I. EXECUTIVE SUMMARY

The work on Task 3. Testing of Previously Synthesized Catalysts has been completed during this quarter. Another test (run SA-0025) of catalyst with nominal composition 100 Fe/5 Cu/6 K/24 SiO_2 was not successful (low activity), when a purified n-octacosane was used as the initial slurry medium. After this test, we decided to discontinue using the n-octacosane as the start-up fluid, and in all subsequent tests Ethylflo 164 oil was used as the start-up medium. Three successsfull slurry reactor tests were completed with the Ethylflo 164 oil as the initial liquid medium: run SB-0665 with the 100 Fe/5 Cu/6 K/24 SiO_2 catalyst, and runs SB-0045 and SA-0705 with the 100 Fe/3 Cu/4 K/16 SiO_2 catalyst. These tests were conducted with the objective to verify the catalyst activity/selectivity performance in runs SB-1931 (100 Fe/5 Cu/6 K/24 SiO_2 catalyst) and SB-0261 (100 Fe/3 Cu/4 K/16 SiO_2 catalyst). The latter two tests were conducted during our previous DOE Contract DE-AC22-89PC89868. High syngas conversions (65-85%) and low methane and gaseous hydrocarbon selectivities were obtained in all three tests. In view of the fact that the initial two tests with these two catalysts were conducted 3-4 years ago, and that different start-up fluids were employed in recent tests, the reproducibility of results in multiple tests of the same catalyst may be regarded as quite satisfactory. The 100 Fe/5 Cu/6 K/24 SiO_2 catalyst was more stable in the original test (SB-1931) than in two recent tests (SB-3354 and SB-0665), whereas the opposite trend was observed in tests with the 100 Fe/3 Cu/4 K/16 SiO_2 catalyst. Selectivities in multiple tests with the same catalyst were even more reproducible. In runs SB-0045 and SA-0705 reactor space-time-yield was increased by 41-46% (relative to baseline conditions: 1.48 MPa; 2.4 Nl/g-Fe/h) by increasing reaction presure and gas space velocity to 2.17 MPa and 3.5 Nl/g-Fe/h, respectively.

During the reporting period we completed synthesis of about 100 g of catalyst with nominal composition 100 Fe/3 Cu/4 K/16 SiO_2 (S-3416-2), and of another batch (173 g) of the same catalyst (S-3416-3). Also, we synthesized two additional batches of catalyst with nominal composition 100 Fe/5 Cu/6 K/24 SiO_2, in the amounts of 240 g (S-5624-3) and 200 g (S-5624-4). These amounts are sufficient for all planned tests with these two catalysts for the entire duration of this contract. The synthesized catalysts were characterized by atomic absorption, and BET surface area and pore size distribution measurements.

II. DETAILED DESCRIPTION OF TECHNICAL PROGRESS

II. 1 Task 3. Testing of Previously Synthesized Catalysts

Five tests were conducted during the past quarter. A test designated SA-0025, with 100 Fe/5 Cu/6 K/24 SiO_2 catalyst, in our slurry reactor system A (SA) was not successful (low activity). The operability of the SA reactor was then checked in the test SA-0415 using the commercial Ruhrchemie catalyst. Results from this test suggested that the catalyst poisoning by impurities in n-octacosane was a probable cause of low catalyst activity in run SA-0025. After that three successful tests were conducted using the Ethylflo 164 oil as the initial slurry medium (run SB-0665 with 100 Fe/5 Cu/6 K/24 SiO_2 catalyst, and runs SB-0045 and SA-0705 with 100 Fe/3 Cu/4 K/16 SiO_2 catalyst). With completion of these three tests, the work on Task 3. Testing of Previously Synthesized Catalysts in slurry reactor was completed on schedule.

