

## I. EXECUTIVE SUMMARY

A slurry reactor test (run SA-0376) was completed during the reporting period, following the catalyst pretreatment with H<sub>2</sub> at 280°C for 8 h (Task 6. Pretreatment Effect Research). This pretreatment resulted in catalyst activity similar to the one obtained utilizing our baseline reduction procedure (H<sub>2</sub> at 240°C for 2 h), and higher methane and gaseous hydrocarbon selectivities (about 10-20% higher).

One fixed bed and one slurry reactor test were completed under Task 7. Calcination Effect Research. For run FB-0236, the last of the four tests with catalyst B (100 Fe/5 Cu/6 K/24 SiO<sub>2</sub>) to study calcination effects in a fixed bed reactor, the catalyst was calcined at 700°C for 1 h in a furnace (referred to as flash calcination). After the reduction with H<sub>2</sub> at 250°C for 4 h, the catalyst was tested at 250°C, 1.48 MPa, 2.0 NI/g-cat/h, and synthesis gas feed with H<sub>2</sub>/CO=0.67 for 120 h. Catalyst activity was similar to the one obtained using our baseline calcination procedure (300 °C for 5 h), but gaseous hydrocarbon selectivities were slightly higher.

The effect of flash calcination was also studied in a slurry test SB-0676 using catalyst C (100 Fe/3 Cu/4 K/16 SiO<sub>2</sub>). The catalyst calcined at 700°C (SB-0676) had significantly lower activity than the catalyst calcined at 300°C (runs SB-2145 and SB-2145). Also, methane and gaseous hydrocarbon selectivities were higher on the catalyst calcined at 700°C. However, they were stable with time, unlike those in runs SA-1665 and SB-2145 which increased with time and eventually led to similar values as those obtained in run SB-0676. This suggests that the catalyst calcined at high temperature has a more stable structure, which did not change during FT synthesis.

The work on catalyst characterization by temperature programmed and isothermal reduction was initiated on a variety of iron catalysts, with different amounts of promoters. These studies are complementing our work on Task 6, and provide additional insight into the effect of pretreatment procedures on the reduction behavior of iron catalysts.

## II. OBJECTIVES AND SCOPE OF WORK

The overall contract objectives are to: (1) demonstrate repeatability of performance and preparation procedure of two high activity, high alpha iron Fischer-Tropsch catalysts synthesized at Texas A&M University (TAMU) during the DOE Contract DE-AC22-89PC89868; (2) seek potential improvements in the catalyst performance through variations in process conditions, pretreatment procedures and/or modifications in catalyst synthesis; (3) investigate performance of catalysts in a small scale bubble column slurry reactor, and (4) investigate feasibility of producing catalysts on a large scale in collaboration with a catalyst manufacturer. 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 SiO<sub>2</sub>) and C (100 Fe/3 Cu/4 K/16 SiO<sub>2</sub>). 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) , differential thermal analysis (DTA) 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 FT 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 - March 28, 1997)

The objectives of this task are: (1) Provide basic characterization (by AA, BET, XRPD) of synthesized catalysts, and used catalysts (by XRPD, Mössbauer spectroscopy) in support of other tasks of the project; (2) Attempt to identify and quantify "surface" species on the catalyst after exposure to CO and/or synthesis gas by temperature programmed techniques (TPR/ TPD/ TPO/ TPRX) coupled with on-line gas analysis by mass spectrometry and gas chromatography.

Task 9. Catalyst Testing in a Bubble Column Slurry Reactor (October 1, 1996 - March 28, 1997)

A laboratory bubble column slurry reactor (BCSR) shall be designed, constructed and used for testing of catalysts B and C to quantify differences in the reactor space-time-yield and hydrocarbon selectivities between the STSR and the BCSR. This unit will be approximately 2.5 cm (~1 in) in diameter and 1.5 m (~5 ft) tall, with the effective (unexpanded or static) slurry volume of about 500 cm<sup>3</sup>.

