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DEVELOPMENT AND PROCESS EVALUATION OF
IMPROVED FISCHER-TROPSCH SLURRY CATALYSTS

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I. ABSTRACT

Eleven tests of different activation/reduction conditions were performed in fixed bed reactors using a 100Fe/3Cu/0.2K catalyst to study the effect of reduction procedure on catalyst activity, selectivity, and stability. CO reduced catalysts were initially more active than H₂ reduced catalysts, and had more desirable selectivity behavior. CO reduced catalysts produced less methane and C₂-C₄ products and more C₅+ products than the catalysts reduced with H₂. Of the CO reduced catalysts, reductions at 250 °C for 8 h and 280 °C for 24 h gave the most active and stable catalysts, with the 280 °C reduction giving better selectivity. Reduction of the catalyst at high pressure (1.48 MPa) with CO at 280°C for 24 h decreased catalyst activity and stability as compared to ambient pressure. The pressure had a minor effect on catalyst selectivity. Reduction of the catalyst with synthesis gas, (H₂/CO) = 0.68, 280 °C, 24 h duration also lowered the activity and stability of the catalyst compared to the catalyst reduced with pure CO, while the selectivity of the catalysts were similar.

Two tests have been made of the Ruhrchemie LP 33/81 iron-based catalyst in fixed bed reactors. Different reduction procedures were followed in each test, using both the manufacturer's recommended H₂ reduction and the standard CO reduction (280 °C, 8 h) used in the current investigation. The reduction procedure had little effect on catalyst activity, however, the H₂ reduced catalyst produced less C₂ - C₄ products and more C₅⁺ products. The activity of the Ruhrchemie catalyst was comparable to the activity of United Catalysts, Inc. C-73 fused iron, and less than the precipitated iron catalysts tested in the current study.

Two tests of a 100 Fe/0.3 Cu/0.2 K precipitated catalyst have been made in a slurry reactor. The first test of the catalyst was ended due to line plugging and catalyst deactivation. The second test was successful, and 18 mass balances were performed during 550 hours of operation. Process variables were studied over a range of values: 220-265 °C, 0.79-2.96 MPa, 1-4 NL/g-cat·h, using (H₂/CO) feed ratios of 0.67 and 1.0. The catalyst did not deactivate, and no major operational problems were encountered during the run.

X-ray photoelectron and Fourier Transform infrared spectroscopies have been used to characterize the effects of Cu and K promoters and of various calcination/reduction treatments on the chemical state and behavior of surface sites on precipitated iron catalysts. Treatment of the unreduced precipitates in H₂ at 300°C, even in the presence of Cu promoter, results primarily in Fe²⁺ formation on the surfaces of these materials, whereas treatment in CO leads to complete reduction of surface iron to the zero-valent state. Reduction in CO causes deposition of surface carbon and generates a more energetically heterogeneous array of surface iron sites than results from treatment in H₂. Water formed during exposure of CO-reduced catalysts to a H₂/CO synthesis gas mixture effects partial re-oxidation of reduced surface iron sites to Fe²⁺, and also causes extensive migration of potassium promoter to the surfaces of iron crystallites. Impregnation of a 100Fe/5Cu precipitate with various amounts of SiO₂ binder/support results in substantial increases in surface areas that are maintained after calcination and reduction treatments.

II. OBJECTIVE AND SCOPE OF WORK

The objective of this contract is to develop a consistent technical data base on the use of iron-based catalysts in Fischer-Tropsch (F-T) synthesis reactions. This data base will be developed to allow the unambiguous comparison of the performance of these catalysts with each other and with state-of-the-art iron catalyst compositions. Particular attention will be devoted to generating reproducible kinetic and selectivity data and to developing reproducible improved catalyst compositions. To accomplish these objectives, the following specific tasks will be undertaken.

TASK 1 - Project Work Plan

The objective of this task is to establish a detailed project work plan covering the entire period of performance of the contract. This includes estimated costs and manhours expended by month for each task.

TASK 2 - Slurry Catalyst Improvement

The primary purpose of this task is to develop improved iron-based catalysts, both precipitated and supported, that show enhanced activity and selectivity in slurry phase testing. This will be accomplished by gaining systematic understanding of the role of promoters, binders, supports and activation procedures in determining the activity and selectivity of iron-based catalysts. The catalyst development program will incorporate extensive physical and chemical characterization of these materials with the objective to establish correlations between the physical/chemical properties of these catalysts and the corresponding catalytic behavior for synthesis gas conversion.

TASK 3 - Process Evaluation Research

The purpose of this task is to subject the most improved catalysts (based on activity and selectivity) to a thorough process evaluation. This involves long term stability studies, investigation of a wide range of process variables, and determination of kinetic parameters.

TASK 4 - Economic Evaluation

The aim of this task is to develop the relative economic impact for each improved catalyst composition and compare these economics with the economics of using the base case catalyst. Data obtained from tasks 2 and 3 will be used to generate a product yield structure, Fischer-Tropsch reactor residence time, and key process flow rates. These economic studies will include relative capital costs, operating costs, and required revenues for each catalyst, as well as a sensitivity study of the assigned relative values of the principal products (i.e. diesel and gasoline).

III. SUMMARY OF PROGRESS

The effect of reductant type, temperature, and duration on catalyst activity, selectivity, and stability has been studied in ten fixed bed reactor tests. A high pressure reduction was also tested to determine the influence of reduction pressure. CO, H₂, and (H₂/CO) = 0.68 gases were used as reductants. Reductions were performed at 250, 280, and 310 °C for durations of 8 and 24 hours. Following reduction, all catalysts were tested at a fixed set of operating conditions (250 °C, 1.48 MPa, (H₂/CO) = 1) for up to 120 h on stream.

For the catalysts reduced with CO at 8 h duration, low reduction temperatures gave the most active and stable catalysts. Product selectivity improved with increased reduction temperature, as the fraction of olefins in the product increased and the weight percent of higher molecular weight products increased. With 24 h reduction durations, reducing at 280 °C gave a more active and stable catalyst, while the reduction temperature had a minimal effect on catalyst selectivity. Reduction of the catalyst at 280 °C for 24 h was found to be the most desirable taking both activity and selectivity under consideration. A test was made using a high pressure reduction (1.48 MPa) at the best conditions (280 °C, 24 h) to evaluate the catalyst reduced at conditions suitable for *in situ* slurry reactor reductions. The catalyst selectivity did not change appreciably from the catalyst reduced at ambient pressure, however, catalyst activity and stability decreased significantly.

The initial activity of catalyst reduced with H₂ were lower than that of catalyst reduced using CO, but the activity of H₂ reduced catalyst

increased with time on stream while the activity of CO reduced catalyst declined with time on stream. The selectivity of CO reduced catalyst was superior to that of H₂ reduced catalyst. Reduction with H₂ tended to form catalyst which produced more methane and C₂-C₄ products as compared to catalyst reduced with CO at the same temperature and duration. One additional test was made using synthesis gas (H₂/CO = 0.68) as the reductant at the best reduction conditions (280°C, 24 h duration) for CO reductant. The activity of this catalyst was inferior to that of the catalyst reduced using pure CO, and superior to the H₂ reduced catalyst. The selectivity behavior of the CO and synthesis gas reduced catalysts were similar.

Two tests have been made using Ruhrchemie LP 33/81 iron based catalyst in fixed bed reactors. Different reduction procedures were used for each test: the manufacturer's recommended procedure (H₂, 220°C, 1 h) and the standard reduction procedure used in our investigation (CO, 280°C, 8 h). The catalysts were tested over a range of process conditions: 220 up to 265°C, 1.48 - 2.96 MPa, 0.75 - 4 NL/g-cat·h, using (H₂/CO) = 1 feed gas, to provide a comparison of the reduction procedures as well as a comparison to United Catalysts, Inc. C-73 fused iron and the catalysts developed in the current investigation.

The activity of the Ruhrchemie catalyst reduced using the two different procedures was found to be comparable at the same process conditions. The strongest effect on reduction procedure was on catalyst selectivity. The recommended H₂ reduction produced a catalyst more selective to higher molecular weight products than the CO reduced catalyst, an effect opposite of that found with precipitated iron catalysts. The CO reduced catalyst formed more olefinic product than the H₂ reduced catalyst.

The activity of a CO reduced 100 Fe/3 Cu/0.2 K precipitated catalyst prepared during this investigation was higher than the activity of the Ruhrchemie catalyst. The selectivity of the precipitated catalyst was similar to that of the CO reduced Ruhrchemie catalyst. United Catalyst, Inc. C-73 fused iron catalyst had similar activity to the Ruhrchemie catalyst at the same process conditions. The H₂ reduced Ruhrchemie catalyst produced less methane and C₂ - C₄ products, and more C₅⁺ products, than the C-73 fused iron catalyst.

A slurry reactor run using 100 Fe/0.3 Cu/0.2 K precipitated catalyst was made, and three mass balances were performed at 220, 235, and 250°C, 1.48 MPa, 2 Nl/g-cat·h, (H₂/CO) = 1. The run was terminated after 110 hours on stream due to line plugging and catalyst deactivation. A successful retest of this catalyst was made, and 18 mass balances were performed during 550 hours of operation. The catalyst was reduced *in situ* at 250°C, 0.77 MPa, for 8 hours using CO reductant. Process variables were studied over the range 220 - 265°C, 0.79 - 2.96 MPa, 1 - 5 Nl/g-cat·h, (H₂/CO) = 0.67 and 1.0.

