currently understood but may be tentatively attributed to the specific catalyst-handling procedure used in this lab and to the differences in the activation treatments between the two tests.

Task 3. Construction of a Catalyst Preparation Plant and Development of a Baseline Catalyst

Under Task 3, preliminary catalyst-preparation equipment was built in the laboratory for determining the significance of various catalyst preparation parameters. These data were then used for final design of the catalyst preparation equipment.

Several Fe-Cu catalysts were prepared at different pH levels by the coprecipitation of the nitrates of Fe and Cu with Na_2CO_3 solution. The preparation parameters and the properties for 12 of these catalysts are listed in Table 1. The precipitates were washed with water, dried, and then calcined. The catalysts were examined by STEM, XRD, DSC, TGA, TPR, and nitrogen adsorption. Only one of these catalysts were tested for its Fischer-Tropsch performance.

Determination of pH's for Precipitating Fe and Cu

A ferric nitrate ($Fe(NO_3)_3$) solution with 5.0 wt.% Fe was titrated against 1N solutions of Na_2CO_3 and NH_4OH at room temperature (Figures 9 and 10). In both cases, the Fe precipitation started to occur at a pH of about 2. Similarly, a solution of copper nitrate ($Cu(NO_3)_2$) with 0.5 wt-% Cu started to precipitate at a pH of about 5 (Figures 11 and 12). However, in the presence of $Fe(NO_3)_3$, $Cu(NO_3)_2$ precipitated at lower pH's.

Description of DSC and TGA Experiments

Catalyst 5685-61 was prepared by the coprecipitation of $Fe(NO_3)_3$ and $Cu(NO_3)_2$ solutions with a Na_2CO_3 solution (100:1 Fe:Cu, by weight) at a pH of 3.5. According to STEM examination of the catalyst after drying at 110°C, the catalyst was made up of 2 to 4 nanometer (nm) amorphous Fe-Cu particles. Another catalyst, 5685-53, (100:1 Fe:Cu) precipitated with Na_2CO_3 at a pH of 4.3 showed similar morphology to catalyst 5685-61. These two catalysts were used for establishing the reproducibility of DSC experiments, which are useful for determining the calcination temperature requirement of Fe-Cu catalysts.

In DSC experiments, the uncalcined catalyst is heated from room temperature to 600°C at 5°C/min under air flow, and the heat flow to or from the catalyst is measured. The results obtained with catalyst 5685-53 in two separate runs are described in Figure 13. A minimum in the DSC curve indicates the occurrence of an endothermic reaction. The minimum at 40 to 50°C is probably related to water evolution from the catalyst. A maximum in the DSC curve indicates the occurrence of an exothermic reaction. The maximum observed at about 390°C is probably related to the formation of Fe_2O_3 from goethite, α-FeO(OH); this formation apparently illustrates the calcination temperature requirement for the catalyst. Secondary maxima appear at about 200°C. Not presently clear is whether the presence of multiple maxima indicates the presence of catalyst particles with different calcination temperature requirements or whether it indicates that calcination is a multistep process.

The results summarized in Figure 13 also indicate that the DSC experiments were quite reproducible. No more than 5°C difference is observed between the calcination temperature requirements measured in two separate runs with the same catalyst.

Catalyst 5685-53 was also evaluated in a TGA experiment, which involves measuring the percent of weight loss as the catalyst is heated up to 600°C at 5°C/min under air flow (Figure 14). The TGA experiment also provides the derivative of the catalyst weight loss with respect to time. A maximum in the derivative curve illustrates the temperature at which the rate of weight loss becomes maximum. Three maximas, at 56°C, 217°C, and 360°C, were observed. These maxima may correspond to the minimum and maxima observed in the DSC experiments at 40 to 50°C, 200°C, and 390°C. Not presently clear is why the high-temperature maxima (or minimum) differ by 20 to 50°C between the DSC and TGA experiments.

During the TGA experiment, catalyst 5685-53 lost about 12% weight between 100°C (the temperature at which significant fraction of the free water should have evolved) and 600°C. A 12.4% weight loss would occur for the reaction of 2FeO(OH) to Fe_2O_3 and H_2O. This reaction presumably is the major calcination reaction.

The DSC results obtained with catalyst 5685-61 in two separate runs and the TGA results are described in Figures 15 and 16. For this catalyst, the secondary maximum at about 250°C is less apparent. Also the high-temperature maximum occurs at a lower temperature. These

DSC results again indicate that these experiments are quite reproducible, but this time, the high-temperature maxima for duplicate measurements on the same catalyst were 12°C apart.

Description of TPR Experiments

Catalyst 5685-145 with 100:1 Fe:Cu (by weight) was prepared by the coprecipitation of $Fe(NO_3)_3$ and $Cu(NO_3)_2$ with Na_2CO_3 solution at a pH of 6.5, followed by drying at 110°C and calcining at 410°C. Based on XRD measurements on a similar catalyst, the Fe-Cu crystallite size in this catalyst is expected to be between 6 and 11 nm. Catalyst 5685-145 was used for establishing the reproducibility of TPR experiments, which are useful for determining the reduction temperature requirement of Fe-Cu catalysts.