Task 10. Scale-Up of a Catalyst Synthesis Procedure (April 1, 1996 - March 28, 1997)

By the end of the first eighteen months of this project, the repeatability of the catalyst performance and catalyst preparation procedure shall be demonstrated. Subsequently, if the performance of the catalysts is found satisfactory by DOE the Contractor shall work with a catalyst manufacturer on synthesis of a large batches (~100 lb) of catalysts B and C. The cost estimate for the catalyst preparation will be provided upon reviewing details of the preparation procedure, and submitted to DOE for approval. Upon the DOE approval the Contractor will test catalysts synthesized by a catalyst manufacturer in a STSR.

### **III. DETAILED DESCRIPTION OF TECHNICAL PROGRESS**

#### **III. 1 Task 1. Project Work Plan**

The work on this task was completed. No additional activity to report.

#### **III. 2 Task 2. Engineering Modifications and Training of New Personnel**

The work on this task was completed. No additional activity to report.

#### **III. 3 Task 3. Testing of Previously Synthesized Catalysts**

The work on this task was completed. No additional activity to report.

#### **III. 4 Task 4. Reproducibility of Catalyst Preparation**

The work on this task was completed. No additional activity to report.

#### **III. 5 Task 5. The Effect Of Source of Potassium and Basic Oxide Promoter**

The work on this task was completed. No additional activity to report.

#### **III. 6 Task 6. Pretreatment Effect Research**

Work on pretreatment effect research has continued in this quarter. A slurry reactor test (SA-0376) was completed with catalyst C (100 Fe/3 Cu/4 K/16 SiO<sub>2</sub>), in which the catalyst was reduced with hydrogen at 280°C for 8 h. The detailed description of the test results is given below, followed by comparison of results using three different hydrogen reduction procedures.

##### **III. 6. 1 Run SA-0376 with 100 Fe/3 Cu/4 K/16 SiO<sub>2</sub> Catalyst**

About 18 g of the catalyst (< 270 mesh in size) was loaded for the test, together with 300 g Durasyn 164 oil as the initial slurry medium. The pretreatment conditions applied were: H<sub>2</sub> at 280°C, 0.78 MPa (100 psig), 950 cm<sup>3</sup>/min for 8 h. In comparison with the standard reduction conditions for this catalyst (240°C, 0.78 MPa for 2 h), the higher reduction temperature (280°C vs. 240°C) and longer reduction duration (8 h vs. 2 h) were employed, but the gas flowrate was significantly lower (950 vs. 7,500 cm<sup>3</sup>/min).

Following the reduction, the catalyst was first tested at 260°C, 1.48 MPa, syngas molar feed ratio of 0.67 ( $H_2/CO = 0.67$ ) and gas space velocity of 1.4 NI/g-cat/h. As shown in Figure 1, the CO conversion was about 83-80 %, ( $H_2+CO$ ) syngas conversion 77-76 %, and the  $H_2/CO$  usage ratio was 0.56-0.57 under these conditions. Methane selectivity after the reduction was low (2.8 mol%), but it gradually increased to 4.0 mol% at about 100 h and then leveled out (Figure 2a). Similarly, the  $C_1+C_2$  selectivity increased from 5.8 to 8 mol% (Figure 2b) and the  $C_2-C_4$  selectivity from 13 mol% to 15 mol% (Figure 2c).

At 168 h on stream, the space velocity was increased to 2.3 NI/g-cat/h. This reduced CO and syngas conversions to 66 and 62 %, respectively, but did not result in change of the usage ratio. Selectivity to gaseous hydrocarbons continued to increase with time, reaching 4.3 mol% for methane (Fig. 2a) and 16.5 mol % for  $C_2-C_4$  gaseous hydrocarbons (Fig. 2c).

At 254 h, the reaction pressure was increased to 2.17 MPa and space velocity to 2.05 NI/g-cat/h, a proportional increase relative to the baseline conditions of 1.48 MPa and 1.4 NI/g-cat/h employed in the test. After 9 h at these conditions, the CO and the syngas conversions were 79 and 75 %, respectively. These values are similar to those measured at 167 h on stream (the last measurement at 1.48 MPa and 1.4 NI/g-cat/h), indicating no loss in catalyst activity between 167 and 256 h on stream. During the next 90 h, the CO conversion decreased from 79 to 72 %, and the syngas conversion from 75 to 68 %. Gaseous hydrocarbon selectivities were not affected by catalyst deactivation during this period of time, and variations in data were mainly caused by fluctuations in the reactor temperature.