Catalyst activity appeared to increase during the run, as the (H₂ + CO) conversion at 250°C, 1.48 MPa, (H₂/CO) = 1, 2 Nl/g-cat·h was 55.6% at 104 hours on stream and increased to 67.1% at 494 hours on stream. The increase in activity may have been due to an initially incomplete reduction of the catalyst, with continued activation during synthesis testing. The catalyst did not deactivate during the course of the run, including balances at high pressure (up to 2.96 MPa). The space time yield was found to increase linearly with pressure over the range 0.79-2.96 MPa.

Three silica-supported iron precipitates have been prepared, having

the nominal compositions $100\text{Fe}/5\text{Cu}/4.2\text{K}/8\text{SiO}_2$, $100\text{Fe}/5\text{Cu}/4.2\text{K}/25\text{SiO}_2$, and $100\text{Fe}/5\text{Cu}/4.2\text{K}/100\text{SiO}_2$. The surface areas of these materials, following calcination for 5 hrs at 300°C and subsequent reduction in CO for 5 hrs at the same temperature, are 94, 150, and $250\text{ m}^2/\text{g}$, respectively. These values are substantially higher than that ($38\text{ m}^2/\text{g}$) of an unsupported $100\text{Fe}/3\text{Cu}$ precipitate after similar treatment. Pore volume distributions have been determined for each of the three silica-supported materials, but are not accurate indicators of average pore size because a significant fraction of pores in these high surface area materials are smaller than the minimum size ($\sim 60\text{ \AA}$) detectable with the mercury porosimetry equipment used for these measurements.

X-ray photoelectron (XPS) spectroscopy has been extensively employed to characterize the effects of copper and potassium promoters and of various calcination/reduction treatments on the chemical state and extent of reduction of surface atoms/ions on certain of the precipitated iron catalysts. The $100\text{Fe}/3\text{Cu}/0.2\text{K}$ composition has been used for most of these measurements. After prior calcination at 300°C , treatment of the latter catalyst in H_2 at 300°C , although resulting in complete reduction of Cu^{2+} in the copper promoter to Cu^0 , effects only partial reduction of surface iron species. The latter exist primarily in the Fe^{2+} state following such H_2 treatment. Reduction of the calcined catalyst in CO at 300°C , by contrast, leads to complete reduction of surface iron to the zero-valent state, and is accompanied by deposition of surface carbon due to disproportionation. Subsequent exposure of the reduced catalyst to a $2/1\text{ H}_2/\text{CO}$ synthesis gas mixture at 250°C causes re-oxidation of a portion of the surface iron to Fe^{2+} , as a result of the water that is formed as a by-

product of the methanation reaction.

An additional significant finding of these XPS studies is that surface water, generated either during H_2 reduction treatment or as a result of the H_2/CO reaction, causes extensive phase separation and/or migration of the potassium promoter to the surface of the iron crystallites. The rate of this process appears to be very high, suggesting that surface enrichment in potassium may be the predominant condition throughout the synthesis reaction on the unsupported catalysts. Such surface enrichment in potassium occurred to only a slight extent, on the other hand, on the supported $100Fe/5Cu/100SiO_2$ material, indicating that the homogeneously distributed silica matrix effectively inhibits the migration process.

Fourier Transform infrared (FT-IR) spectroscopy studies of adsorbed nitric oxide (NO) have also been continued on various silica-supported iron catalysts, in an effort to further characterize the nature and behavior of surface iron sites. These investigations have confirmed the XPS finding that treatment of dispersed iron in H_2 at $300^\circ C$ leads to a mixture of Fe^{2+} and Fe^0 surface states. Reduction treatment in CO at $300^\circ C$, although not yielding FT-IR evidence for complete reduction to zero-valent iron, appears to form a more energetically heterogeneous array of surface sites than that resulting from treatment in H_2 .

IV. DETAILED DESCRIPTION OF TECHNICAL PROGRESS

TASK 1 - Project Work Plan

The project work plan was completed during the first quarter of this project and the detailed work plan was submitted to APCI.

TASK 2 - Slurry Catalyst Improvement

2.1. Task 2.4 - Activation/Reduction Procedure Research

2.1.1. Activation/Reduction Procedure Tests in Fixed Bed Reactors.

The activation/reduction procedure followed can have a significant effect on subsequent catalyst activity, selectivity, and stability. Eleven different sets of reduction conditions were tested in fixed bed reactors to evaluate the influence of the reduction parameters (reductant type, temperature, and duration) on subsequent catalyst performance. All but one of the reductions were conducted at atmospheric pressure. A precipitated, unsupported 100Fe/3Cu/0.2K (3 parts Cu and 0.2 parts K per 100 parts Fe, by weight) catalyst was used in all tests, which was first calcined in air at 300 °C for 5 h, crushed and sized to 30/60 mesh, and diluted 1:8 by volume with glass beads of the same mesh size range. Following reduction, the catalysts were gradually brought to synthesis conditions following the procedure described in the Technical Progress Report for the period 1 July - 30 September 1987, and were tested at a fixed set of operating conditions (250 °C, 1.48 MPa, 2 NL/g-cat·h, (H₂/CO) = 1) for up to 120 h, during which time two mass balances were made at approximately 40 and 90 h on stream. Conversions were measured regularly throughout the entire run.

Using CO as the reductant, 8 hour reduction procedures were used at three different temperatures: 250 (run FA-25-2737), 280 (run FA-25-3077) and 310 °C (run FA-25-2847). The results obtained for each of these three runs are summarized in Table 1. Three runs were made using the 280 °C, 8 hour CO reduction. The first run, FA-25-2667 (reported in the Technical Progress Report for the period 1 July - 30 September 1987) ended prematurely after an electrical power failure interrupted the run. A second attempt was made using the same reduction conditions, run FB-25-2727, but a flow interruption after about 40 hours on stream caused catalyst deactivation. Run FA-25-3077 was a successful test of the catalyst reduced at 280 °C and 8 h. Two CO reductions of 24 hour duration were made at 250 (run FA-25-2857) and 280 °C (run FA-25-2967). The results obtained from each of these runs are summarized in Table 2.

A single test was made with a catalyst reduced at high pressure (1.48 MPa), run FA-25-3517, reducing the catalyst with CO for 24 hours at 280 °C. *In situ* reductions with slurry bed reactors require higher pressure than fixed bed reactors in order to prevent excessive evaporation of the slurry liquid. This test was made to evaluate a catalyst reduced at a pressure suitable to slurry reactors. Table 3 summarizes the results of this run.

Two procedures of 8 hour duration using H₂ as the reductant were tested at 250 (run FB-25-3087) and 280 °C (run FB-25-2957), and the results of these runs are summarized in Table 4. A flow interruption occurred at approximately 105 hours on stream during run FB-25-3087, and the run was terminated before a second mass balance was completed. As the results from the first balance indicated that these reduction conditions did not lead to improved catalyst behavior, the run was not repeated. Two additional H₂

reduction procedures using 24 hour durations were tried. The results obtained at 250 (run FA-25-3237) and 280 °C (run FB-25-3227) reduction temperatures are given in Table 5.

A run was also made using synthesis gas as the reductant (run FB-25-3377), which is summarized in Table 6. The catalyst was reduced at 280 °C for 24 hours using an $(H_2/CO) = 0.68$ feed gas.

2.1.2. Discussion of Results

Tests with CO as reductant

An activity plot, (H_2+CO) conversion versus time at testing conditions, is shown in Figure 1 for the five ambient pressure CO reduction procedures. The reductions at 250 °C for 8 h and 280 °C for 24 h show similar activity and are the most stable, however the activity for all CO reductions decline with time. The selectivity behavior of the 280 °C, 24 h reduction is superior to that of the 250 °C, 8 h reduction, Figure 2. Average values of the (1+2)-olefins/n-paraffin ratio and weight percent of hydrocarbon distribution of balances 1 and 2 are given in this figure. The reduction at higher temperature leads to lower weight percent of methane and C_2-C_4 products. The (1+2)-olefins/n-paraffin ratios are also slightly higher with the 280 °C reduction.

The effects of both activation temperature and duration may also be studied in Figures 1 and 2. For the 8 h reductions, the lowest temperature, 250 °C, gives the best activity and stability behavior. The catalyst reduced at 280 and 310 °C behave similarly, but are less active and less stable than the catalyst reduced at 250 °C. Selectivity is improved for the 8 h duration as the reduction temperature is increased.

The higher reduction temperatures result in catalysts which produce less methane and C_2-C_4 products, with improvements in the weight percent of higher molecular weight products. The (1+2)-olefins/n-paraffin ratios also tend to increase as the reduction temperature increases. At 24 h reduction durations, comparisons can be made at 250 and 280 °C. With the longer duration, higher temperature favors a more stable catalyst, while the selectivities of the two catalysts are about the same.