In TPR experiments, the calcined catalyst is heated from room temperature to 800°C at 2°C/min under 5% H_2 in argon flow and the uptake of H_2 is measured. The results obtained with catalyst 5685-145 in two separate runs are described in Figure 17.

The first major TPR peak occurs between 140 and 160°C. In an attempt to identify the crystalline phases present at 150°C, another portion of catalyst 5685-145 was heated from room temperature to 150°C in 2 hours under 5% H_2 in argon flow, maintained at 150°C for 1 more hour, and then analyzed by XRD (Figure 18). A magnetite (Fe_3O_4) phase was observed to be present along with a maghemite (γ-Fe_2O_3) phase.

The peak between 140 and 160°C was equivalent to about 0.15 millimole (mmole) H_2/g catalyst. Because this catalyst contains 0.11 mmole Cu/g catalyst, the TPR peak at 140 to 160°C may be partly attributed to the reduction of Cu.

The second major TPR peak occurs between 160 and 200°C. A portion of catalyst 5685-145 that was heated at 250°C under 5% H_2 in argon flow in 4 hours and maintained there for 1 more hour showed only magnetite phase, but no Fe_2O_3 (Figure 19).

The third major TPR peak occurs between 200 and 680°C. At higher temperatures, further H_2 uptake occurs. A portion of catalyst 5685-145 was heated to 800°C under 5% H_2 in argon flow in 6.5 hours and held there for 1 more hour. This catalyst showed metallic iron (α-Fe) along with wustite (α-FeO) (Figure 20).

These results suggest that the reduction of Fe-Cu catalyst may be occurring in at least three steps at specified temperature ranges:

- Step 1a. $Fe_2O_3 \longrightarrow Fe_3O_4$ at 140 to 160°C

  $CuO \longrightarrow Cu$ (possibly)

  1b. $Fe_2O_3 \longrightarrow Fe_3O_4$ at 160 to 200°C
- Step 2. $Fe_3O_4 \longrightarrow FeO$ at 200 to 680°C
- Step 3. $FeO \longrightarrow Fe$ at more than 680°C

Why two peaks may be associated with Fe_3O_4 formation from Fe_2O_3 is not presently clear.

The results summarized in Figure 17 indicate that duplicate TPR results obtained with the same catalyst are quite reproducible. No more than a 10°C difference occurs between the position of each corresponding TPR maxima.

The TPR results show that the complete reduction of Fe-Cu catalysts requires temperatures in excess of 800°C. However, temperatures higher than 300°C are not typically required to generate active catalysts. Thus, the reduction of the catalyst surface relative to the bulk occurs at much lower temperatures, as also discussed by M. P. Rosynek et al.[3] Nevertheless, the TPR experiments are useful for monitoring differences between different Fe-Cu catalysts because the reduction behavior of these catalysts, as examined by TPR, is expected to vary sensitively with their chemical and morphological properties.

Use of DSC for Determining Calcination Temperature Requirement for Fe-Cu Catalysts

Previously described DSC measurements on 100:1 Fe:Cu catalyst 5685-53 precipitated at 4.3 pH showed a high-temperature maximum peak at about 390°C. Another catalyst precipitated at the same 4.3 pH was calcined at 275°C for 2 hours. The XRD measurements showed this catalyst to have 37.8% crystalline α-Fe_2O_3 only. A portion of catalyst 5685-53 calcined at 380°C and another portion calcined at 450°C showed 79 and 80% α-Fe_2O_3, which was the only detected crystalline phase. These results indicate that essentially maximum crystalline α-Fe_2O_3

is obtained when calcination is done at the temperature that corresponds to the high-temperature maximum in the DSC measurement and that the amount of α-Fe_2O_3 does not significantly increase at higher calcination temperatures. Because neither DSC nor XRD measurements show that any phase of transformation seems to take place in the Fe-Cu catalyst at temperatures higher than those corresponding to the high-temperature maximum in the DSC experiment (-T_c), a calcination temperature higher than T_c may be necessary.

Catalyst 5685-75 (100:1 Fe:Cu, by weight) was prepared by the coprecipitation of $Fe(NO_3)_3$ and $Cu(NO_3)_2$ with a solution of Na_2CO_3 at a pH of 9.7. The DSC measurement on this catalyst showed a high-temperature maximum at 443°C (Figure 21). A portion of this catalyst was calcined at 380°C and another portion at 450°C, each for 2 hours. The XRD measurements showed the catalyst calcined at 380°C to be 77% α-Fe_2O_3 and the catalyst calcined at 450°C to be 87% α-Fe_2O_3. These results again indicate that the amount of α-Fe_2O_3 is maximized when calcination is done at the high temperature DSC maximum.