From 344 to 349 h on stream, a power outage occurred, causing slurry reactor temperature to cool down to 100°C. The run was terminated at 350 h on stream after taking a slurry sample for catalyst characterization. Additional slurry samples were withdrawn during the test at : 0 h (after the reduction), 134 h and 230 h on stream, respectively. Table 1 summarizes major events for run SA-0376.

### Pretreatment Effect Results - Comparison

So far, three different pretreatment procedures have been studied with the 100 Fe/3 Cu/4 K/16 SiO<sub>2</sub> catalyst in slurry reactor tests. They are: (1) standard or baseline procedure with H<sub>2</sub> at 240°C for 2 h (runs SA-1665 and SB-2145); (2) H<sub>2</sub> at 250°C for 4 h (run SB-3425); and (3): H<sub>2</sub> at 280°C for 8 h (run SA-0376). Comparison of the catalyst activities and selectivities in tests after different pretreatments are shown in Figures 3 and 4. The catalyst in run SA-0376 was reduced under the most severe conditions (the highest reduction temperature and the longest duration). Its activity, represented by the apparent rate constant (assuming the first order reaction in hydrogen partial pressure) in Figure 3, was similar to those observed in runs SA-1665 and SB-2145 following the standard reduction procedure (the lowest reduction temperature and the shortest duration), but was markedly lower than the activity in run SB-3425. This demonstrates that the use of severe reduction conditions does not necessarily result in higher activity. Previous studies in our laboratory with iron based catalysts without silicon oxide, have shown that the use of more severe reduction conditions may result in very low catalyst activity. Methane and gaseous hydrocarbon selectivities in run SA-0376 were similar to those obtained in run SB-3425, 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, which showed that the use of more severe reduction conditions often results in higher gaseous selectivities. Reduced catalysts in runs SA-0376 and SB-3425 were in the form of magnetite and  $\alpha$ -Fe, whereas the catalyst reduced at the standard conditions was in the form of magnetite (see section III. 8. 2 of the report and Figure 14).

### **III. 7 Task 7. Calcination Effect Research**

One fixed bed and one slurry reactor test were completed during the reporting period. For run FB-0236, the last of the four tests with catalyst B (100 Fe/5 Cu/6 K/24 SiO<sub>2</sub>) to study calcination effects in a fixed bed reactor, the catalyst was calcined at 700°C for 1 h in a furnace (referred to as flash calcination, Quarterly Technical Progress Report for October-December,

1995). After the reduction with H<sub>2</sub> at 250°C for 4 h, the catalyst was tested at 250°C, 1.48 MPa, 2.0 NI/g-cat/h, and synthesis gas feed with H<sub>2</sub>/CO=0.67 for 120 h. The effect of flash calcination was also studied in a slurry test SB-0676 using catalyst C (100 Fe/3 Cu/4 K/16 SiO<sub>2</sub>).

### III. 7. 1 Fixed Bed Reactor Test of Catalyst B (100 Fe/5 Cu/6 K/24 SiO<sub>2</sub>)

Results illustrating catalyst activity and gaseous hydrocarbon selectivities in run FB-0236 are shown in Figures 5 and 6, together with results from previous three tests using different calcination conditions (Quarterly Technical Progress Report for October-December, 1995). Some of the early decrease in the syngas conversion in run FB-0236 was due to fluctuations in bed temperature (Figures 5a and 5b). After 70 h on stream, the catalyst calcined at 700°C for 1 h, had similar CO and syngas conversions as those calcined at lower temperatures (300 to 500°C, for 5 h). The usage ratio was similar (0.58 - 0.60) in all four tests (Figure 5c). On the other hand, the catalyst calcined at 700°C had higher methane and C<sub>2</sub>-C<sub>4</sub> gaseous hydrocarbon selectivities (Figure 6), perhaps due to the presence of hot spots in the reactor. In general, the flash calcination or the use of higher calcination temperatures (400 and 500°C) did not result in improved catalyst performance (in terms of either activity or selectivity) in comparison to our baseline calcination procedure in air at 300 °C for 5 h.