The effect of reduction duration can be seen at 250 and 280 °C. At 250 °C, the 24 h duration produced the least stable of all the catalysts, however, the selectivity is better than the 8 h reduction as less methane and C_2-C_4 products are produced. The stability with a 280 °C reduction is superior when longer reduction durations are used.

Although the activities for the CO reduced catalysts decreased with time, the selectivities remained relatively stable between the two balances performed at approximately 40 and 90 hours on stream. The selectivities for the first and second balances of the 250 °C, 8 h and the 280 °C, 24 h reductions are compared in Figure 3. The (1+2)-olefins/n-paraffin ratios and weight percent of methane and C_2-C_4 products remained essentially constant between the two balances, but there was some minor shifting between products in the C_5-C_{11} and $C_{12}+$ ranges.

The activity behavior of the tests made with catalysts reduced with CO at 280 °C for 24 h at ambient and high (1.48 MPa) pressure are compared in Figure 4. The catalyst reduced at ambient pressure was found to be more active and more stable than the catalyst reduced at high pressure. The reduction pressure did not have a strong effect on catalyst selectivity, as shown in Figure 5. The weight percent hydrocarbon distribution obtained

using the different reduction pressures was the same for both procedures. The (1+2)-olefins/n-paraffin ratios were higher for the catalyst reduced at higher pressure, however, this may have been caused by the significantly higher conversions obtained with the ambient pressure reduction. As the ($H_2 + CO$) conversion increases, the partial pressure of H_2 relative to CO also increases (as long as the usage ratio is lower than the feed ratio). Also, higher conversions lead to longer residence times in the reactor due to gas contraction upon reaction. Both these effects (the increase in the H_2/CO partial pressure ratio and the longer residence times) favor hydrogenation of olefinic products at high (H_2+CO) conversion, decreasing the (1 + 2)-olefins/n-paraffin ratio.

Tests with H_2 as reductant

The activity plot of (H_2+CO) conversion versus time at testing conditions for the H_2 reduction procedures is shown in Figure 6. The activities of all H_2 reductions are stable, and tend to gradually increase with time. The activities of the 250 °C, 8 and 24 h activations were comparable and significantly higher than the activities obtained using a reduction temperature of 280 °C. The shorter 8 h reduction at 280 °C gave a more active catalyst than the 24 h reduction at the same temperature.

The effects of reduction temperature and duration on catalyst selectivity are shown in Figure 7. The hydrocarbon weight percent distribution was not strongly affected by the H_2 reduction procedure followed, regardless of the reduction conditions. The (1+2)-olefins/n-paraffin ratios did not change significantly with the duration of the reduction, however, the ratios decreased as the reduction temperature decreased from 280 to 250 °C, at both 8 and 24 h reduction durations. This

trend may be caused by the significantly higher (H_2+CO) conversions obtained with the catalysts reduced at 250 °C.

As with the CO reduced catalysts, the time on stream did not significantly alter catalyst selectivity. The weight percent hydrocarbon distribution and (1+2)-olefins/n-paraffin ratios of the H_2 reduced catalysts at 250 °C, 8 h and 280 °C, 8 h are compared in Figure 8. Only minor differences in catalyst selectivity were observed between the first and second balances of both runs.

Comparison of CO and H_2 reductions

The activity and stability of the CO and H_2 reduced catalysts at selected conditions are compared in Figure 9, where the (H_2+CO) conversion is plotted against time at conditions for 8 h reduction durations at 250 °C with CO and H_2 as reductants, and 24 h reductions using CO at 280 °C and H_2 at 250 °C. The initial activity of the CO reduced catalysts is always higher than the H_2 reduced catalysts, but the activity of H_2 reduced catalysts continues to increase with time. After about 100 h at conditions, the (H_2+CO) conversions of the four catalysts shown are approximately equal.

A comparison of the effect of reductant type on catalyst selectivity is given in Figure 10 for the same tests shown in Figure 9. At all conditions, CO reductions give superior weight percent hydrocarbon distributions than the corresponding H_2 reduction, as the weight percent of methane and C_2-C_4 products is lower for catalysts reduced with CO. The CO reduced catalysts produced more C_5+ products. The (1+2)-olefins/n-paraffin ratios are slightly lower for the catalysts reduced with CO, however, this

may be caused by the higher (H_2+CO) conversions obtained with CO reductant, as discussed previously. Thus, although the activity of these catalysts are similar, the selectivity behavior of the CO reduced catalysts is more desirable than that for catalysts reduced using H_2 .

Test using (H_2/CO) = 0.68 reductant

The activity of the catalysts reduced using pure CO and (H_2/CO) = 0.68 as a function of time at conditions are compared in Figure 11. The reduction temperature and duration were the same for both tests (280 °C, 24 h). The CO reduced catalyst was more active and more stable than the catalyst reduced with mixed gas. The catalyst reduced at 280 °C and 24 h with pure H_2 had yet lower activity, about 30% (H_2+CO) conversion throughout the run.

The selectivity behavior of the H_2 , (H_2/CO) = 0.68, and CO reduced catalysts are compared in Figure 12. The weight percent hydrocarbon distribution of the CO and mixed gas reductions were similar, with some minor shifting of products between the C_5-C_{11} and $C_{12}+$ product ranges. As seen with other H_2 reductions, the catalyst reduced with H_2 favored the formation of methane and C_2-C_4 products, with correspondingly lower weight percents of the higher molecular weight products (C_5+). The (1+2)-olefins/n-paraffin ratios were higher for the catalyst reduced with synthesis gas as compared to the catalysts reduced with either pure H_2 or CO, particularly the CO reduced catalyst. The ratios may have been enhanced by the low conversions obtained with the synthesis gas or H_2 reduced catalyst.

2.2. Task 2.2 - Binder/Support Effect Research.

2.2.1. Fixed Bed Tests of Ruhrchemie Catalyst LP 33/81

Two tests have been made in fixed bed reactors using a Ruhrchemie iron-based catalyst, designated LP 33/81, obtained through Air Products and Chemicals, Inc. The chemical composition of the catalyst was not provided, but is believed to be similar to the catalyst used initially by SASOL in their fixed bed ARGE reactors. According to Dry (in "Catalysis - Science and Technology", v. 1, 1981) the composition of the Ruhrchemie catalyst is $100\text{Fe}/5\text{Cu}/5\text{K}_2\text{O}/24\text{SiO}_2$, by weight.

Different reduction procedures were followed in these two tests: in run FA-99-3357, the manufacturer's recommended procedure was followed, while in run FB-99-3477, the standard reduction procedure employed in our investigation (CO , 280°C , 8 h) was followed. (The Ruhrchemie catalyst was assigned a code of "99" for run number designations). The manufacturer recommended that the catalyst be reduced at 220°C , atmospheric pressure for 1 hour, using pure H_2 flowing at a linear (superficial) gas velocity of 150 cm/s at reduction temperature and pressure.

Run FA-99-3357

Nine mass balances were performed during run FA-99-3357, and the results are summarized in Table 7. The effect of temperature was studied at two space velocities: 220°C (balance 1), 235°C (balance 2), and 250°C (balance 3) at $2\text{ Nl/g-cat}\cdot\text{h}$, and 235°C (balance 7), 250°C (balance 8), and 265°C (balance 6) at $0.75\text{ Nl/g-cat}\cdot\text{h}$. At the higher space velocity, the balance at 220°C gave unexpected results for the weight percent hydrocarbon distribution, as methane and $\text{C}_2\text{-C}_4$ product percentages were

high and the heavier product fractions were low compared to 235 and 250 °C. The total yield for this balance was low (138 g/Nm³ (H₂ + CO) converted) and the system may not have been at steady state with respect to the high molecular weight products. Wax may have been accumulating in the reactor during this period. At the 0.75 Nl/g-cat·h space velocity, the weight percent of methane and C₂-C₄ products in the hydrocarbons increased with temperature, as expected, with corresponding decreases in the fractions of heavier products (C₅+ and C₁₂+).

The effect of space velocity is shown over the widest range for 250 °C, 0.75 (balance 5), 2 (balance 3), and 4 Nl/g-cat·h (balance 4). No clear trend in weight percent hydrocarbon distribution was seen. The (1+2)-olefins/n-paraffin ratios increased with increasing space velocity, which suggests that the olefins may be primary products in the synthesis. At higher space velocity (and lower conversion) the olefins would have less opportunity to be hydrogenated to form paraffins.

The catalyst partially deactivated before balance 9, which was a repeat of the conditions used in balance 2 (235 °C, 1.48MPa, 2 Nl/g-cat·h). These two balances were made approximately 168 hours apart. The (H₂+CO) conversion dropped from 45 to 36.5% over the interval. The deactivated catalyst also had a tendency to produce lighter products, as the weight percent of methane and C₂-C₄ products in the hydrocarbons was greater in balance 9. The percentage of heavier products decreased accordingly. The deactivation was probably begun by the severe conditions (265 °C) used during balance 6.