II. 1. 1 Run SA-0025 with 100 Fe/5 Cu/6 K/24 SiO_2 Catalyst

A test in our slurry reactor system A (SA), designated run SA-0025, with 100 Fe/5 Cu/6 K/24 SiO_2 catalyst was carried out during January. This was the fourth test with this catalyst. Two previous tests (SB-2764 and SB-3064) with this catalyst were not successful, which was believed to be due to catalyst poisoning by impurities in n-octacosane (the initial slurry medium), whereas good results were obtained in test SB-3354 using the Ethylflo 164 oil as the initial slurry medium (Quarterly Report for September 1 - December 31, 1994). The purpose of this test was to check reproducibility of results obtained during the previous DOE Contract DE-AC22-89PC89868 in run SB-1931 with the same catalyst, in a different reactor system, after taking additional precautions in purification of n-octacosane.

About 10.5 g of catalyst (< 270 mesh in size) and 310 g of normal octacosane (as slurry medium) were used for this test. Prior to loading, the octacosane was purified by washing with THF for 10 min, instead of usual 5 min duration. The catalyst was reduced with H_2 at 250°C for 4 h, and then tested at 260°C, 1.48 MPa (200 psig), 2.1 Nl/g-cat/h and synthesis gas molar feed

ratio of 0.67 ($H_2/CO = 0.67$). After 9 hours on stream, the syngas conversion reached only about 19 %, whereas methane selectivity was 2 mol%. Subsequent reduction of gas space velocity to 1.8 Nl/g-cat/h (at 22 h on stream) and increase of the Autoclave reactor head temperature to 260°C (44 h on stream) did not result in increase of the catalyst activity. The syngas conversion remained low at about 18%, until the test was terminated after 63 h on stream.

In order to determine the cause of low activity in this test we have done the following: (1) Sent samples of n-octacosane for trace halogen analysis, and (2) Performed another test in the slurry A reactor system to check its operability. Results from these tests are described below.

Impurities in n-Octacosane

After the test SA-0025, samples of fresh n-octacosane (before purification with THF), and from the slurry reactor (after the purification) were sent for trace bromine analysis to two different Laboratories. According to analysis done at the Galbraith Laboratories, Inc. (Knoxville, TN) the as received n-octacosane had 530 ppm bromine, and the purified one less than 10 ppm bromine. The VHG Labs Inc. (Manchester, NH), using TOX (total organic halogen) method, detected higher level of impurities. They reported 0.7 wt% total halogens (as bromine) in fresh n-octacosane, and less than 0.005 wt% (50 ppm) in the purified sample. Both results show that the amount of bromine in octacosane was substantially reduced with THF washing. However, it can not be ruled out that the residual ppm level of bromine had a detrimental effect on the catalyst activity. The presence of trace sulfur was also detected by Galbraith Laboratories in used octacosane samples (Quarterly Report for September 1 - December 31, 1994). Therefore, we believe that the presence of impurities in n-octacosane had resulted in catalyst poisoning in the test SA-0025, as well as in the earlier tests SB-2764 and SB-3064 with the same catalyst. Results from Run SA-0415 with the Ruhrchemie catalyst (reported below) lend support to this hypothesis. We do not plan to use n-octacosane as the initial slurry medium in future tests.

II. 1. 2 Run SA-0415 with Ruhrchemie LP 33/81 Catalyst

This test was conducted following the unsuccessful run SA-0025 with 100 Fe/5 Cu/6 K/24 SiO_2 catalyst, in order to check whether low catalyst activity in this test was due to the use of n-octacosane in the slurry reactor A system (SA). We used the commercial Ruhrchemie LP 33/81 catalyst (nominal composition 100 Fe/5 Cu/4.2 K/25 SiO_2) for this purpose, and Ethylflo 164 oil (a hydrogenated 1-decene homopolymer liquid - C_{30}, obtained from the former Ethyl Co.) was used as the initial slurry medium to replace n-octacosane. Also, to check the effect of gas circulation on the catalyst performance, the side hole in the bottom part of the Autoclave reactor stirrer shaft was intentionally plugged with bolt and nut before loading, so that any gas circulation through the interior of the stirrer shaft would be minimized during the run. About 5.0 grams of the catalyst (< 270 mesh in size) was employed in this test. The catalyst was reduced with H_2 at 250°C for 4 h, and then tested at 260°C, 1.48 MPa (200 psig), 1.8 Nl/g-cat/h and feed ratio H_2/CO = 0.67. During 46 hours of testing, the total syngas ($CO+H_2$) conversion was between 65 and 69 % (Figure 1a), whereas the H_2/CO usage ratio was between 0.62 and 0.67. Methane selectivity varied between 3.2 and 3.6 mol% (Figure 1b). These values are in good agreement with the ones obtained in run SB-3254 (Quarterly Report for September 1 - December 31, 1994) using the same catalyst, and the same reduction and process conditions. Results from these two tests show that the catalyst performance is reproducible in both reactor systems (slurry A and B reactors). Blocking the hole in the stirrer shaft had no adverse effects on catalyst performance, i.e., it did not affect the gas circulation inside the Autoclave reactor. The problems encountered in run SA-0025 (low activity) were probably due to the use of n-octacosane as the start-up liquid.