### III. 7. 2 Run SB-0676 with 100 Fe/3 Cu/4 K/16 SiO<sub>2</sub> Catalyst

For this slurry test, the catalyst was calcined at 700°C for 1 h in a furnace (flash calcination procedure). In order to achieve uniform heating during the calcination, the catalyst (total of 20 grams) was distributed evenly into four preheated crucibles each containing a thin layer of catalyst.

About 16 g of the calcined catalyst (< 270 mesh in size) was loaded into the reactor together with 300 g of Durasyn 164 oil as the initial slurry medium. After the reduction with hydrogen at 240°C, 0.78 MPa for 2 h (the standard conditions for catalyst C), the catalyst was tested initially at 260°C, 1.48 MPa, syngas molar feed ratio of 0.67 and gas space velocity of 1.4 NI/g-cat/h. The CO and syngas conversions were stable at about 67 and 63 %, respectively



(Figures 7a and 7b). The H<sub>2</sub>/CO usage ratio was about 0.55-0.56 (Figure 7c). Initial methane selectivity was relatively high, about 4.0 mol%, but it stayed below 4 mol% during the remainder of the test (Figure 8a). The C<sub>1</sub>+C<sub>2</sub> selectivity varied between 7.3 and 8.0 mol%, whereas C<sub>2</sub>-C<sub>4</sub> selectivity was about 14 mol% (Figures 8b and 8c).

At 166 h on stream, the reaction pressure and feed gas space velocity were increased to 2.17 MPa and 1.8 NI/g-cat/h, respectively. This resulted in temporary increase of the CO and syngas conversions, followed by continued decrease afterwards. The CO conversion decreased from 68 to 61 % during the next 130 h on stream, whereas the syngas conversion decreased from 64 to 57 %. During the same period of time methane selectivity decreased from 3.8 to 3.3 mol%, and (C<sub>1</sub>+C<sub>2</sub>) hydrocarbon selectivity decreased from 7.2 to 6.5 mol%. The run was terminated after 305 h on stream. Major events for run SB-0676 are summarized in Table 2.

A major problem during the test was wax removal from the reactor. Wax withdrawal was slow even during the first 50 h on stream (when the slurry "wax" was mainly Durasyn-164 liquid oil), requiring the use of pressure drop of 0.7 MPa across the filter (with pore size of 0.5 μm). The pressure drop was increased to 2.1 MPa several days later to facilitate the wax removal. After 240 h, it became virtually impossible to withdraw the wax from the reactor. After the test about 440 g of slurry was removed from the reactor, whereas normally this amount is about 250 g, therefore, a large amount of product wax had accumulated in the reactor during the latter portion of the test.

After the test, the filter was removed and cleaned in an ultrasonic bath, but it still could not remove liquid from the reactor (low molecular weight hydrocarbon solvent - Varsol). This filter seems to be blocked. We plan to replace this filter with a new one with the average pore size of 2.0 μm for future tests in the slurry B reactor.

### Comparison of Results from Runs SB-0676, SB-2145 and SA-1665

Results from two tests SB-2145 (Quarterly Technical Progress Report for July-September, 1995) and SB-2145 (Quarterly Technical Progress Report for April-June, 1995), in which the catalyst was calcined at 300°C for 5 h, are compared with those obtained in run SB-0676 in Figures 9 and 10. Figure 9 compares the catalyst activity among the three tests in terms of the apparent rate constant (assuming the first order reaction in hydrogen partial pressure). The catalyst calcined at 700°C (SB-0676) had significantly lower activity than the catalyst calcined at 300°C (runs SB-2145 and SB-2145). This trend is in agreement with the findings from the fixed bed reactor tests, and lower activity is mainly due to the loss of surface area during high temperature calcination (see Table 3). Methane and gaseous hydrocarbon selectivities were higher on the catalyst calcined at 700°C (Figure 10, data at 1.48 MPa only). However, they were stable with time, unlike those in runs SA-1665 and SB-2145 which increased with time and eventually led to similar values as those obtained in run SB-0676. This suggests that the catalyst calcined at high temperature has a more stable structure, which did not change during FT synthesis.