Run FB-99-3477

The Ruhrchemie catalyst was tested again in run FB-99-3477, reducing the catalyst using CO at 280 °C for 8 h. 8 mass balances were performed which are summarized in Table 8. The effect of temperature can be seen at 2 Nl/g-cat·h at 220, 235, and 250 °C in balances 1, 2, and 4, respectively. The weight percent of methane and C₂-C₄ products increase from 220 to 235 °C as expected, but decrease slightly as the temperature is increased further to 250 °C. The amount of higher molecular weight products decreases from 220 to 235 °C, and remains relatively constant between 235 and 250 °C. At lower space velocity, 0.75 Nl/g-cat·h, two temperatures were used: 235 (balance 6) and 250 °C (balance 5). The weight percent of methane and C₂-C₄ products in hydrocarbons followed the expected trend, increasing with temperature, with a slight decrease in the high molecular weight products (C₅+).

The effect of space velocity was studied at 235 °C at 0.75, 2, and 4 Nl/g-cat·h in balances 6, 2, and 3, respectively. Higher space velocity favored formation of lighter products, as the methane and C₂-C₄ weight percents increased as the space velocity was increased. The weight percent of heavy product decreased with an increase in space velocity. No clear trend was seen with space velocity for the olefin/paraffin ratios.

Balance 7 was a repeat of the conditions used in balance 2 (235 °C, 1.48 MPa, 2 Nl/g-cat·h) and the catalyst had not deactivated significantly over the 120 h period between balances. At 63 hours on stream (balance 2) the (H₂ + CO) conversion was 43.7% while at 183 hours on stream (balance 7) the conversion was still 42.9%. Some slight changes in catalyst selectivity were observed, as the amounts of methane and C₂-C₄ products in

the hydrocarbon fraction decreased with time on stream. The (1+2)-olefins/*n*-paraffin ratios remained constant between the two balances. Further evidence that the catalyst activity remained stable is given in balance 8, compared to either balance 2 or 7. The (H₂+CO) conversion obtained at higher pressure (2.96 MPa) and higher space velocity (3.94 Nl/g-cat·h) was approximately equal to that obtained at lower pressure. The space time yield was found to be approximately proportional to pressure: 0.039 (balance 2) and 0.038 (balance 7) mols (H₂+CO)/g-cat·h at 1.48 MPa compared to 0.074 mols (H₂+CO)/g-cat·h at 2.96 MPa.

Effect of reduction procedure and comparison of catalysts

The Ruhrchemie catalyst can be compared with the precipitated iron catalysts at 1.48 MPa, 2 Nl/g-cat·h, at 220, 235, and 250 °C. The Ruhrchemie catalyst tests using the two different reduction procedures and the 100 Fe/3Cu/0.2K catalyst (run FA-25-2447, reported in the Technical Progress Report for the period 1 July-30 September 1987) are compared in Table 9. A comparison of the Ruhrchemie catalyst with United Catalyst, Inc. C-73 fused iron (run FA-01-1537, reported in the Technical Progress Report for the period 1 April - 30 June 1987) is shown in Table 10.

The activities of the Ruhrchemie catalyst reduced at different conditions are comparable to one another at the same operating conditions. The reduction procedure has the strongest effect on catalyst selectivity. The manufacturer's recommended H₂ reduction produces a catalyst more selective towards higher molecular weight products than the CO reduced catalyst. The differences are most pronounced in the C₂-C₄ and C₁₂+

fractions: reduction with CO causes the catalyst to produce more C_2-C_4 products and less $C_{12}+$ products than the catalyst reduced with H_2 . This effect is opposite that found with the precipitated iron catalyst studied under the activation/reduction procedure effect research task of this study. The CO reduced catalyst tends to produce more olefinic product than the H_2 reduced catalyst.

A comparison of the Ruhrchemie catalyst tests with a test of a 100 Fe/3Cu/0.2K precipitated iron catalyst is also made in Table 9. The precipitated iron catalyst prepared for this study is more active than the Ruhrchemie catalyst, based on CO and (H_2 +CO) conversion, at the same operating conditions. The weight percent of hydrocarbon distribution is similar to that of the CO reduced Ruhrchemie catalyst, thus produces more C_2-C_4 products and less $C_{12}+$ products than the H_2 reduced Ruhrchemie catalyst. A comparison with United Catalyst, Inc. C-73 fused iron, Table 10, shows that the activity of the two commercial catalysts are comparable at the same operating conditions. The Ruhrchemie catalyst produces less methane and C_2-C_4 products, and more C_5+ products, than does the fused iron catalyst, although the (1+2)-olefins/n-paraffin ratios from the fused catalyst are usually higher than the corresponding ratios obtained with the Ruhrchemie catalyst.

2.3. Task 2.5 - Slurry Reactor Kinetic Studies.

2.3.1. Run SA-05-2777, 100Fe/0.3 Cu/0.2K.

A nominal 100Fe/0.3 Cu/0.2K calcined, precipitated catalyst was used in this run. This was the first test of a precipitated iron catalyst in a slurry reactor for the present investigation. The catalyst was ground to

less than 325 mesh and loaded into the reactor with an excess of purified n-octacosane. The catalyst was reduced *in situ* using CO at 280 °C, 0.77 MPa for 8 hours. Line plugging occurred down-stream of the reactor during the reduction period due to evaporation of the n-octacosane from the reactor, and several flow interruptions occurred. Following the reduction, the reactor was purged with helium, and the gas feed and reactor stirring were discontinued to allow the catalyst to settle. After a short settling period, the excess n-octacosane was withdrawn through a dipleg which was preset to give a static slurry volume of about 440 cm³.

Three mass balances were performed following the reduction, at 220, 235, and 250 ° with (H₂/CO) = 1, 1.48 MPa, and 2 Nl/g-cat·h, and the (H₂+CO) conversions were measured at 26.1, 32.2, and 44.3%, respectively. The exit flow rates were unstable during the balances, probably due to partially blocked lines. The catalyst also appeared to be deactivating with time on stream. After 110 hours on stream, the run was terminated prematurely due to a block in the inlet feed line and catalyst deactivation.

2.3.2. Run SA-05-2967, 100 Fe/0.3 Cu/0.2 K.

This run was made as a retest of the unsuccessful run SA-05-2777, using the 100Fe/0.3 Cu/0.2K catalyst. A hard paraffin wax (FT-300, from Dura Commodities, New York) was used as the slurry liquid, and an excess of the wax was loaded with the catalyst (< 325 mesh) into the reactor prior to reduction. The catalyst was reduced *in situ* using CO at 250 °C, 0.77 MPa for 8 hours. Following reduction, the excess wax was withdrawn from the reactor to a preset static slurry volume of about 440 cm³. A total of 18

mass balances were made during the run, and the run was voluntarily terminated after about 550 hours of operation. The results obtained during the run are summarized in Table 11.

Wax accumulated in the reactor during the synthesis was withdrawn only three times during the course of the run, with withdrawals of 163, 395, and 148 g of wax after balances 7, 12, and 18, respectively. Several methods were tested to allocate the wax collected over multiple periods to individual mass balances. The simplest was to assume that the wax was accumulated in the reactor at a constant rate between withdrawals, regardless of operating conditions. Under this assumption, the rate of wax accumulation in the reactor was 0.79 g/h in balances 1-7, 2.2 g/h in balances 8-12, and 0.55 g/h in balances 13-18. This method of wax allocation often gave poor mass closures and unrealistic estimates of total product yield.

Two methods of wax allocation based on mass closures were also tried. The first method assumed that the amount of wax produced at a given set of conditions was proportional to discrepancy of the total closure obtained during the mass balance period. The amount of wax needed to obtain 100% closure for all balances was then normalized to agree with the actual amount of wax withdrawn. The second allocation method distributed the wax in order to optimize the carbon and hydrogen atomic closures obtained during the mass balance periods. With the exception of balance 12, this method gave good total mass closures, and in most cases, reasonable values for the total yield. Balance 12 had inherently poor atomic C-H closures, thus the total closure allocation was used to estimate the amount of wax accumulated during this period. The optimized C-H closure allocation was

used for all remaining periods.

The effect of space velocity, shown in Figure 13, was studied at 250 °C, 1.48 MPa with nominal (H_2/CO) feed ratios of 1.0 (balances 5, 3 and 16, and 4) and 0.67 (balances 12 and 15, 10, and 11) at 1, 2, and 4 $Nl/g\text{-cat}\cdot h$. The (H_2+CO) conversion decreased approximately linearly with space velocity. The catalyst appeared to become more active with time on stream, as shown by the ($H_2 + CO$) conversions obtained in balances 3 and 16 at 250 °C, 1.48 MPa, (H_2/CO) = 1 with 2 $Nl/g\text{-cat}\cdot h$ space velocity. During balance 3 (approximately 106 h on stream) the (H_2+CO) conversion was 55.6%, while during balance 16 (approximately 494 h on stream) the conversion had increased to 67.1%. At the same process conditions using a 0.67 (H_2/CO) feed ratio, the (H_2+CO) conversion was roughly constant at 345 and 445 hours on stream, 80.8 (balance 12) and 84.7% (balance 15), respectively. The increasing catalyst activity may be due to continuing catalyst activation during synthesis testing. The *in situ* catalyst reduction conditions of 250 °C for 8 h may not have completely reduced the catalyst, however, catalyst activation would have continued at the elevated synthesis temperature with mixed feed gas.