II. 1. 3 Run SB-0665 with 100 Fe/5 Cu/6 K/24 SiO_2 Catalyst

This test was conducted to check reproducibility of results obtained in run SB-3354 with the same catalyst, the same initial slurry medium and the same reactor (SB). Ten grams of the catalyst (< 270 mesh in size) from the original preparation batch was loaded for the test, and

Ethylflo 164 oil was used as the initial slurry medium. Major events during the run are shown in Table 1 and detailed results from four mass balances are summarized in Table 2. Following the reduction with H_2 at 250°C for 4 h, the catalyst was initially tested at 260°C, 1.48 MPa (200 psig), synthesis gas molar feed ratio of 0.67 ($H_2/CO = 0.67$) and space velocity of 2.0 Nl/g-cat/h for 46 h, then at 1.8 Nl/g-cat/h for 87 h and finally at 1.6 Nl/g-cat/h for 240 h. Changes in catalyst activity (in terms of CO, H_2+CO conversions and usage ratio) as well as selectivity (CH_4, $C_1 + C_2$ and $C_2 - C_4$ hydrocarbons) are shown in Figures 2 and 3, as a function of gas space velocity and time on stream. Initially the catalyst exhibited high activity, but it deactivated with time. The CO and (H_2+CO) conversions after 7 h at the initial conditions were about 84 and 82 %, respectively, they decreased to 76 and 72 % at 46 h (Figure 2a, and 2b). Catalyst deactivation continued when the space velocity was lowered to 1.8 Nl/g-cat/h, at the end of this period of testing the CO and (H_2+CO) conversions became 71 and 67 %, respectively. However, the catalyst was more stable afterwards. From 160 to 300 h on stream at gas space velocity of 1.6 Nl/g-cat/h, the CO conversion remained between 71 % and 68 %, whereas syngas conversion was between 68 % and 65 %. The catalyst activity suddenly increased between 307 and 326 h on stream, the CO conversion went up from 67 to 73% overnight, whereas syngas conversion increased from 64 % to 69 %. The catalyst activity then stabilized at 70 % CO conversion and 67 % syngas conversion during the next 72 h. The (H_2/CO) usage ratio was about 0.56 initially (Figure 2c), but it gradually increased to 0.58, indicating a decrease in WGS reaction activity with time.

Low molecular weight hydrocarbon selectivities increased during the first 160 h of testing, and then remained relatively stable as the catalyst activity stabilized. As shown in Figure 3a, during the first 160 h of testing the methane selectivity increased from 2.5 to 3.5 mol%, and then varied between 3.4 and 3.7 % during the next 220 h of testing. Similar trends were also observed for C_2, C_3, C_4 olefins and n-paraffins. For example, during the first 160 h of testing, ethylene selectivity increased from 1.3 to 2.1 %, ethane from 1.3 to 1.6 %, propylene from 3.8 to 4.8 %, propane from 0.7 to 0.9 %, (1+2) butene from 3.0 to 3.6 % and n-butane from 0.7 to 0.9

%; afterwards, these selectivities showed little change with time. The final total $C_1 + C_2$ selectivity was about 7.5 mol% (Figure 3b), and selectivity to C_2 - C_4 hydrocarbons (including isomers) was 15 mol% (Figure 3c).

