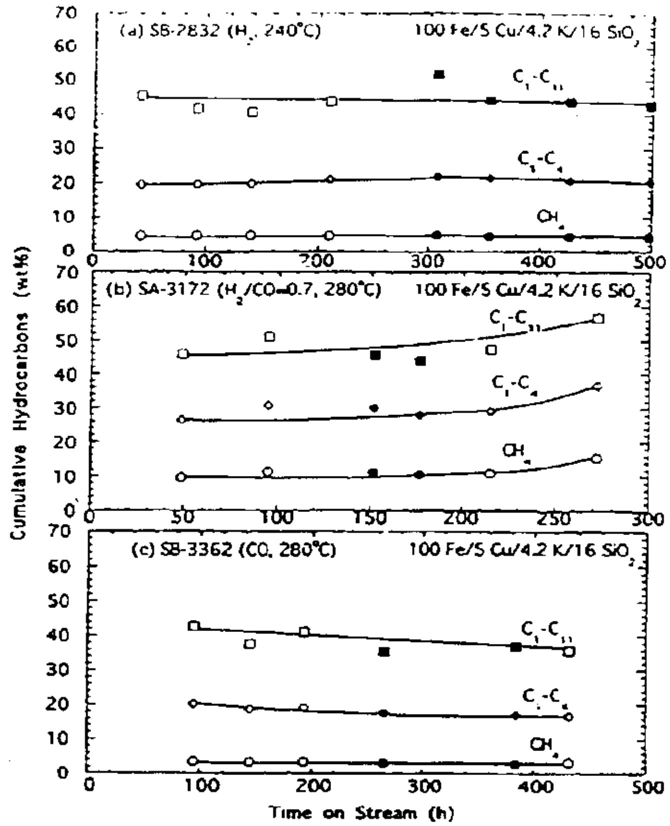

Figure 6. Effect of time-on-stream on hydrocarbon product distribution (FT synthesis conditions: T=260°C, (H_2/CO)=0.67; open symbols: P=1.48 MPa, SV=1.5 Nl/g-cat/h; solid symbols: P=2.17 MPa, SV=2.2 Nl/g-cat/h).

Table 10 Summary of Results for Pretreatment Effect Study with 100 Fe/5 Cu/4.2 K/16 SiO_2 Catalyst

Test designation	SB-2832		SA-3172		SB-3362	
Temperature, °C	260	260	260	260	260	260
Pressure, MPa	1.48	2.17	1.48	2.17	1.48	2.17
SV, Nl/g-cat/h	1.50	2.20	1.44	2.10	1.50	2.20
Time-on-stream, h	41-210	308-500	49-95	150-180	95-200	240-400
CO conversion, %	83-88	71-78	81-89	80-81	76-78	67-70
(H_2+CO) conv., %	78-81	69-75	80-86	78-80	73-75	66-68
STY, mmol/g-cat/h	53-54	67-73	50-55	73	50	66
k, mmol/g-cat/h	260-277	214-254	326-372	342	246	221
(H_2/CO) usage ratio	0.58-0.59	0.58-0.62	0.61-0.62	0.63-0.64	0.58-0.60	0.63
Hydrocarbon selectivity, wt%						
CH_4	4.6	4.5	10.4	10.8	3.5	2.9
C_2-C_4	15.5	16.7	18.2	18.2	15.8	14.4
C_5-C_{11}	22.0	24.4	19.8	15.0	21.2	19.0
C_{12+}	57.9	54.4	51.6	56.0	59.5	63.7
Olefin content, wt%						
C_2-C_4	68	72	54	60	74.5	78.5
C_5-C_{11}	73	73	78	80	80.0	80.3

H_2/CO=0.67 for all tests

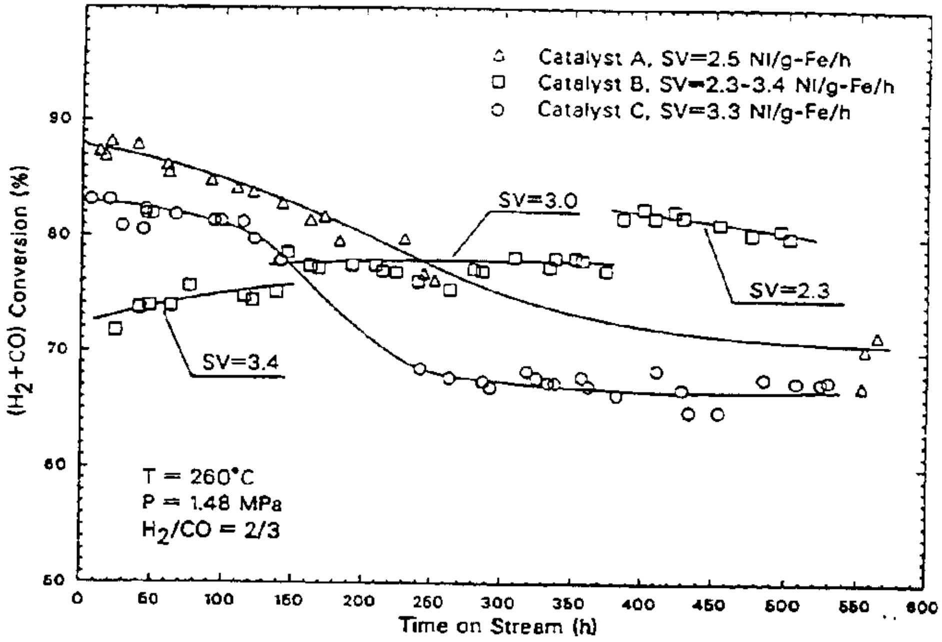

Figure 7. (H2+CO) conversion versus time-on-stream in slurry reactor tests of iron/silica FTS catalysts