Experiments were later conducted with catalysts 5685-111 and 5685-61 to determine whether an extended low temperature calcination would lower the final calcination temperature requirement. Catalyst 5685-111 was prepared by coprecipitating $Fe(NO_3)_3$ and $Cu(NO_3)_2$ (10:1 Fe:Cu) at a pH = 9.5 with ammonia solution. For this catalyst, the high temperature DSC maximum occurred at 458°C (Figure 22). During another DSC experiment, this catalyst was brought to 374°C at 5°C/min and then maintained isothermally for 1.5 more hours (Figure 23).

The catalyst was then subjected to a standard DSC experiment, which indicated that the high temperature DSC peak position and shape had not essentially changed (Figure 24).

However, catalyst 5685-61, which had a maximum DSC peak at about 380°C was brought to 350°C during the DSC experiment and then maintained isothermally for 2 more hours (Figure 25). A subsequent standard DSC experiment did not show the 380°C peak anymore (Figure 26).

These two sets of results show that a low temperature calcination may lower the final calcination temperature requirement when the first calcination temperature is 30°C lower, but not when it is 100°C lower than the temperature at which the maximum in the DSC curve appears.

Effect of Calcination Temperature

Two separate portions each of 100:1 Fe:Cu catalysts 5685-53 and 5685-75 prepared at 4.3 and 9.7 pH, respectively, were calcined at 380 and 450°C and later examined by STEM, TPR, and N_2 adsorption to determine the effect of calcination temperature on Fe-Cu catalysts.

Catalyst prepared at 4.3 pH and calcined at 380°C showed 4 to 6 nm Fe-Cu particles in the STEM examination. The particle size was much larger (5 to 20 nm) for the catalyst

calcined at 450°C. The particle size remained large (10 to 40 nm) at calcination temperatures of 380 and 450°C for the catalyst prepared at a 9.7 pH.

Nitrogen adsorption measurements on a 4.3 pH catalyst calcined at 380 and 450°C are summarized in Figures 27-29. The results indicate that higher temperature calcination decreases the total pore volume from 0.22 to 0.17 cc/g, increases the average pore radius from 5.2 to 6.2 nm and decreases the total surface area from 83 to 53 m^2/g. Similarly for 9.7 pH catalysts, higher temperature calcination increases the average pore radius from 5.2 to 8.9 nm and decreases the total surface area from 74 to 41 m^2/g (Figures 30-32).

The results of TPR experiments with two different portions of catalyst 5685-53 precipitated at a 4.3 pH are summarized in Figure 33. The following differences were found with the portion calcined at 450°C relative to the portion calcined at 380°C:

- The low temperature TPR peak, which seems to be related to the Fe_2O_3 to Fe_3O_4 reaction, increased in magnitude and also shifted to 20°C lower temperature.
- The TPR peak between 350 and 700°C expanded by 20°C to higher temperature and increased in magnitude.

These results indicate that selection of suitable calcination temperatures for Fe-Cu catalysts is important because the morphological properties of iron catalysts, as determined by STEM and N_2 adsorption, are influenced significantly by the calcination temperature.

Furthermore, variations in TPR spectra also were observed with changes in calcination temperature. This observation suggest that the chemical properties of catalysts may also have been influenced by calcination temperature.

Effect of pH

Six catalysts were prepared by the precipitation of solutions containing $Fe(NO_3)_3$ and $Cu(NO_3)_2$ (100:1 Fe:Cu) with Na_2CO_3 solution at pH's of 3.5, 4.3, 5.5, 6.5, 7.9, and 9.7, respectively. These catalysts were characterized by DSC, TGA, STEM, TPR, and XRD to evaluate the effect of the pH of precipitation on Fe-Cu catalysts.

Catalysts 5685-61, 5685-53, 5709-73, and 5709-49 precipitated at a pH of 3.5, 4.3, 5.5, and 6.1 respectively, and dried at 110°C showed amorphous-looking Fe-Cu particles of 2 to 4 nm in the STEM examination (Figures 34 and 35). Catalyst 5685-69 precipitated at a pH of 7.9 and had 20 to 35% crystalline material with 10 to 20 nm of Fe-Cu particles (Figure 36). The rest of the catalyst was amorphous with 2 to 4 nm particles. Catalyst 5685-75 precipitated at a higher pH of 9.7 was 35 to 45% crystalline with 10 to 40 nm Fe-Cu particles (Figure 36). To identify the nature of the crystalline material, catalyst 5685-75 was also analyzed by XRD, which indicated 30.1% of the catalyst to be crystalline α-Fe_2O_3. A minor amount of goethite phase was also detected in XRD (Figure 37).

Because high-pH catalysts showed increased amounts of crystalline Fe_2O_3 with large iron particles, a low pH and a high pH catalyst were calcined and then analyzed by STEM to determine whether differences in catalyst morphology observed after the 110°C drying step still existed after calcination. The STEM micrographs for catalysts with pH's of 4.3 and 9.7 after calcination at 380 and 450°C are in Figures 38 and 39. The low-pH catalyst was composed of 4 to 6 nm Fe-Cu particles after calcination at 380°C, and the high-pH catalyst was composed of 10 to 40 nm particles. Similarly, after 450°C calcination, the low-pH catalyst had 5 to 20 nm particles, and the high-pH catalyst had 10 to 40 nm particles. These results indicate that the Fe-Cu particle size increases with the increase in pH of precipitation, and these differences persist through the calcination step.