Comparison of Data from Runs SB-1931, SB-3354 and SB-0665

Figure 4 compare the conversions and usage ratio among the three tests with the 100 Fe/5 Cu/6 K/24 SiO_2 catalyst. In the original test SB-1931 (with n-octacosane as the initial slurry medium), the CO and syngas conversions were stable with time. However, in the two recent tests SB-3354 and SB-0665 (with Ethylflo 164 oil as the initial slurry medium) the catalyst deactivated during the first 150 h of testing (Figures 4a and b). Comparison of catalyst activity is observed better in Figure 5, where the apparent first order rate constant, k, is plotted as a function of time. The apparent rate constant depends on temperature only, which was kept constant in all three tests, and thus provides a direct comparison of the catalyst activity. Initial activities in all three tests were about the same, k = 340-350 mmol/g-Fe/h/MPa. In run SB-1931, the apparent rate constant gradually decreased from 350 to 300 mmol/g-Fe/h/MPa over a 400 hour period. However, in run SB-3354, the rate constant decreased from 340 to 250 mmol/g-Fe/h/MPa during the first 150 h of testing. It was then stable at this value during the next 150 hours of testing at SV = 1.6 Nl/g-cat/h; and then dropped further to 200 mmol/g-Fe/h/MPa during testing at SV = 1.2 Nl/g-cat/h. In run SB-0665, the initial activity was 350 mmol/g-Fe/h/MPa at 20 h , but the rate constant decreased from 350 to 250 mmol/g-Fe/h/MPa in 120 hours, and then stabilized at 220 mmol/g-Fe/h/MPa between 180 to 370 h of testing.

Low selectivities of methane and other gaseous hydrocarbons obtained in run SB-1931 were generally reproduced in recent tests SB-3354 and SB-0665 (Figure 6). For example, selectivities to methane and C_2 - C_4 hydrocarbons during run SB-3354, were similar to those obtained in run SB-1931 (2.5-3% and 12-13 mol%, respectively); whereas the corresponding values in run SB-0665 were slightly higher (i.e. 2.5-3.6% and 12-15 mol%, respectively).

II. 1. 4 Run SB-0045 with 100 Fe/3 Cu/4 K/16 SiO_2 Catalyst

This was the first of the two slurry reactor tests with this catalyst which were completed during the reporting period. The objective of this test was to check reproducibility of results obtained during the previous DOE Contract DE-AC22-89PC89868 in a slurry reactor test designated SB-0261 with the same catalyst (n-octacosane as the initial slurry medium).

About 7.0 g of catalyst (< 270 mesh in size), from the same preparation batch as that used in run SB-0261, was used in the test. Replacing n-octacosane, 340 g of Ethylflo 164 oil (a hydrogenated 1-decene homopolymer liquid - C_{30}, obtained from Ethyl Co.) was used as the initial slurry medium. After reduction with H_2 at 250°C for 2 h, the catalyst was tested at 260°C, 1.48 MPa (200 psig), 1.4 Nl/g-cat/h and syngas molar feed ratio of 0.67 ($H_2/CO = 0.67$). During the next 255 h on stream, the CO conversion was stable at about 87 - 89 %, the syngas conversion at 81 - 83 % (Figure 7a and 7b). The usage ratio, a measure of the water-gas-shift (WGS) activity, was about 0.55 - 0.56 (Figure 7c). Methane selectivity was low, 1.8 - 2.5 mol% (Figure 8a); the lumped selectivity of $C_1 + C_2$ was 4.6 - 5.6 % (Figure 8b), and total C_2 - C_4 was around 10.5 % (Figure 8c). At 257 h on stream, the reaction pressure and space velocity were increased proportionally to 2.17 MPa (300 psig) and 2.05 Nl/g-cat/h, respectively. The catalyst maintained its activity and stability during testing at higher pressure. The CO and syngas conversion decreased slightly to about 83 - 86 %, and 78 - 81 %, respectively, whereas the usage ratio increased to 0.57 - 0.58. The methane selectivity was between 2.5 to 2.2 mol%. The total $C_1 + C_2$ selectivity was 5.5 mol%, and that of C_2 - C_4 hydrocarbons was 11 mol%. The test was terminated after 400 h on stream. Table 3 lists major events during the test, whereas Table 4 gives the summary results for six mass balances.