At the same process conditions, the (H_2/CO) = 0.67 feed ratio favored higher conversions over the (H_2/CO) = 1 feed ratio. Also, the lower feed ratio accelerated wax production. During balances 8-12, of 91 h duration, 395 g of wax were produced, whereas during balances 1-7, of 177 h duration, only 163 g of wax were produced. Balances 8-12 were all run using the lower (H_2/CO) feed ratio, and balances 1-7 were run using an (H_2/CO) = 1 feed ratio. Also, balances 1-7 consisted of 5 balances (1-5) at the same

temperature, pressure, and space velocity as balances 8-12, plus two additional balances at other process conditions. Thus wax production must have been much higher at the lower feed ratio.

A plot of the space time yield versus pressure is given in Figure 14. The space time yield was found to vary roughly linearly with pressure over the range of pressures studied. The precipitated catalyst did not deactivate at high pressure in the slurry reactor as was found in the fixed bed tests of these catalysts.

2.4. Catalyst Characterization.

During the past quarter, we have completed the synthesis and physical property characterization of the three silica-supported, precipitated iron catalysts that will be studied during this investigation. We have also employed x-ray photoelectron spectroscopy (XPS) and Fourier Transform infrared spectrophotometry (FT-IR) techniques to further characterize the surface chemical natures of both supported and unsupported iron catalysts and to gain insight into the effects of copper and potassium promoters on the reduction and surface behaviors of these materials. Details of research progress in these areas are provided in the following sections.

2.4.1. Characterization of Silica-Supported Iron Catalysts

Three promoted, silica-supported iron catalysts were prepared following the procedure described in Appendix I, with the nominal compositions: $100\text{Fe}/5\text{Cu}/4.2\text{K}/8\text{SiO}_2$, $100\text{Fe}/5\text{Cu}/4.2\text{K}/25\text{SiO}_2$, and $100\text{Fe}/5\text{Cu}/4.2\text{K}/100\text{SiO}_2$. BET- N_2 surface areas of these materials, prior to KHCO_3 impregnation and following calcination for 5 hrs at 300 °C and subsequent reduction in CO for 5 h at the same temperature, are tabulated

below and shown in Figure 15.

Silica Content (parts/100 Fe)	Surface Area (m ² /g)
0	38
8	94
25	150
100	250

The surface area of a silica-free 100Fe/3Cu prepared previously and subjected to the same calcination/reduction treatment is included for comparison purposes. It is clear that the presence of even small amounts of added SiO₂ result in substantial increases in post-reduction surface area of the precipitated catalysts. Furthermore, although the increase in specific surface area (based on total weight of Fe + Cu + SiO₂; open points of Figure 15) with increasing SiO₂ content is approximately linear up to a SiO₂ level of 25 parts/100 parts Fe, additional increase in the SiO₂ content to 100 parts/100 parts Fe does not result in a proportionally further enhancement of surface area. This behavior probably reflects an inherent limitation caused by the surface area of the SiO₂ itself. Specific surface areas calculated on the basis of weights of the Fe and Cu components only (closed points in Figure 15) are a nearly linear function of SiO₂ content.

Pore volume distributions for each of the three silica-containing catalysts, as measured by mercury porosimetry following calcination for 5

h at 300 °C and reduction in CO for 5 h at the same temperature, are shown in Figures 16-18. Comparative results for CO- and H₂-reduced samples of the silica-free 100Fe/3Cu precipitate are shown in Figures 19 and 20, respectively. Porosimetry data for the three silica-supported materials are internally consistent and show a marked difference in pore distribution profile between the 8SiO₂ material on the one hand and the 25SiO₂ and 100SiO₂ materials on the other. The former catalyst exhibits a well-defined maximum at a pore diameter of ~150-200Å, while the latter two materials do not display any well-defined maxima in their profiles. It should be noted, however, that the upper pressure limit of the porosimetry equipment employed for these measurements is 60,000 psi, which corresponds to a minimum accessible pore diameter of ~60Å. However, in order for low molecular weight solid materials to have total surface areas of $\geq 150 \text{ m}^2/\text{g}$, as were measured for the 25SiO₂ and 100SiO₂ precipitates after reduction in CO, they must contain a substantial fraction of pores smaller than 60Å. Hence, pore volume distributions determined by mercury porosimetry are not quantitatively useful in comparing the pore size properties of materials having a wide range of surface areas.

2.4.2. XPS Studies of Catalyst Surface Properties

Previous studies during this project using the temperature-programmed reduction (TPR) technique have demonstrated the influence of copper and potassium promoters on the reduction behaviors of precipitated iron catalysts. Although the information obtained from these measurements has revealed the overall chemical features of the reduction process, the TPR method is a bulk technique whose sensitivity is not limited to the behavior

of surface species on which adsorption and catalytic reactions occur. Thus, the XPS technique is a valuable complementary method for investigating the chemical nature and state of reduction of sites on catalyst surfaces because it probes primarily the uppermost few layers of a solid. Incident radiation (viz., Al K_{α} x-rays) causes ejection of core electrons from various of the occupied electron energy levels of atoms/ions in the solid. Although the incident x-rays are very penetrating, the escape depth of the ejected electrons is only 10 to 20Å, resulting in pseudosurface sensitivity. The binding energy of the ejected electrons from each energy level can be calculated from the relationship:

$$\text{B.E.} = h\nu - \text{K.E.} - \psi_s \quad (1)$$

where B.E. and K.E. are the binding energy and kinetic energy, respectively, of the ejected electrons; ν is the frequency of the incident x-rays, and ψ_s is the work function of the spectrometer. XPS spectra provide a sensitive measure of the chemical state and extent of reduction of surface atoms/ions because, for a given atomic energy level, the binding energy of core electrons is influenced by the oxidation state of the species. The binding energy of electrons from the $2p_{3/2}$ level in iron, for example, is ~707 eV for zero-valent, metallic Fe^0 and ~711 eV for Fe^{3+} species in Fe_2O_3 .

XPS spectra in the Fe 2p region are shown in Figure 21 for unpromoted, precipitated iron catalysts that had been calcined at 300 °C and then treated in H_2 at the same temperature. The Fe 2p photoelectron spectra of ferric and ferrous oxides are particularly complex, due to the extensive

coupling that occurs between the core holes created by photoemission and the high spin states of iron species. Spectrum (a) in Figure 21 is characteristic of Fe_2O_3 . It is clear that subsequent treatment in H_2 (spectrum (b)) does not effect reduction to Fe^0 , but leads to a complicated spectrum containing evidence for primarily Fe^{2+} , together with smaller amounts of both Fe^{3+} and Fe^0 . The intensities of all peaks following H_2 treatment are markedly decreased from that for the original calcined material, presumably due to increases in oxide particle size. In contrast to the effect of H_2 exposure, treatment of a calcined sample in CO at 300 °C leads to virtually quantitative reduction to metallic iron, as shown by spectrum (a) in Figure 22, which exhibits the narrower peak and lower binding energy of Fe^0 and which lacks the characteristic 3d $\rightarrow$ 4s shake-up satellite peaks of Fe^{3+} spectra. It is significant that subsequent exposure of the CO-reduced iron sample to a 2/1 H_2 /CO synthesis gas mixture at 250 °C results in the re-formation of oxidized iron, as shown in spectrum (b) of Figure 22. Oxidation of reduced iron is presumably caused by the water that is generated as a by-product of the synthesis reaction.

The XPS technique has been employed to further investigate the behaviors of copper and potassium promoters during the calcination, reduction, and reaction of precipitated iron catalysts. The composition chosen for extensive study of promoter effects is 100Fe/3Cu/0.2K, for which extensive TPR and other characterization data exist. Figures 23 to 26 present XPS spectra in the iron 2p, carbon 1s/potassium 2p (both occur within the same spectral region), copper 2p, and oxygen 1s regions for both dried, but otherwise untreated samples (spectra (a)) and samples that had

been calcined at 300 °C (spectra (b)). The intensities of the iron peaks increase following calcination (Figure 23,) due to removal of surface water and consequent increase in surface iron atom concentration. Figure 24 reveals the presence of adventitious surface carbon (peak at ~285 eV) that remains after calcination, as well as surface carbonate species (small peak at ~289 eV). Surface potassium, which would give peaks at 294 and 297 eV in this region, is, as expected, not detectable either before or after calcination due to its low (~0.2 %) concentration. Figure 25 indicates that oxidized copper may either partially segregate or migrate to the surface of precipitate crystallites during calcination, as shown by the marked increase in intensity in the Cu 2p peak at ~934 eV following calcination. Surface oxygen prior to calcination (spectrum (a) in Figure 26) resembles that in FeOOH and/or $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$, as indicated by the single broad peak centered at ~531 eV. Treatment in O_2 at 300°C, however, results in generation of a narrow peak at 529 eV (spectrum (b)), which is characteristic of oxygen in Fe_2O_3 (the remaining shoulder at 531 eV is due to Al_2O_3 on the aluminum sample holder).