### **III. 8 Task 8 Catalyst Characterization**

#### **III. 8.1 BET Measurement Results**

Results of BET measurements illustrating the effect of calcination temperature on the pore size distribution of catalysts B (100 Fe/5 Cu/6 K/24 SiO<sub>2</sub>, from batch-3) and C (100 Fe/3 Cu/4 K/16 SiO<sub>2</sub>, from batch- 4) are shown in Figures 11 and 12, respectively. The pore diameter varied between 2.0 and 20.0 nm for the catalysts studied (calcined from 300 to 700°C). The pore size data clearly show that the pore diameter of the catalyst slightly increases with the increase in calcination temperature. In general, both the surface area and the pore volume decrease with either increase in calcination temperature or increasing time at a fixed calcination temperature (Table 3). The surface area of catalyst C (100 Fe/3 Cu/4 K/ 16 SiO<sub>2</sub> from batch 4) decreased from 310 to 108 m<sup>2</sup>/g-cat , whereas the surface area of catalyst B (100 Fe/5 Cu/6 K/24 SiO<sub>2</sub>

from batch 3) decreased from 258 to 100 m<sup>2</sup>/g-cat when the calcination temperature increased from 300 to 700°C. The pore volumes of both catalysts decreased from about 0.5 cm<sup>3</sup>/g at 300°C to 0.3 cm<sup>3</sup>/g at calcination temperature of 700°C.

### III. 8. 2 XRD Measurement Results

#### II. 8. 2. 1 XRD Measurements of Catalyst Samples from Slurry Reactor Tests Conducted Under Task 6

Figure 13 illustrates changes in bulk iron phases with time on steam during run SA-0376 with catalyst C (100 Fe/3 Cu/4 K/16 SiO<sub>2</sub> from batch 4). Metallic iron ( $\alpha$ -Fe) and small amounts of magnetite (Fe<sub>3</sub>O<sub>4</sub>) were found (Figure 13-A) in the sample withdrawn immediately after the hydrogen reduction (TOS = 0 h). During FT synthesis the relative amounts of iron carbide and magnetite increased with time on stream (Figures 13-B to 13-D), whereas the catalyst activity gradually decreased.

Figure 14 illustrates the effect of hydrogen reduction temperature and duration on bulk iron phases of catalyst C (100 Fe/3 Cu/4 K/16 SiO<sub>2</sub> from batch 4). At a reduction temperature of 240°C and reduction time of 2 h catalyst C (run SB-2145) was reduced primarily to magnetite and possibly to  $\alpha$ -Fe (Figure 14-A.). After the reduction at a higher temperature (250°C) and longer duration (4 h) both magnetite and, to a smaller extent, metallic iron were found in the reduced sample (Figure 14-B). As the reduction temperature and time were increased further (280°C, 8 h) the catalyst from run SA-0376 (Figure 14-C) was in the form of  $\alpha$ -Fe with small amounts of magnetite. Results show that the degree of reduction increases with the use of more severe reduction conditions.

#### III. 8.2. 2 XRD Measurements of Catalyst Samples from Fixed Bed and Slurry Reactor Studies Conducted Under Task 7

Used catalyst samples from runs FB-2975, FA-2925 (Quarterly Technical Progress Report for October-December, 1995) and FB-0236 were characterized by X-ray diffraction. Prior to reaction tests the catalysts were calcined at different temperatures ranging from 300 to 700°C followed by reduction in hydrogen at 250°C for 4 h. After that, they were tested in a fixed

bed reactor for about 120 to 140 h, and at the end of each run catalyst samples from the top and bottom portions of the bed were collected and analyzed by X-ray diffraction. The pseudo-hexagonal iron carbide ( $\epsilon'$ -Fe<sub>2,2</sub>C) was the only phase found in all the six samples (top and bottom portions) at the end of these three runs (Figure 15).