This test was very successful, and produced similar activity, methane and gaseous hydrocarbon selectivities as those obtained in test SB-0261, but the catalyst was more stable in the current test than in the original test.

II. 1. 5 Run SA-0705 with 100 Fe/3 Cu/4 K/16 SiO_2 Catalyst

This second test with the 100 Fe/3 Cu/4 K/16 SiO_2 catalyst was carried out in a different reactor system (SA) than the original one (SB), therefore, it also served as a check of effects of the use of different reactors on our results. About 8.9 g of catalyst (< 270 mesh in size) was used for the test. The same type of hydrogenated homopolymer oil as that used in the run SB-0665 was used in this test as the initial slurry medium. This oil is now designated as Durasyn 164 (previously Ethylflo 164 oil), and is manufactured by Albemarle Co., Baton Rouge, La. After reduction with H_2 at 250°C for 2 h, the catalyst was first tested at 260°C, 1.48 MPa (200 psig), 1.4 Nl/g-cat/h and syngas molar feed ratio of 0.67 ($H_2/CO = 0.67$). Changes in catalyst activity and selectivity with time on stream are shown in Figures 9 and 10. The catalyst lost some activity initially, but then stabilized after 80 h of testing. For example, the initial CO and (H_2+CO) syngas conversions at 8 h on stream were 92 and 85 %, respectively. At 80 h on stream they decreased to 87 and 82 %, respectively; and then remained at these levels during the next 180 h of testing (Figure 9a and 9b). The H_2/CO usage ratio, a measure of the WGS activity, was around 0.56 (Figure 9c). With decrease in FTS activity, the selectivity to methane and other low molecular weight hydrocarbons increased with time. Methane selectivity went up from 1.9 mol% to 3.3 %, whereas total C_2-C_4 selectivity increased from 8 to 13 mol% (Figure 10a and 10c). At 264 h on stream, the reaction pressure and space velocity were increased proportionally to 2.17 MPa (300 psig) and 2.05 Nl/g-cat/h, respectively, in order to increase the reactor space-time-yield. The CO and syngas conversions remained at 84 and 79 %, respectively, during the next 100 h of testing. Afterwards the activity started to decrease gradually, e.g., the CO conversion decreased to 80 % at the end of 260 h of testing at higher pressure (526 h on stream), whereas the syngas conversion decreased to 75 %. Methane selectivity was stable during this period, about 3 mol%. The total $C_1 + C_2$ selectivity was about 7 mol%. The final lumped C_2 - C_4 hydrocarbon selectivity was about 14 mol%. The test was terminated after 526 hour on stream. The major events during the test are listed in Table 5. Total of five mass balances were completed during the run and the results are summarized in Table 6.

Comparison of Data from Runs SB-0261, SB-0045 and SA-0705

Comparison of conversions and the usage ratio among three tests with the 100 Fe/3 Cu/4 K/16 SiO_2 catalyst is made in Figure 11, of the apparent rate constant in Figure 12 and of gaseous hydrocarbon selectivities in Figure 13. During the first 100 h of testing, the CO and syngas conversions were very similar in all three tests (see Figures 11a and 11b). This good reproducibility of the catalyst activity is also reflected in Figure 12, in which the apparent reaction rate constant varied between 250 - 270 mmol/g-Fe/h/MPa during this period of time. In the original run SB-0261, the catalyst deactivated after 100 h on stream. By contrast, the catalyst in the two recent runs SB-0045 and SA-0705 was more stable over a long period of time. The selectivity to methane and low molecular weight hydrocarbons was also reproducible, especially between runs SB-0261 and SB-0045 (Figure 13). For example, the methane selectivity was around 2 mol% in run SB-0261, and it varied between 2.2 and 2.5 mol% in run SB-0045 during 500 hours of testing while maintaining high activity (Figure 13a). On the other hand, slightly higher selectivities of low molecular weight products were obtained in run SA-0705. In the latter test, methane selectivity varied between 2.0 and 3.2 mol%, total $C_1 + C_2$ selectivity was about 7 mol%, and C_2 - C_4 selectivity was 13 - 14 mol% (Figures 13b and c). Some of these discrepancies may be due to the use of different reactor systems, and we will examine this issue in future tests. In general, the results from two tests in the two reactor systems were similar.