Catalysts precipitated at 3.5, 4.3, 7.9, and 9.7 pH were also examined by DSC after the drying step at 110°C (Figure 40). The minima observed at 40 to 50°C are probably related to water evolution. The DSC maximum high temperature peak decreases in magnitude and shifts to higher temperature from 367 to 444°C with an increase in pH from 3.5 to 9.7. All catalysts, regardless of pH, have a secondary maximum at about 250°C. Catalyst with a 7.9 and 9.7 pH also have a low temperature maximum at about 100°C, but catalysts with a 3.5 and 4.3 pH do not. The DSC maximum at about 100°C is apparently related to the formation of large iron oxide particles that are observed during STEM examination of the high-pH catalysts that were dried at 110°C.

The high-pH catalysts that were dried at 110°C lost less weight during the TGA experiment between 100 and 600°C relative to the low-pH catalysts: 5.3% for 7.9 pH catalyst and 4.0% for 9.7 pH catalyst relative to 12% for 3.5 and 4.3 pH catalysts (Figures 14, 16, 41, and 42). Less weight loss during the TGA experiments with high-pH catalysts that were dried at 110°C relative to low pH catalysts that were dried at 110°C is expected because the significant fraction of the reaction of 2FeO(OH) to Fe_2O_3 and H_2O with high-pH catalysts seems to occur during the 110°C drying step before the TGA experiments.

The DSC and TGA experiments show distinct features for catalysts precipitated at different pH's, indicating that the properties of iron catalysts are significantly influenced by the pH of precipitation. These results suggest that DSC and TGA techniques may play a key role for the characterization of Fe-Cu catalysts in the future.

The effect of the pH of precipitation on the properties of Fe-Cu catalysts was further demonstrated by the TPR experiments (Figures 43 and 44). The TPR experiments show that catalysts with a pH of 9.7 can be reduced at lower temperatures relative to 4.5 pH catalysts, regardless of the calcination temperature. Not presently clear is whether these differences in reproducibility of Fe-Cu catalysts precipitated at different pH's are mainly caused by differences in the catalyst particle sizes that were previously discussed.

Effect of Cu Level

Three catalysts were prepared by the coprecipitation of solutions containing different ratios of $Fe(NO_3)_3$ and $Cu(NO_3)_2$ (100:0.5 Fe:Cu, 100:1 Fe:Cu, 100:5 Fe:Cu, by weight) with Na_2CO_3 solution at 6.1 to 6.5 pH. A fourth catalyst with 100:5 Fe:Cu was precipitated at 9.5 pH. These catalysts were characterized by DSC, TGA, STEM, XRD, and TPR to evaluate the effect of Cu level.

In the STEM examination, catalyst 5685-139 with 100:0.5 Fe:Cu showed partly crystalline morphology with 2 to 6nm particles after the 110°C drying step (Figure 45). The XRD analysis of the same catalyst indicated these crystallites to be goethite (Figure 46). As explained previously, crystallites observed with high-pH catalysts (7.9 and 9.5 pH) after 110°C drying were hematite (α-Fe_2O_3) and not goethite (α-FeO(OH)).

Catalysts 5709-49 and 5685-135 with 100:1 Fe:Cu and 100:5 Fe:Cu, respectively, did not show crystallites and had amorphous-looking 2 to 4 nm particles (Figure 45 and 47). These results indicate that Cu may suppress the formation of goethite at 110°C. Because large hematite particles would result from large goethite particles during calcination, the Cu level may be a key variable to control Fe-Cu particle size in the finished catalyst.

Because large hematite particles were formed at 110°C with high pH catalysts and Cu suppressed the formation of large goethite particles at the same temperature, a high-pH catalyst

was prepared to determine whether formation of large hematite particles could be prevented by the use of a high Cu level. Catalyst 5709-37 with 100:5 Fe:Cu was prepared at a pH of 9.5. The amorphous nature of this catalyst indicates that a high Cu level indeed suppressed the formation of large hematite particles at 110°C (Figure 47).

The high and low Cu catalysts 5685-139 (100:0.5 Fe:Cu) and 5685-135 (100:5 Fe:Cu) precipitated at a pH of 6.1 to 6.5 also showed different features in the DSC and TGA experiments (Figures 48 and 49). The weight loss between 100 and 600°C with the low-Cu catalyst, which did not have hematite (α-Fe_2O_3), but only goethite (α-FeO(OH)) crystallites, was about 12%. This weight loss is similar to the weight loss observed with low-pH samples that had no hematite crystallites. These two sets of results are consistent because the weight loss during the TGA experiments between 100 and 600°C is probably attributed to the formation of hematite from FeO(OH). Not presently clear is why the weight loss is less with the high-Cu catalyst because that catalyst did not show hematite formation at 110°C.