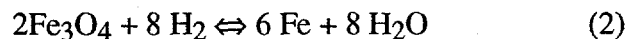
Figure 16 illustrates changes in bulk iron phases with time on stream during run SB-0676 with catalyst C (100 Fe/3 Cu/4 K/16 SiO<sub>2</sub>) from batch 4. This catalyst was calcined at 700°C for 1 h prior to testing. Magnetite was found in the sample withdrawn immediately after the hydrogen reduction (TOS=0 h) as shown in Figure 16-A. Both magnetite and the pseudo-hexagonal iron carbide were found in the samples withdrawn during FT synthesis (Figures 16-B to 16-D).

Figure 17 shows the effect of calcination temperature on the reduction behavior of Catalyst C (100 Fe/3 Cu/4 K/16 SiO<sub>2</sub> from batch 4). Both the catalysts were reduced with hydrogen at 240°C for 2 h. Both magnetite and, to a smaller extent, metallic iron were found after the reduction in the catalyst sample calcined at 300°C (run SB-2145, Figure 17-A). The catalyst calcined at 700°C (SB-0676) was reduced to magnetite only (Figure 17-B).

### III. 8.3. Temperature Programmed Reduction (TPR) Measurements

Temperature-programmed reduction (TPR) and isothermal reduction studies were performed using 5%H<sub>2</sub>/95%N<sub>2</sub> 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%H<sub>2</sub>/95%N<sub>2</sub> (flow rate of 40 ml/min) from room temperature to 800°C at a heating rate of 20°C/min. In order to quantify the degree of reduction, CuO standard was used for the calibration of the peak areas.

A typical TPR profile for the unpromoted iron sample is given in Figure 18-A, the two peaks in the thermogram correspond to the characteristic two-step reduction of Fe<sub>2</sub>O<sub>3</sub> that was observed for most of the catalysts studied:



### III. 8. 3.1 Effect of Potassium Promotion

The effect of potassium promoter on the reduction behavior in H<sub>2</sub> of copper-free calcined iron catalysts is illustrated in Figure 18 (their degree of reduction results are summarized in Table 4). Potassium addition had virtually no effect on either the position or the area of the TPR peak at 380°C that corresponds to Fe<sub>3</sub>O<sub>4</sub> formation. However, increasing levels of potassium promoter caused a marked increase in the reduction temperature (Figures 18-A to 18-D) for the second stage of the reduction process (Fe<sub>3</sub>O<sub>4</sub> to α-Fe). The reduction temperature maxima (T<sub>m</sub>), for the second stage of reduction, for unpromoted iron sample (Figure 18-A) is about 595°C, but it increased to about 630°C for the 100 Fe/1 K catalyst (Figure 18-D). However, the total degree of reduction was not influenced by the potassium levels in the catalyst samples (Table 4). The results (from Figure 18 and Table 4) also show that the peak area ratio of the first and second peak is about 1: 8. This is consistent with the theoretical value for complete reduction of iron oxide to zero valent iron, according to the two step process described by equations (1) and (2).

### III. 8. 3. 2 Effect of Copper Promotion

Figure 19 illustrates the effect of copper promotion on the reduction of iron oxide. The 100 Fe/0.3 Cu catalyst has two peaks between 400 and 700°C, indicating the presence of different types of iron phases in the sample. The addition of copper to the catalyst facilitates the reduction of iron oxide. The reduction temperature maxima (T<sub>m</sub>) for the first reduction step decreased from 360 to 260°C (Figures 19-B and 19-C) when the copper levels are increased from 0.3 to 3 parts per 100 parts of iron. With further increase in copper promotion (100 Fe/5 Cu) the

reduction temperature decreases to 230°C (Figure 19-D). The 100 Fe/5 Cu catalyst also shows a second peak at 280°C. The existence of two peaks ( $T_m = 230$  and 280°C) in the low temperature region may be attributed to the presence of two different kinds of iron oxide species in the sample. The position of the second temperature maxima, also shifts to lower temperatures with the addition of copper (Figures 19-A to 19-D).