Concluding Remarks on Multiple Tests with 100 Fe/3 Cu/4 K/16 SiO_2 and 100 Fe/5 Cu/4 K/24 SiO_2 Catalysts

Three tests were conducted with each of the two catalysts. In the original tests conducted in 1991 (SB-0261 with the 100 Fe/3 Cu/4 K/16 SiO_2 catalyst, and SB-1931 with the 100 Fe/5 Cu/6 K/24 SiO_2 catalyst) n-octacosane was used as the initial medium. In the four tests conducted in December 1994, and January 1995 Ethylflo 164 oil was used as the starting fluid, due to problems encountered in three tests using n-octacosane as the start-up fluid (low activity in all three tests). The effect of reactor set-up (slurry A vs. slurry B reactor system) was

investigated in two recent tests with the 100 Fe/3 Cu/4 K/16 SiO_2 catalyst (runs SB-0045 and SA-0705). In view of the fact that the initial two tests with these two catalysts were conducted 3-4 years ago, and that different start-up fluids were employed, the reproducibility of results in multiple tests of the same catalyst may be regarded as quite satisfactory. The 100 Fe/5 Cu/6 K/24 SiO_2 catalyst was more stable in the original test (SB-1931) than in two recent tests (SB-3354 and SB-0665), whereas the opposite trend was observed in tests with the 100 Fe/3 Cu/4 K/16 SiO_2 catalyst. Selectivities in multiple tests with the same catalyst were even more reproducible.

II. 2 Task 4. Reproducibility of Catalyst Preparation

The objective of this task is to demonstrate reproducibility of catalyst preparation procedure on a laboratory scale. During the reporting period we have completed synthesis of about 100 g of catalyst with nominal composition 100 Fe/3 Cu/4 K/16 SiO_2 (S-3416-2), and of another batch (173 g) of the same catalyst (S-3416-3). Also, we have synthesized two additional batches of catalyst with nominal composition 100 Fe/5 Cu/6 K/24 SiO_2, in the amounts of 240 g (S-5624-3) and 200 g (S-5624-4). The synthesized catalysts were characterized by atomic absorption spectroscopy (AAS), and BET surface area (SA) and pore size distribution (PSD) measurements. Results are described in a section describing the progress on Task 8. Catalyst Characterization.

II. 3 Task 5. The Effect Of Source of Potassium and Basic Oxide Promoters

The objective of this task is to investigate effects of two different sources of potassium and addition of another promoter (CaO) on the catalyst performance. We have completed the literature review of different synthesis procedure and catalyst compositions employed in previous studies, and are ready to synthesize catalysts needed for testing in fixed bed and slurry reactors.

II. 4 Task 8. Catalyst Characterization

Several batches of catalysts with nominal compositions 100 Fe/3 Cu/4 K/16 SiO_2 (S-3416) and 100 Fe/5 Cu/6 K/24 SiO_2 (S-5624) were synthesized using the procedure developed in our laboratory (Bukur et al., 1990). Different batches of the catalyst with the same nominal composition are designated with the serial number (catalyst code) followed by an Arabic numeral designating the specific batch (e.g., S-3416-2 refers to batch 2 of the catalyst with nominal composition 100 Fe/3 Cu/4 K/16 SiO_2).