Catalysts 5685-139, 5685-61, and 5685-135 with 100:0.5 Fe:Cu, 100:1 Fe:Cu and 100:5 Fe:Cu, respectively, were all calcined at 410°C and then examined by TPR (Figure 50). The low temperature peaks between 100 and 180°C are probably related to the onset of Fe_3O_4 formation or to the reduction of Cu, as discussed previously. The position of the low temperature peak decreased in temperature as the Cu level increased.

The higher temperature peaks between 180 and 210°C are apparently related to the Fe_3O_4 formation reaction. These peak positions were similar for catalysts with 100:5 Fe:Cu and 100:1 Fe:Cu but occurred at a higher temperature with catalyst having 100:0.5 Fe:Cu. These results are consistent with those obtained by other investigators and suggest that Cu may enhance the reduction of Fe_2O_3 to Fe_3O_4.

The portions of the TPR experiments at temperatures higher than 250°C, which involve reduction of Fe_3O_4 to metallic Fe by FeO formation were different with the three catalysts containing different levels of Cu. However, no obvious trend in the ease of reduction to metallic Fe with Cu level was observed.

Effect of Potassium

Catalysts 5685-139 with 100:0.5 Fe:Cu and catalysts 5685-135 with 100:5 Fe:Cu were impregnated with potassium (K), in the form of potassium carbonate (K_2CO_3). The TPR behavior of these catalysts were compared before and after K impregnation. Results summarized in Figures 51 and 52 indicate that although K may inhibit the reduction of Fe_2O_3 to Fe_3O_4, it certainly enhances the reduction of Fe_3O_4 to metallic Fe.

Catalysts Precipitated with NH_4OH

Different DSC features of 100:1 Fe:Cu catalysts 5685-75 and 5685-111 prepared by precipitation at 9.5 to 9.7 pH using Na_2CO_3 and NH_4OH solutions, respectively, were previously described (Figures 21 and 22). The STEM examination of these catalysts after 110°C drying indicated that although Na_2CO_3-derived catalyst was partly crystalline, with 10 to 40 nm Fe-Cu particles, NH_4OH-derived catalyst had only amorphous-looking particles no larger than 2 to 4 nm. These two catalysts were later calcined at 450°C and further characterized to determine whether differences between them would continue to exist through the catalyst finishing steps. The STEM examination indicated that although the average Fe-Cu particle size was approximately the same with both catalysts, the particle size distribution was wider with Na_2CO_3-derived catalyst (10 to 40 nm) relative to NH_4OH-derived catalyst (25 to 30 nm) (Figure 53). According to TPR experiments, although Fe_3O_4 formation seems to have shifted to about 20°C higher temperature, reduction to metallic Fe seems to have been enhanced with the NH_4OH-derived catalyst (Figure 54).

Summary of the Effect of Catalyst-Preparation Parameters

The observed effects of various catalyst preparation parameters is summarized in the following paragraphs:

- A pH of at least 2 is required to precipitate an iron nitrate solution by using sodium carbonate or ammonia solutions. A pH of at least 5 is required to precipitate Cu nitrate solution. However, in the presence of iron nitrate, the precipitation of Cu occurs at lower pH's.
- An increase in calcination temperature decreases the surface area and pore volume of precipitated Fe-Cu catalysts. Therefore, the calcination temperature should be no higher than that required for forming Fe_2O_3 from FeO(OH).
- The amount of crystalline Fe_2O_3 in a precipitated Fe-Cu catalyst is maximized when calcination is conducted at the high temperature maximum in the DSC curve. This result suggests that DSC experiments may be useful for determining the calcination temperature requirement for Fe-Cu catalysts.
- According to DSC measurements, the calcination temperature requirement for precipitated 100:1 Fe:Cu catalysts prepared from Na_2CO_3 increased from about 380°C to about 450°C as the pH of precipitation increased from 3.5 to 9.5.
- The Na_2CO_3-derived Fe-Cu catalysts prepared at a pH of ≤ 6.5 had small amorphous particles. The catalysts prepared at a pH of ≥ 7.9 were increasingly crystalline, with large hematite (α-Fe_2O_3) particles, after 110°C drying. These morphological differences remained through the calcination step. This result indicates that the pH of precipitation is the key variable for controlling the Fe-Cu particle size.
- The Na_2CO_3-derived 100:0.5 Fe:Cu catalyst prepared at a pH of 6.5 had large goethite (α-FeO(OH) particles. The 100:1 Fe:Cu and 100:5 Fe:Cu catalysts

prepared at same pH had small amorphous particles. Because large goethite particles lead to large hematite particles during calcination, the Cu level may also be a key variable for controlling the Fe-Cu particle size.