The effect on the various catalyst surface species of reduction in CO at 300 °C (spectra (a)) of calcined 100Fe/3Cu/0.2K samples, followed by subsequent exposure to a 2/1 H_2 /CO synthesis gas mixture at 250 °C (spectra (b)) is shown in Figures 27 to 30. CO treatment at 300 °C leads to quantitative reduction of both iron and copper to the metallic state, as shown by the generation of the characteristic peaks at 707 eV and 932 eV in Figures 27 and 28, respectively. The concentration of surface carbon approximately doubles as a result of treatment in CO, as indicated by a comparison of the 285 eV peak intensity in spectrum (a) of Figure 29 to

that in Figure 24 (note the difference in ordinate scale between the two figures). Surface potassium is still not detectable after sample reduction in CO.

XPS spectra following subsequent exposure of the CO-treated sample to a 2/1 H_2 /CO synthesis gas mixture at 250 °C show evidence for slight re-oxidation of iron (spectrum (b) in Figure 27), but the effect is much less pronounced than that observed for an unpromoted catalyst (Figure 22). Copper appears essentially unchanged following exposure to H_2 /CO (Figure 28). The most dramatic effect of the H_2 /CO treatment is that shown in Figure 29. Surface potassium, which, as expected, had been undetectable following calcination and CO treatment due to its low concentration, increases markedly as a result of exposure to syngas. This observation indicates that potassium (oxide) undergoes either a phase separation or extensive migration to the surface of iron crystallites during H_2 /CO treatment. This behavior is almost certainly induced by the water and (possibly) CO_2 that are formed during H_2 /CO reaction, which may promote a complex process involving formation of KOH, K_2CO_3 , and K_2O . The rate of potassium migration has not been quantitatively determined, but it appears to be very high, suggesting that the potassium-enriched surface condition may be predominant throughout the H_2 /CO reaction process.

The behavior of a H_2 -reduced sample of 100Fe/3Cu/0.2K, in comparison to that of the CO-treated material discussed above, is shown in Figures 31 to 34. Treatment of a calcined sample in H_2 at 300 °C does not result in measurable reduction to metallic iron, but leads primarily to Fe^{2+} formation (spectrum (a) in Figure 31). H_2 treatment is, however, sufficient to produce zero-valent copper (Figure 32). In marked contrast to the

behavior observed following reduction in CO, treatment in H_2 results in an even more pronounced surface enrichment in potassium (Figure 33) than that caused by exposure of a CO-reduced catalyst to syngas. This behavior is consistent with the postulate that potassium migration is induced by water, since partial reduction of surface Fe^{3+} to Fe^{2+} produces water as a by-product, whereas either partial or complete reduction in CO generates only CO_2 . Figure 33 also reveals that considerable surface carbonate species are formed following H_2 treatment, as indicated by the peaks at 289 eV in both spectra. The origin of this CO_3^{2-} species is not yet clear.

Preliminary XPS results have also been obtained for one of the silica-supported iron precipitates ($100Fe/5Cu/100SiO_2$) whose preparation has been described in a previous section of this report. Spectra (a) in Figures 35 to 39 are for a sample that had been calcined at 300 °C, while spectra (b) were obtained following H_2 treatment at 300 °C and subsequent exposure to 1 atm of a 2/1 H_2 /CO synthesis gas mixture. As observed for the unsupported $100Fe/3Cu/0.2K$ catalyst, treatment of the silica-supported material in H_2 at 300 °C results in only partial reduction of surface Fe^{3+} to Fe^{2+} , with little evidence for metallic iron formation (Figure 35). Again Cu^{2+} is effectively reduced to metallic copper by H_2 treatment, as shown in Figure 36. However, both H_2 treatment and exposure to H_2 /CO result in much less migration of potassium to the surface (Figure 37) than was observed with the silica-free catalyst (Figure 33). Evidently, the presence of the homogeneously (?) distributed silica matrix effectively inhibits the potassium migration and/or segregation process.

2.4.3. FT-IR Studies of Surface Iron Species

We have also continued to employ FT-IR measurements of adsorbed molecules, particularly nitric oxide (NO), to further probe the influence of calcination and reduction treatments and promoter effects on surface iron species. As described in a previous report of this series, adsorption of NO on surface iron sites results in infrared bands due to the N-O stretching vibration, the frequency of which is dependent on the oxidation state of the iron species. Figure 40 contrasts the adsorption behaviors of an unpromoted 25 wt% Fe/SiO₂ catalyst (whose adsorption behavior effectively mimics that of the precipitated iron catalysts, but has much greater infrared transmittance) following H₂ and CO reduction treatments at 300 °C. Adsorption of NO on the H₂ reduced material (spectrum (a)) results in N-O stretching bands at both 1740 and 1818 cm⁻¹, indicating the presence of both metallic Fe⁰ and unreduced Fe²⁺ sites, respectively. Similar bands are observed for the sample treated in CO (spectrum (b)); however, the intensities of both bands are markedly decreased, indicating blockage of adsorption sites by surface carbon resulting from CO disproportionation. In addition, the band widths are greater than those observed for the H₂ treated sample, suggesting that CO reduction leads to a more energetically heterogeneous array of adsorption sites than results from H₂ treatment.

Figure 41 shows the comparative effects of copper and potassium promoters on the NO adsorption behavior of catalysts that had been calcined at 300 °C, cooled in O₂ to 25°C, and then exposed to H₂ under ambient conditions. As reported previously, the effect of added K₂O is to decrease the frequency of the N-O stretching vibration (spectrum (c)) on oxidized iron sites, while copper has no effect on band position compared to that on

the unpromoted catalyst. However, the band frequency on each of the three catalysts is 20 to 30 cm^{-1} lower than that observed with a H_2 -free surface. This behavior suggests that adsorbed H_2 may act as an electronic surface modifier for oxidized iron sites in a manner similar to that of K_2O promoter.

The extent of disproportionation that occurred when a catalyst containing 1 wt% of added Cu was reduced in CO at 300 °C was sufficiently great that no subsequent adsorption of NO could be detected, due to site blockage by surface carbon species. Similar treatment of an unpromoted catalyst in CO, on the other hand, does not cause complete site blockage, as shown by spectrum (b) in Figure 42. Reduction in a 2/1 H_2/CO syngas mixture at 300 °C, however, led to substantial formation of metallic Fe^0 sites, as evidenced by the complex set of bands centered at $\sim 1730 \text{ cm}^{-1}$ (spectrum (a) in Figure 42) that was observed following exposure to NO at 25°C, as well as to an array of Fe^{2+} sites, indicated by the broad band at $\sim 1810 \text{ cm}^{-1}$. The presence of copper promoter appears to significantly enhance disproportionation of CO on these silica-supported iron catalysts.

TASK 3 - Process Evaluation Research

No work on this task was scheduled during this quarter.

TASK 4 - Economic Evaluation

No work on this task was scheduled during this quarter.

Table 1. Summary of results for 8 hour duration CO reduction procedures at 250 (FA-25-2737), 280 (FA-25-3077), and 310 °C (FA-25-2847).

Run	FA-25-2737			FA-25-3077			FA-25-2847	
	250			280			310	
Reduction Temperature (°C)								
Period	1	2		1	2		1	2
Date	10/03/87	10/06/87		11/06/87	11/08/87		10/14/87	10/16/87
Time on Stream (h)	72.0	120		72.5	122		72.0	110
Balance Duration (h)	6.0	6.0		6.0	6.0		6.0	6.0
Average Temperature (°C)	250	250		250	250		250	250
Maximum Δ Temperature (°C) ^b	2.0	2.0		4.0	5.0		4.0	3.0
Pressure (MPa)	1.48	1.48		1.48	1.48		1.48	1.48
H ₂ /CO Feed Ratio	1.08	1.07		1.09	1.09		1.09	1.09
Space Velocity (NI/g-cat·h) ^a	2.04	2.04		2.04	2.04		2.04	2.04
GLSV (h ⁻¹) ^c	264	264		224	224		246	246
CO Conversion (%)	91.5	86.9		76.6	68.6		85.1	77.7
H ₂ +CO Conversion (%)	78.7	73.1		68.6	61.2		71.4	64.8
H ₂ /CO Usage	.79	.74		.87	.86		.75	.74
STY (mols H ₂ +CO/g-cat·h) ^a	.072	.067		.062	.056		.065	.059
P _{CO₂} · P _{H₂} /P _{CO} · P _{H₂O}	18.8	12.8		4.6	3.9		16.4	13.8
Weight % of Outlet								
H ₂	2.51	2.99		2.82	3.26		3.02	3.39
H ₂ O	5.69	6.09		7.57	6.90		4.13	3.47
CO	8.33	12.8		21.8	28.8		13.9	20.6
CO ₂	62.4	58.9		47.1	41.9		54.9	51.0
Hydrocarbons	18.5	16.9		15.3	13.7		16.3	13.6
Oxygenates	.64	.47		.82	.81		.67	.43
Wax ^d	2.02	1.86		4.63	4.67		6.99	7.46
Yield (g/Nm ³ H ₂ + CO Converted)								
CH ₄	20.8	20.1		13.5	13.3		12.7	12.6
C ₂ -C ₄ Hydrocarbons	59.3	61.1		50.3	52.8		51.8	50.4
C ₅ -C ₁₁ Hydrocarbons	55.2	56.4		57.2	64.8		64.1	61.2
C ₁₂ + Hydrocarbons	24.9	20.2		65.5	66.1		80.1	87.7
Wax ^d	15.8	15.7		43.4	50.0		62.6	74.9
Oxygenates	4.99	4.00		7.68	8.72		6.02	4.33
Total	165	162		194	206		215	216
1+2 Olefins/n-Paraffin Ratio								
C ₂	.34	.39		.69	.76		1.41	1.62
C ₃	3.46	3.60		4.77	4.91		7.45	7.37
C ₄	3.73	3.80		4.56	4.61		6.37	6.39
C ₈	1.46	1.64		2.24	2.20		3.67	4.30
C ₁₀	1.35	1.40		1.78	1.52		3.14	3.50

^a Based on unreduced catalyst

^c Based on effective bed volume

^b Maximum axial temperature difference

^d Unanalyzed products collected from hot trap

Table 1 (cont'd). Summary of results for 8 hour duration CO reduction procedures at 250 (FA-25-2737), 280 (FA-25-3077), and 310 °C (FA-25-2847).