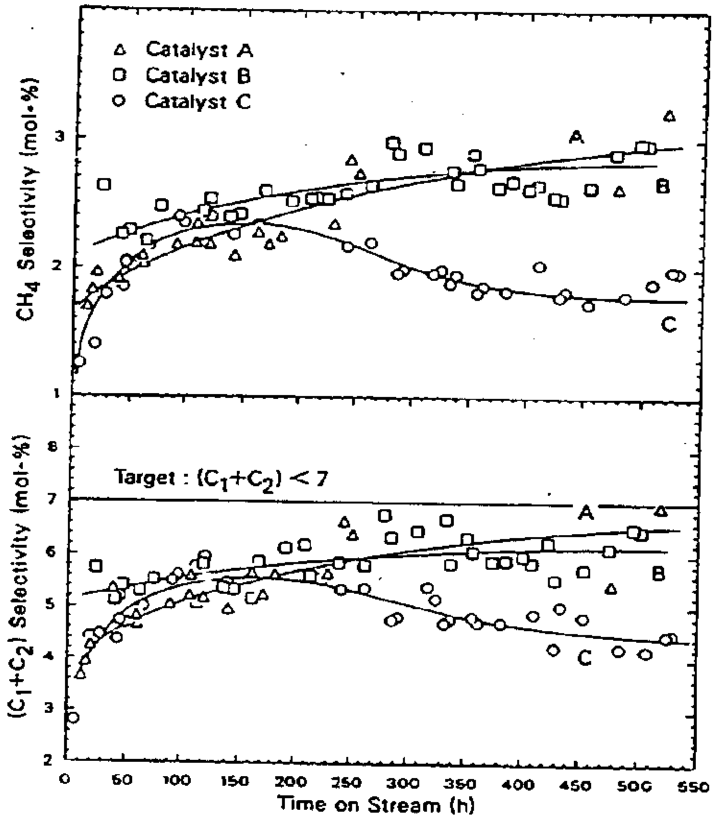

Figure 8. Effect of time-on-stream on methane and (methane+ethane+ethylene) selectivities in slurry reactor tests of iron/silica FTS catalysts

Table 11 Catalyst Target Performance

ACTIVITY

(H_2+CO) conversion, %	88
CO conversion, %	90
$Nm^3(H_2+CO)$ reacted/(g-Fe·h)	2.6
STY (kg C_3^+/m^3 reactor/day)	900

HYDROCARBON SELECTIVITY

(g $HC/Nm^3(H_2+CO)$ reacted)	≥178
(g $C_3^+/Nm^3(H_2+CO)$ reacted)	≥166
(C_1+C_2), wt%	6.7-8.0

PROCESS CONDITIONS

(H_2/CO) feed ratio = 0.6-1.0	Pressure (bar) = 1-20
Space velocity = 2-4 (Nm^3/kg-Fe·h)	Temperature (°C) = 230-300

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

Table 12 Comparison of Catalyst Performance in Slurry Reactors

Run ID	TAMU Catalyst B	Ruhrchemie SA-0888	UCI SA-3391	UOP (1991)	Mobil's Run** CT-256-13
Process Conditions:					
Temp. (°C)	260	250	265	265	257
Pressure (MPa)	1.48	1.48	2.10	2.10	1.48
SV (Nl/g-Fe/h)	2.2-3.4	3.8	2.4	2.4	2.3
Feed (H_2/CO)	0.66-0.69	0.67	0.7	0.7	0.73
TOS (h)	40-520	0-343	227-322	15-370	475
% (H_2+CO) Conv.	74-84	40-43	73-80	69	82
Usage Ratio	0.56-0.62	0.74-0.84	0.58-0.62	0.57	0.59
Rate Const at 260°C (rel)	100	79	40	33	49-70
Hydrocarbon Selectivities (wt-%):					
CH_4	3.0	4.7	4.4		2.7
C_2-C_4	10.5	20.6	16.5		11.1
C_5-C_{11}	16.0	23.2	23.6		18.1
$C_{12}+$	70.5	51.5	55.5		68.1
C_1+C_2	6.1	10.8	9.2		5.6
Hydrocarbon Selectivities (mol-%):					
CH_4	2.7		3.9	4.5	
C_1+C_2	5.8		8.7	5.8*	

*$CH_4+C_2H_6$ only

**Slurry Bubble Column Reactor Test