- The formation of Fe_3O_4 from Fe_2O_3 occurred at lower temperatures with Na_2CO_3-derived 100:5 Fe:Cu and 100:1 Fe:Cu catalysts relative to 100:0.5 Fe:Cu catalyst prepared at a 6.1 to 6.5 pH. This result indicates that Cu enhances the reduction of Fe_2O_3 to Fe_3O_4.
- The formation of Fe_3O_4 from Fe_2O_3 occurred at a higher temperature. The formation of metallic Fe from Fe_3O_4 occurred at a lower temperature after K_2CO_3 impregnation of Na_2CO_3-derived catalysts prepared at a 6.1 to 6.5 pH. This result indicates that although K may inhibit the reduction of Fe_2O_3 to Fe_3O_4, it may enhance the reduction of Fe_3O_4 to metallic Fe.
- The NH_4OH-derived 100:1 Fe:Cu catalyst precipitated at a 9.5 pH had small amorphous particles, but Na_2CO_3-derived catalyst prepared at the same pH had large hematite particles after 110°C drying. However, after 450°C calcination, the average particle sizes were similar for both catalysts. This result indicates that the use of NH_4OH relative to Na_2CO_3 does not provide an obvious advantage.
- The complete reduction of precipitated Fe-Cu catalysts require temperatures in excess of 800°C. Because reduction temperatures no higher than 300°C can lead to very active catalysts, the reduction of Fe-Cu catalyst surface must be occurring at much lower temperatures than those required for bulk reduction.

Catalyst Preparation Plant

In the catalyst preparation plant (Figure 55a), metal was not used as a material of construction for any wetted section to avoid catalyst contamination that may occur through the dissolution of metallic components in contact with acidic solutions. The materials of construction for the process lines, fittings, and reactor were either Teflon or polypropylene. The Fe-Cu nitrate and the sodium carbonate (Na_2CO_3) feed solutions are in two separate 15-gallon feed tanks. During the experiment, the weight of these solutions is continuously measured by two scales. The feed solutions are pumped separately to a precipitation reactor.

The detailed drawings of the precipitation reactor are in Figures 55b, 55c, 55d, 55e, and 55f. The reactor was designed specifically to prevent plugging during the precipitation of Fe and Cu. The two feed solutions get in contact with each other in a vertical rotating mixer zone. One of the pH probes is located at the outlet of the vertical mixing zone. Small strips attached to the end of the mixer help minimize, to some extent, the buildup of precipitate on the surface of the pH probe. Nevertheless, this pH probe did not provide reliable pH measurements (because of solids buildup). More reliable pH measurements were possible with another probe located 1 inch lower in the reactor. The surface of this second probe was kept relatively clean by means of a small horizontal water (deionized) stream.

The product, slurry, is pumped from the reactor directly to a centrifugal filter. The filter bags had 1 to 3 nm pore dimension and were supplied by Ketema, Inc. The specifications for the bags were Ketema STK 02-010S0-12 inch TOLHURSH olefin composition. The centrifuge effectively filters the precipitate and rejects the rest of the solution. Typically, the filter bag is replaced every 2 hours. However, during these 2 hours, the filtration rate is slower than the feed rate to the centrifuge. The excess slurry is collected in a 55-gallon drum. Following the termination of the run, the supernatant solution is decanted from the top of the drum. The concentrated slurry is pumped to the centrifuge for further collection of solids. After recovery, the solid precipitate is washed with water in separate batches. Typically, 100 grams of water was required for every gram of catalyst to achieve a sodium level less than 5 weight parts per million (wppm). Typically, 80 to 90% of the Fe and Cu pumped to the precipitation reactor was recovered from the washing step.

Drying, Calcination, Impregnation, and Calcination

Following the washing step, the catalyst was dried in an oven at 110°C for 24 hours. The oven-dried material was ground to more than 40 mesh and then calcined under 3 L/min air flow in a quartz tube furnace for 2 hours. Typical batch sizes for calcination have been 500 to 600 grams of catalyst. The calcined material was then ground to 140 to 400 mesh. Typically, 30% of the calcined material became more than 400 mesh and rejected from the rest of the catalyst preparation.

The calcined catalyst was then impregnated with a potassium carbonate (K_2CO_3) solution in a rotary impregnator. The impregnating solution to catalyst weight ratio was 1.26. Following 20 minutes of contact of the catalyst with the sclution, steam was injected to the impregnator jacket to boil off the water. The evolution of water took another 2 hours. The catalyst recovery during the impregnation step is typically more than 98%.

Following impregnation, the catalyst was recalcined under air at 380°C for 2 hours. The calcined catalyst was then sieved again to recover 140 to 400 mesh portion. The additional fines (more than 400 mesh) produced in this step is typically more than 5% of the calcined material.

Catalysts Prepared in the Plant

A total of 16 runs were performed in Plant 752. Some of these catalysts from these different runs were combined to make larger batches of catalysts. The preparation parameters and the properties of these catalysts that were actually evaluated in Fischer-Tropsch synthesis are summarized in Table 1. The same table also lists the batch size for the final finished catalysts as well as the pilot plant run numbers at which they were tested.

Example of Catalyst Characterization

As outlined previously, several different portions were obtained from any given precipitation run in Plant 752. These portions were separately filtered, washed, dried, calcined, and characterized

by STEM to check the uniformity of the preparations. Only portions that had similar size Fe-Cu oxide particles and with comparable Fe:Cu ratios were combined to make larger batches.