Run	FA-25-2737		FA-25-3077		FA-25-2847	
Reduction Temperature (°C)	250		280		310	
Period	1	2	1	2	1	2
Weight % of Hydrocarbons						
CH ₄	13.0	12.7	7.22	6.76	6.10	5.95
Ethane	7.54	7.92	4.55	4.15	3.33	3.95
Ethylene	2.39	2.88	2.93	2.93	4.37	4.48
Propane	3.42	3.32	1.83	1.82	1.15	1.11
Propylene	11.3	11.4	8.33	8.50	8.16	7.82
n-Butane	2.46	2.60	1.59	1.59	0.99	0.94
1+2 Butenes	8.87	9.55	7.01	7.08	6.11	5.80
C ₄ Isomers	1.06	1.06	.74	.73	.69	.66
n-Pentane	2.69	3.19	2.07	2.01	1.61	1.87
1+2 Pentenes	5.74	6.95	5.99	5.68	5.68	6.71
C ₅ Isomers	1.55	1.77	.90	.75	.56	.91
n-Hexane	2.42	2.75	1.50	1.93	.69	.68
1+2 Hexenes	3.56	4.09	3.34	4.50	3.17	2.80
C ₆ Isomers	2.77	1.04	.67	.73	.75	.71
n-Heptane	1.49	1.69	1.14	1.13	.62	.55
1+2 Heptenes	2.37	2.74	2.12	2.56	2.33	2.04
C ₇ Isomers	.79	.94	.57	.52	1.05	.59
n-Octane	1.39	1.26	.92	.89	.54	.52
1+2 Octenes	1.99	2.03	2.02	1.93	1.96	2.21
C ₈ Isomers	.52	.83	.41	.55	1.14	.57
n-Nonane	.99	.88	1.00	.93	.54	.52
1+2 Nonenes	1.48	1.35	1.93	1.96	1.89	2.03
C ₉ Isomers	.55	.46	.47	.41	1.40	.52
n-Decane	.82	.74	.97	1.21	.57	.54
1+2 Decenes	1.09	1.02	1.71	1.81	1.77	1.87
C ₁₀ Isomers	.47	.44	.46	.28	1.22	0.63
n-Undecane	.63	.54	.86	1.21	.54	.51
1+2 Undecenes	.75	.67	1.27	1.53	1.50	1.56
C ₁₁ Isomers	.43	.37	.36	.35	1.17	.56
C ₂ -C ₄	37.0	38.7	27.0	26.8	24.8	23.8
C ₅ -C ₁₁	34.5	35.7	30.7	32.9	30.7	28.9
C ₁₂ +	15.6	12.8	35.1	33.6	38.4	41.4
Wax ^d	9.87	9.95	23.3	25.4	30.0	35.4

^d Unanalyzed products collected from hot trap

Table 2. Summary of results for 24 hour CO reduction procedures at 250 (FA-25-2857) and 280 °C (FA-25-2967).

Run	FA-25-2857		FA-25-2967	
	250		280	
Reduction Temperature (°C)				
Period	1	2	1	2
Date	10/15/87	10/17/87	10/26/87	10/28/87
Time on Stream (h)	72.0	120	73.0	122.0
Balance Duration (h)	6.0	6.0	6.0	6.0
Average Temperature (°C)	250	251	251	251
Maximum Δ Temperature (°C) ^b	6.0	5.0	5.0	5.0
Pressure (MPa)	1.48	1.48	1.48	1.48
H ₂ /CO Feed Ratio	1.08	1.08	1.09	1.09
Space Velocity (NI/g-cat·h) ^a	2.05	2.05	2.04	2.04
GHSV (h ⁻¹) ^c	248	248	245	245
CO Conversion (%)	63.6	56.0	88.6	84.1
H ₂ +CO Conversion (%)	56.9	50.0	76.2	74.5
H ₂ /CO Usage	.86	.85	.79	.85
STY (mols H ₂ +CO/g-cat·h) ^a	.052	.046	.069	.068
P _{CO₂} · P _{H₂} / P _{CO} · P _{H₂O}	2.56	3.52	25.1	6.0
Weight % of Outlet				
H ₂	3.40	4.17	2.67	2.55
H ₂ O	8.11	5.40	3.07	8.11
CO	32.2	42.4	11.1	15.1
CO ₂	34.6	34.1	56.2	51.3
Hydrocarbons	16.1	9.78	15.8	16.1
Oxygenates	.76	.47	.27	.81
Wax ^d	4.75	3.66	10.9	6.0
Yield (g/Nm ³ H ₂ + CO Converted)				
CH ₄	13.8	13.8	15.4	14.4
C ₂ -C ₄ Hydrocarbons	51.4	48.7	55.6	51.9
C ₅ -C ₁₁ Hydrocarbons	95.6	51.2	48.8	56.7
C ₁₂ + Hydrocarbons	88.4	53.8	95.6	63.8
Wax ^d	56.7	45.6	87.9	50.6
Oxygenates	9.01	5.91	2.18	6.85
Total	258	173	218	194
1+2 Olefins/n-Paraffin Ratio				
C ₂	.73	.88	.51	.53
C ₃	4.61	5.03	4.48	4.42
C ₄	4.39	4.59	4.28	4.31
C ₈	2.15	2.20	2.11	1.87
C ₁₀	1.96	1.91	1.43	1.44

^a Based on unreduced catalyst

^c Based on effective bed volume

^b Maximum axial temperature difference

^d Unanalyzed products collected from hot trap

Table 2 (cont'd). Summary of results for 24 hour CO reduction procedures at 250 (FA-25-2857) and 280 °C (FA-25-2967).

Run	FA-25-2857		FA-25-2967	
	250		280	
Reduction Temperature (°C)	1	2	1	2
Period				
Weight % of Hydrocarbons				
CH ₄	5.54	8.22	7.14	7.73
Ethane	3.46	4.24	4.35	4.97
Ethylene	2.35	3.48	2.05	2.44
Propane	1.41	1.89	1.98	2.03
Propylene	6.22	9.08	5.47	8.56
n-Butane	1.26	1.77	1.60	1.74
1+2 Butenes	5.34	7.83	6.62	7.23
C ₄ Isomers	.57	.80	.75	.80
n-Pentane	1.68	2.36	1.99	2.38
1+2 Pentenes	4.89	9.50	5.07	6.07
C ₅ Isomers	.83	1.77	.51	.57
n-Hexane	1.41	1.29	1.36	1.59
1+2 Hexenes	2.93	2.80	2.80	3.22
C ₆ Isomers	.58	.76	1.97	.71
n-Heptane	1.16	.86	.76	1.15
1+2 Heptenes	2.18	1.63	1.41	2.03
C ₇ Isomers	.46	.55	.37	.52
n-Octane	1.39	.65	.56	1.08
1+2 Octenes	2.93	1.40	1.15	1.99
C ₈ Isomers	.64	.24	.23	.29
n-Nonane	1.61	.63	.57	1.12
1+2 Nonenes	3.33	1.33	.93	1.81
C ₉ Isomers	.86	.33	.15	.32
n-Decane	1.73	.69	.57	1.11
1+2 Decenes	3.32	1.30	.80	1.57
C ₁₀ Isomers	1.09	.39	.17	.32
n-Undecane	1.63	.65	.52	1.02
1+2 Undecenes	2.69	1.06	.61	1.20
C ₁₁ Isomers	1.03	.39	.17	.29
C ₂ -C ₄	20.6	29.1	25.8	27.8
C ₆ -C ₁₁	38.4	30.6	22.7	30.4
C ₁₂ +	35.5	32.1	44.4	34.2
Wax ^d	22.8	27.2	40.8	27.1

^d Unanalyzed products collected from hot trap

Table 3. Summary of results for high pressure (1.48 MPa) CO reduction at optimum reduction temperature (280 °C) and duration (24 h), run FA-25-3517.