### III. 8. 3. 3 Effects of Silica, Potassium and Calcium Oxide on the Reduction Behavior of Copper Promoted Iron Catalysts

Figure 20 illustrates the effects of addition of silica, potassium and calcium oxide on the reduction behavior of copper promoted iron catalyst. Comparing Figures 20-B and 20-C, one can see that the first and the second peaks of iron reduction shift from 260°C to 330°C and 570°C to 630°C, respectively, with addition of silica. Thus, the addition of silica inhibits the reduction of iron catalyst. From Figures 20-C and 20-D it follows that the addition of potassium to the doubly promoted iron catalyst (100 Fe/3 Cu/16 SiO<sub>2</sub>) has virtually no effect on the reduction behavior of the iron. However, the addition of CaO to the triply promoted iron catalyst retards the first step of iron reduction (Figures 20-A and 20-D). The added silica and calcium oxide may be stabilizing or blocking the iron oxide species. It is also evident from literature (Jones and McNicol, 1986) that the standard free energy change ( $\Delta G^\circ$ ) values for the reduction of calcium oxide and silica are high (~350 kJ/mole<sup>-1</sup> for CaO and ~175 kJ/mole<sup>-1</sup> for silica).

The qualitative trends observed in Figure 20 with the catalysts containing 3 parts of Cu per 100 parts of iron, are also seen with catalysts containing 5 parts of Cu (Figure 21).

### III. 8. 4 Isothermal Reduction

In isothermal reduction, catalyst samples of about 400 to 500 mg were used. The temperature was ramped at a constant rate of 5°C/min to a final temperature of 280°C. Then the catalyst sample was maintained at this temperature for 8 h in a flow of 5% H<sub>2</sub>/95% N<sub>2</sub> (40 ml/min).

#### III. 8. 4. 1 Effect of Potassium Promoter

Figure 22 illustrates the effect of potassium addition on the degree of reduction of iron. The results show that the degree of reduction increases rapidly up to a reduction time of about 250 minutes and then levels off with further increase in reduction time. Also, the results show that both the rate and the degree of reduction decrease with increase in potassium levels in the catalyst.

#### III. 8. 4. 2 Effects of Copper, Potassium and Silica Promoters

Figure 23 demonstrates the effect of addition of silica and potassium promoters on the reduction behavior of an iron catalyst promoted with 3 parts of copper per 100 parts of iron. The results show that the addition of silica and potassium causes an increase in the overall rate and degree of reduction compared to that of copper only promoted catalyst. Since the addition of silica stabilizes or blocks the iron oxide species the observed increase in degree of reduction is contrary to the expected behavior for these catalysts. The total degree of reduction values are about 48% for the silica and copper containing catalysts (Figure 23). The total degree of reduction values obtained from TPR experiments are: 95% for 100 Fe/3 Cu; 92% for 100 Fe/3 Cu/16 SiO<sub>2</sub>, and 74 % for 100 Fe/3 Cu/16 SiO<sub>2</sub>/4 K catalyst. Differences in the degree of reduction values are mainly due to the differences in reduction temperatures. In the TPR experiments the maximum reduction temperatures is about 800°C while the maximum reduction temperature during the isothermal reduction is 280°C.

Figure 24 demonstrates the effect of addition of silica and potassium promoters on the reduction behavior of an iron catalyst promoted with 5 parts of copper per 100 parts of iron. Results show that the addition of silica and potassium causes an increase in the overall rate and degree of reduction compared to that of copper only promoted catalyst. From Figures 23 and 24 it appears that both series of catalysts exhibit the same type of behavior during isothermal reduction at 280°C.