For example, six different portions were obtained during Run 15 (Plant 752). Portion 1B was collected in the filter bag during the precipitation run. Portions 1, 2, 3, 4, and 5 were collected from the 55-gallon drum. The aging times of Fe-Cu precipitate in the product slurry (for portions 1 to 5) were for several days compared to no more than 2 hours for portion 1B.

The STEM results for Run 15 (Plant 752) catalyst is summarized in Table 5a. According to the STEM examination, the Fe-Cu oxide particle size of the various portions, was either 10 to 20 nm or 10 nm and less. Portion 1B had ≤ 10 nm particles, which is identical to the particle size obtained from portions 4 and 5.

On the other hand, the Fe content was highest for portion 1B. This suggests that some dissolution of Cu occurred during the extended aging period.

Details of Preparation for Catalyst 6616-18

Catalyst 6618-18 was tested in the long-term stability test in Run 19, Plant 700B. The precipitation of Run 16 in Plant 752 produced four portions of catalyst. Drying and calcination occurred in the laboratory.

1) 0 to 3 hours of precipitation collected in filter bag during the run

2) 3 to 6 hours of precipitation collected in filter bag during the run

3&4) collected and recovered from the 55-gallon drum after the run

The following table summarizes the characterization results for the calcined portions:

Portion	Na, ppm	STEM Fe-Cu oxide particle size, nm	Average composition* of Fe:Cu (by weight)	Surface area (N_2 adsorption), m^2/g
1	15	<20	100:2.52	59
2	15	5-20	100:2.30	
3	4.5	5-20	100:2.11	90
4	2.4	5-20	100:5.52	
* Semiquantitive analysis				

Calcined portions 2 to 4 were combined and ground to 140 to 400 mesh: 940 grams ended up in the 140 to 400 mesh, and 530 grams ended up in the fines (>400 mesh). The combined batch was analyzed and found to have 67.3% Fe and 100:1.23 Fe:Cu (by weight). A 300-gram portion of the combined portions 2 to 4 was impregnated with potassium carbonate solution. The impregnated catalyst was calcined. The final composition 100:1.15:1.57 Fe:Cu:K (by weight).

The final catalyst, 6616-18, was examined with STEM. The Fe-Cu-K oxide particles were 10 to 20 nm in size.(Figure 55g) The composition for 14 of these particles are reported

in Table 5b. The results in Table 5b reveal that Cu is more uniformly distributed among individual particles than K. The apparent high level of Cu observed during STEM examination of the individual particles (relative to bulk analysis) may result from the fact that the Cu analysis with STEM was not standardized against atomic absorption spectroscopy technique used for bulk Cu analysis. Furthermore, the Cu content of the Fe-Cu-K oxide particles observed during STEM may be higher than the Cu content of amorphous regions of the catalyst, resulting in an overall lower Cu content.

Experimental Fe Catalyst Evaluation in Fixed-Bed

An experimental Fe catalyst, 5709-91, prepared in the lab, was evaluated under Task 3. Two tests were done in the fixed-bed pilot plant in an attempt to provide future direction for the catalyst development work that is to be conducted in a slurry reactor. These studies were later pursued on completion of the slurry pilot plant.

Two runs were conducted: fixed-bed Runs 50 and 51. Catalyst identification, nature of diluents, catalyst and diluent weights, catalyst and diluent mesh-size ranges, and catalyst and diluent bed lengths are summarized in Table 6. For all of these tests, the catalyst was first heated under N_2 flow at 1 atm to 100°C, and then synthesis gas was introduced. The reactor was pressured to 9 to 11 atm with synthesis gas, and the catalyst was heated to 280°C under a synthesis gas flow. The test conditions were changed several times during these runs. Catalyst inlet temperatures (2 inches before the catalyst bed) and maximum temperatures, inlet and outlet

pressures, feed compositions, feed rates, and space velocities at different hours on-stream are also summarized in Table 6.

The results with the experimental Fe catalyst 5709-91 are summarized in Figures 56-63. The catalyst showed a high exotherm of 320°C when the catalyst inlet temperature was 279°C, at about 6 hours on-stream. After 6 hours, the catalyst inlet temperature was lowered to 250°C, the space velocity was lowered from 3.0 to 2.4 NL/hr/gFe, and the feed H_2:CO ratio was lowered from 0.7 to 0.5. Under these conditions, the catalyst maximum temperature was about 259°C. The CO+H_2 conversion gradually declined from 88% to somewhere between 62 and 68% by 200 hours on-stream. During the same period, the CO_2 selectivity, the H_2:CO usage ratio, and the H_2:CO outlet ratio were constant, but the methane selectivity gradually increased to a value of 2.4 to 2.6%. These results indicate that both catalytic activity and hydrocarbon selectivities were changing with time during the first 200 hours. Also, the propylene to propane ratio, which may show the hydrogenation activity of the catalyst, gradually decreased. This observation is consistent with the increase in methane selectivity. Later in the run, the pressure was increased from 13 to 33 atm. At this high pressure, the CO+H_2 conversion was stable at 82 to 83% between 202 and 322 hours on-stream. On the other hand, the propylene to propane ratio continued to decrease, and the methane selectivity gradually increased after an initial decrease.