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

$$W_{SiO2} = 100\% - W_{Fe}\,(M_{Fe2O3}/2M_{Fe}) - W_{Cu}\,(M_{CuO}/M_{Cu}) - W_{K}\,(M_{K2CO3}/2M_{K})$$

$$= 100\% - 1.43\,W_{Fe} - 1.25\,W_{Cu} - 1.77\,W_{K}$$

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

Results of elemental analysis are shown in Table 7, and major findings are summarized below:

(1) For catalyst with nominal composition 100 Fe/3 Cu/4 K/16 SiO_2, both the copper and the silica contents agree well among different batches, however, potassium contents in batch 2 (3.6 parts /100 parts of Fe) and in batch 3 (3.5 parts/100 parts Fe) catalysts are significantly lower than that in batch 1 (5.8-6.7 parts per 100 parts of Fe). The actual potassium content in the catalysts synthesized during the current contract (Batches 2 and 3) is closer to the nominal one ,

than that in Batch 1 (synthesized during the previous contract). However, in order to obtain the desired catalytic performance, we plan to add potassium to the catalyst from batches 2 and 3, to obtain about 5.5 parts of K per 100 parts of Fe. Also, results obtained from different laboratories with the same catalyst batch (S-3416-1) agree well with each other.

(2) For catalyst with nominal composition 100 Fe/5 Cu/6 K/24 SiO_2, the potassium content in batches 2-4 varies from 5.1 to 5.4 parts per 100 parts of Fe, and the copper content varies between 4.1 and 5.4 parts per 100 parts of Fe, both of which are close to the desired nominal catalyst composition. Again, the potassium contents in these batches are slightly lower than that in batch 1 of this catalyst. The silica contents are reasonably similar in all four batches, varying between 21.9 to 26.0 parts per 100 parts of Fe. Results from different laboratories analyzing the same catalyst (S-5624-1) are similar for copper and silica, but show larger discrepancies for the potassium content.

(3) A relatively high sodium content in the catalyst S-3416-3 is due to the use of washing water which was not purified properly. Its potential impact on catalytic results will be evaluated during the catalyst testing, but we do not expect any adverse effects, since sodium can also serve as an alkali promoter.

Surface areas and pore volumes were measured by physical adsorption of nitrogen at 77 K using a Micromeritics Digisorb 2600 instrument, and values obtained are listed in Table 7. Table 7 also lists the surface areas obtained from the single-point BET method on a Micromeritics Pulse Chemisorb 2705 instrument for comparison purposes. Differential pore volume distributions (PSD) obtained by nitrogen adsorption are illustrated in Figure 14. From the surface area and pore size distribution results, it can be seen that:

(1) The surface areas obtained from the single-point method are close to those obtained from the BET plot method (with relative error less than 10%). Such an agreement proves that the former method is applicable to the catalyst system studied.

(2) The surface areas are between 222 and 284 $m^2 g^{-1}$ with 100 Fe /5 Cu/6 K/24 SiO_2 catalyst, and between 245 and 315 $m^2 g^{-1}$ with 100 Fe/3 Cu/4 K/16 SiO_2 catalyst, i.e. the maximum

variation among different batches is about 20%. Also, multiple measurements with the same catalyst (batch 1) were in good agreement.

(3) Pore volumes for all new batches (Batches 2-4) are significantly lower than those of catalysts synthesized in the pervious project (Batch 1 in each series), even though the surface areas are similar as indicated above.

(4) Pore size distributions of catalysts studied are between 2 and 20 nm. For catalyst 100 Fe/5 Cu/6 K/24 SiO_2 series, the pore size distributions of catalysts from batch 1 and 3 are reasonably similar, and both have two major pores. One is a mesopore with the pore diameter of 2.5 nm, and the other is a macropore with the pore diameter of about 10 nm. However, the pore size distribution of batch 2 catalyst is quite different, and it exhibits a very narrow pore size distribution with dominant pores between 2.5 and 4 nm. For catalyst 100 Fe/3 Cu/4 K/16 SiO_2 series, all three batches show similar pore size distributions and have two dominant pores. The mesopores have a diameter of about 2.5 nm and the macropores are between 4 and 10 nm.

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

Plans for the Next Quarter

During the next quarter we plan to: (a) test synthesized catalysts with nominal compositions 100 Fe/5 Cu/6 K/24 SiO_2 and 100 Fe/3 Cu/4 K/16 SiO_2 in slurry reactors (Task 4); (b) synthesize catalysts containing CaO as promoter and catalysts with different source of potassium (Task 5) and initiate their testing in fixed bed and/or slurry reactors; and (c) complete characterization of the newly synthesized catalysts (Task 8).

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