### III. 8. 5 TGA Measurement Results

Isothermal reduction in thermogravimetric analysis (TGA) experiments was conducted using approximately 20 mg catalyst samples. The catalyst sample was purged with helium (40 ml/min) and temperature was ramped at a rate of 5°C/min from a room temperature to 280°C. Then the helium flow was switched to hydrogen (99.995% purity) at 40 ml/min, and the temperature was maintained at 280°C for a total period of 8 h. The degree of reduction was calculated from the weight loss vs. time data.

Figure 25 shows the effects of silica, potassium and calcium oxide on the rate and degree of reduction of iron catalysts promoted with 3 parts of copper per 100 parts of iron. The degree of reduction (open circles) of the 100 Fe/3 Cu catalyst increased with time until about 320 minutes and then leveled off with further increase in reduction time. The degree of reduction of copper promoted iron catalyst decreased from about 85% to 45% when 16 parts of silica was added (solid circles). These results show that the reduction of copper promoted iron catalyst was inhibited by addition of silica, suggesting an interaction between the metal and silica, as proposed by many investigators (Dry, 1981; Anderson, 1984; Lund and Dumesic, 1981). The addition of potassium and calcium oxide to the doubly promoted (with 3 parts Cu and 16 parts silica) did not have much effect on either the rate or the degree of reduction.

Figure 26 shows the effects of silica, potassium and calcium oxide on the rate and degree of reduction of iron catalysts promoted with 5 parts of copper per 100 parts of iron. The results show that both the rate and the degree of reduction of copper promoted catalysts decrease with the addition of silica, potassium and calcium oxide promoters. The degree of reduction of 100 Fe/5 Cu catalyst decreased from about 90% to about 45% with the addition of 24 parts of silica. The degree of reduction was further decreased with the addition of calcium oxide to about 34% (solid squares).

There are some discrepancies in numerical values of the degree of reduction values obtained from three different reduction methods, namely TGA (isothermal), TPR and isothermal reduction in the TPR apparatus. Table 5 summarizes the effect of various promoters on the



degree of reduction of iron catalysts. The degree of reduction of unpromoted iron oxide is about 62% as determined by TPR experiment. Isothermal reduction experiments are in progress for the unpromoted iron catalyst. The degree of reduction of copper promoted catalyst (100 Fe/3 Cu) from TGA experiment is about 86% which is comparable to the value (95%) obtained from TPR (non isothermal) experiment. However, the value obtained from the TPR apparatus under isothermal conditions is only 19%, and is much lower than the value determined from TGA experiment under isothermal conditions. Differences between TGA and TPR-isothermal experimental results may be due to the differences in the partial pressures of the reducing gas (pure hydrogen in TGA experiments vs. 5% hydrogen in the TPR unit), and the use of different amounts of catalyst samples in these two types of experiments.

The same trends, namely significantly higher degrees of reduction during isothermal reduction in the TGA unit in comparison to the TPR unit, were observed with all other catalysts (Table 5). We plan to examine this issue in future experiments.

## References

- Jones, A. and McNicol, B. "Theoretical Aspects" In Temperature-Programmed Reduction for Solid Materials Characterization; Marcel Dekker, Inc: New York, 1986, p. 13.
- Anderson, R. B. The Fischer-Tropsch Synthesis; Academic Press: Orlando, Fla., 1984.
- Dry, M. E " The Fischer-Tropsch Synthesis" In Catalysis Science and Technology Vol. 1; Anderson, J. R.; Boudart, M., Eds.; Springer-Verlag: New York, 1981, pp. 159-255.
- Lund, C. R. F. and Dumesic, J. A. " Strong Oxide-Oxide Interactions in Silica-Supported Fe<sub>3</sub>O<sub>4</sub>". J. Catal. 1981, **69**, 32-43.

### **III. 9 Catalyst Testing in a Bubble Column Slurry Reactor**

The work on this task is not scheduled to begin yet. No activity to report.

### **III. 10 Scale-up of Catalyst Synthesis Procedure**

The work on this task is not scheduled to begin yet. No activity to report.

### **Plans for the Next Quarter**

During the next quarter we plan to: (a) continue with testing of catalysts under Tasks 6 and 7 of the contract, and (b) continue with catalyst characterization of catalysts at various stages of usage (Task 8).