The experimental Fe catalyst 5709-91 was evaluated in an extended 800-hour test in fixed-bed Run 51 (Table 7 and Figures 64-74). The objective was to determine the catalyst

stability at high conversion. Relatively low pressures, typical of what is used in other laboratories, were selected. After an initial 270°C treatment with synthesis gas during the first 26 hours, the catalyst inlet temperature was first lowered to 259°C, then to 240°C by 70 hours on-stream, and finally increased to 247°C by 260 hours on-stream. At this inlet temperature, the maximum catalyst temperature fluctuated between 270°C and 295°C (Figure 64). After 260 hours, other conditions were implemented: 13 atm, 0.7:1 H_2:CO feed ratio, and feed rate of 1.9 NL/hr/gFe. Between 260 and 800 hours, the CO+H_2 conversion gradually decreased from about 90% to about 75%. During the same period, the H_2:CO outlet ratio also decreased because the usage ratio was lower than the feed ratio. The methane selectivity fluctuated between 3.5 and 4.2% and the ethane plus ethylene selectivity increased from 2.0 to 3.0%. The methane and ethane selectivity was about 5.5% at lineout. Because approximately 50% of CO converts to CO_2, based on hydrocarbons and oxygenates only, the overall selectivity to methane and ethane was about 11%. The Anderson-Schulz-Flory distribution plots for hydrocarbons made during the run show the chain-growth probability to be 0.875 between carbon numbers 3 to 15. The chain-growth probability increased for higher carbon numbers and was 0.986 for carbon numbers between 60 and 140 (Figures 72 and 73).

The results indicate that the activity of the experimental Fe catalyst 5709-91 was not stable in the fixed-bed reactor under the current operating conditions: the deactivation rate was about 0.8% conversion/day. These operating conditions are more severe than those typically used in a slurry reactor for which this Fe catalyst is intended. Specifically, the fixed-bed catalyst temperature reached as high as 295°C (compared with 255-280°C for slurry reactors),

which may have enhanced the deactivation rate. Also, at the inlet of the catalyst bed where little water exists, the H_2:CO ratio may have reached a value much lower than the feed ratio (0.7) because of the essential absence of the water gas shift reaction.

Shakedown of Slurry Pilot Plant

The slurry-bed pilot plant was described above (Task 1). Slurry-bed Run 1 was for pilot plant shakedown. The catalyst identification, the nature of the initial wax medium, the catalyst, and initial wax weights are summarized in Table 8. The C_{32} wax medium was from Humphrey Chemical Corp. According to the manufacturer, the major impurity, which is bromine, is introduced during the synthesis, which involves the Wurtz reaction. A detailed analyses of the wax was not made at UOP. The catalyst and the C_{32} paraffin wax medium were loaded into the 1-liter autoclave reactor at 65°C. The 1-liter autoclave was pressure-tested with N_2 at 65°C and 18 atm. After a successful pressure test, the pressure was lowered to 11 atm, and the temperature was increased to 120°C under N_2 flow. Synthesis gas was introduced at 120°C. The temperature was then gradually increased to 280°C under synthesis gas flow. The test conditions were changed several times during this run. Autoclave internal temperatures, pressures, feed compositions, feed rates, and space velocities at different hours on-stream are summarized in Table 8. The mechanical stirring of the slurry medium was achieved by a stirrer connected to the bottom of the autoclave.

The conversions and C_1 and CO_2 selectivities during slurry-bed Run 1 are summarized in Figures 75-79. The catalyst temperature was gradually raised during the first 21 hours from 120°C to 280°C under 2.1 NL/hr/gFe synthesis gas (0.7:1 H_2:CO). At 280°C, three space velocity changes brought the CO+H_2 conversion up to 70% by the end of the activation treatment at 39 hours on-stream. The CO_2 and C_1 selectivities were 41 and 4.1%, respectively. At the end of the activation treatment, the temperature was lowered to 257°C, and the pressure was raised from 13 to 15 atm. With subsequent space velocity changes, 90% CO+H_2 conversion was achieved after 60 hours on-stream at 0.80 NL/hr/gFe. Under these conditions, the CO_2 and C_1 selectivities were 40 and 3.3%, respectively. At 63 hours on-stream, a new feedstock with 0.5:1 H_2:CO ratio was introduced. Following the feedstock change, two additional space velocity changes were made these changes lowered the space velocity to 0.72 NL/hr/gFe. With the low H_2:CO ratio feed gas, the CO+H_2 conversion decreased to somewhere between 70 and 75% at 172 hours on-stream. Run 1 was continued for another 35 hours under identical conditions. The CO+H_2 conversion continued to decrease and was about 57% at the end of the test at 207 hours on-stream. These results indicate that the catalyst was not stable with the low H_2:CO feed gas. Catalyst deactivation was also apparent in the methane selectivity, which gradually increased following the feedstock change.

During this first test in the slurry pilot plant, operational parameters were frequently varied without any noticeable plant upsets. The response of the catalytic performance to operational changes were within expected ranges. Therefore, the shakedown of the slurry pilot plant was considered successful.