Period		1	2
Date		12/20/87	12/22/87
Time on Stream (h)		71.5	119.8
Balance Duration (h)		6.0	7.5
Average Temperature (°C)		250	250
Maximum Δ Temperature (°C) ^b		2.9	3.3
Pressure (MPa)		1.48	1.48
H ₂ /CO Feed Ratio		1.06	1.06
Space Velocity (NI/g-cat·h) ^a		2.04	2.04
Space Velocity (NI/g-Fe·h)		3.00	3.00
GHSV (h ⁻¹) ^c		224	224
CO Conversion (%)		76.5	68.6
H ₂ + CO Conversion (%)		65.1	58.5
H ₂ /CO Usage		.75	.76
STY (mols H ₂ + CO/g-cat·h) ^a		.059	.053
P _{CO₂} · P _{H₂} / P _{CO} · P _{H₂O}		8.9	6.6
Weight % of Outlet			
H ₂		3.24	3.69
H ₂ O		4.94	4.87
CO		21.9	29.8
CO ₂		52.6	46.0
Hydrocarbons		10.4	8.85
Oxygenates		.65	.65
Wax ^d		6.37	6.06
Yield (g/Nm ³ H ₂ + CO Converted)			
CH ₄		10.9	9.51
C ₂ -C ₄ Hydrocarbons		44.2	42.4
C ₅ -C ₁₁ Hydrocarbons		44.0	39.9
C ₁₂ + Hydrocarbons		68.3	71.1
Wax ^d		63.7	66.2
Oxygenates		6.50	7.13
Total		174	170
1 + 2 Olefins/n-Paraffin Ratio			
C ₂		1.56	1.47
C ₃		7.10	6.97
C ₄		6.15	6.04
C ₈		3.48	3.55
C ₁₀		3.24	3.39

^a Based on unreduced catalyst

^c Based on effective bed volume

^b Maximum axial temperature difference
^d Unanalyzed products collected from hot zone

Table 3 (cont'd). Summary of results for high pressure (1.48 MPa) CO reduction at optimum reduction temperature (280 °C) and duration (24 h), run FA-25-3517.

Period		1	2
Weight % of Hydrocarbons			
C ₁ H ₄		6.50	5.84
Ethane		3.25	3.81
Ethylene		4.73	5.22
Propane		1.29	1.20
Propylene		8.71	7.99
n-Butane		1.11	1.04
i+2 Butenes		6.57	6.06
C ₄ Isomers		.75	.70
n-Pentane		1.64	1.55
i+2 Pentenes		6.41	5.28
C ₅ Isomers		.63	.39
n-Hexane		.84	.73
i+2 Hexenes		3.43	3.58
C ₆ Isomers		.86	.82
n-Heptane		.52	.49
i+2 Heptenes		1.81	2.09
C ₇ Isomers		.47	.61
n-Octane		.46	.42
i+2 Octenes		1.56	1.48
C ₈ Isomers		.20	.35
n-Nonane		.47	.43
i+2 Nonenes		1.71	1.54
C ₉ Isomers		.56	.39
n-Decane		.49	.46
i+2 Decenes		1.57	1.54
C ₁₀ Isomers		.61	.48
n-Undecane		.41	.39
i+2 Undecenes		1.16	1.18
C ₁₁ Isomers		.47	.33
C ₁₂ -C ₄		26.4	26.0
C ₅ -C ₁₁		26.3	24.5
C ₁₂ +		40.8	43.6
Wax ^d		38.1	40.6

^d Unanalyzed products collected from hot trap

Table 4. Summary of results for 8 hour H₂ reduction procedures at 250 (FB-25-3087) and 280 °C (FB-25-2957).

Run	FB-25-3087		FB-25-2957	
	250		280	
Reduction Temperature (°C)	1 ^c		1	2
Period				
Date	11/07/87		10/25/87	10/27/87
Time on Stream (h)	71.5		74.0	121.0
Balance Duration (h)	6.0		6.0	6.0
Average Temperature (°C)	250		250	250
Maximum Δ Temperature (°C) ^b	6.0		9.0	8.0
Pressure (MPa)	1.48		1.48	1.48
H ₂ /CO Feed Ratio	1.09		1.09	1.09
Space Velocity (NI/g cat-h) ^a	2.04		2.04	2.04
GHSV (h ⁻¹) ^c	225		245	245
CO Conversion (%)	81.1		61.2	67.5
H ₂ + CO Conversion (%)	65.2		48.0	53.3
STY (mols H ₂ + CO/g cat-h) ^a	.68		.64	.65
P _{CO₂} · P _{H₂} / P _{CO} · P _{H₂O}	.059		.044	.048
Weight % of Outlet	48.4		10.4	13.7
H ₂	3.68		4.56	4.22
H ₂ O	1.42		3.33	3.08
CO	17.9		35.1	29.29
CO ₂	59.0		46.7	51.6
Hydrocarbons	16.8		9.88	10.3
Oxygenates	1.03		.41	.31
Wax ^d	.15		.02	1.20
Yield (g/Nm ³ H ₂ + CO Conver ^d)				
CH ₄	23.3		19.2	18.5
C ₂ C ₄ Hydrocarbons	65.4		61.2	56.8
C ₅ C ₁₁ Hydrocarbons	64.5		53.3	47.3
C ₁₂ + Hydrocarbons	10.7		5.36	20.7
Wax ^d	1.44		.26	14.9
Oxygenates	9.98		5.65	3.84
Total	174		142	147
1 + 2 Olefins/n Paraffin Ratio				
C ₂	.70		1.99	2.35
C ₃	3.69		4.59	4.76
C ₄	2.91		3.63	3.77
C ₈	1.80		2.74	2.96
C ₁₀	1.66		2.76	2.96

^a Based on unreduced catalyst

^c Based on effective bed volume

^b Maximum axial temperature difference

^d Unanalyzed products collected from hot trap
^e Period 2 terminated due to flow interruption

Table 4 (cont'd). Summary of results for 8 hour H₂ reduction procedures at 250 (FA-25-3087) and 280 °C (FB-25-2957).

Run	FB 25-3087	FB-25-2957
Reduction Temperature (°C)	250	280
Period	1 ^c	1
2		
Weight % of Hydrocarbons		
CH ₄	14.2	14.0
Ethane	7.16	5.30
Ethylene	4.70	9.82
Propane	3.38	2.99
Propylene	11.9	13.1
n-Butane	3.10	2.82
1+2 Butenes	8.70	9.90
C ₄ Isomers	.99	1.26
n-Pentane	3.42	3.66
1+2 Pentenes	7.08	8.75
C ₅ Isomers	.68	.69
n-Hexane	2.02	2.18
1+2 Hexenes	4.82	6.27
C ₆ Isomers	.94	1.80
n-Heptane	1.34	1.33
1+2 Heptenes	2.68	3.65
C ₇ Isomers	.58	1.14
n-Octane	1.32	.60
1+2 Octenes	2.34	1.63
C ₈ Isomers	.50	.36
n-Nonane	1.28	.33
1+2 Nonenes	2.20	1.00
C ₉ Isomers	.72	.32
n-Decane	1.24	.37
1+2 Decenes	2.04	1.00
C ₁₀ Isomers	.63	.27
n-Undecane	1.09	.34
1+2 Undecenes	1.65	.88
C ₁₁ Isomers	.78	.33
C ₂ C ₄	39.9	45.2
C ₅ C ₁₁	39.4	36.9
C ₁₂ +	6.52	3.93
Wax ^d	.88	.19

^d Unanalyzed products collected from hot trap

^e Period 2 terminated due to flow interruption

Table 5. Summary of results for 24 hour H₂ reduction procedures at 250 (FA-25-3237) and 280 °C (FB-25-3227).

Run	FA-25-3237		FB-25-3227	
	250		280	
Reduction Temperature (°C)				
Period	1	2	1	2
Date	11/22/87	11/24/87	11/21/87	11/23/87
Time on Stream (h)	70.5	118.5	70.5	89.5
Balance Duration (h)	6.0	6.5	6.5	7.5
Average Temperature (°C)	250	250	250	250
Maximum Δ Temperature (°C) ^b	6.0	8.0	2.0	3.0
Pressure (MPa)	1.48	1.48	1.48	1.48
H ₂ /CO Feed Ratio	1.09	1.09	1.09	1.09
Space Velocity (NI/g-cat·h) ^a	2.04	2.04	2.05	2.05
GHSV (h ⁻¹) ^c	224	224	225	225
CO Conversion (%)	79.0	85.7	31.0	33.1
H ₂ +CO Conversion (%)	62.9	70.2	26.0	27.1
H ₂ /CO Usage	.66	.71	.75	.71
STY (mols H ₂ +CO/g-cat·h) ^a	.057	.064	.024	.025
P _{CO} · P _{H₂} /P _{CO} · P _{H₂O}	29.0	23.6	4.9	4.2
Weight % of Outlet				
H ₂	3.81	3.25	5.65	5.58
H ₂ O	2.18	3.68	2.28	2.98
CO	19.8	13.4	63.3	60.8
CO ₂	57.7	63.3	22.2	23.9
Hydrocarbons	14.6	14.2	5.97	5.59
Oxygenates	.97	.76	.48	.34
Wax ^d	.93	1.35	.17	.79
Yield (g/Nm ³ H ₂ + CO Converted)				
CH ₄	19.5	20.8	16.5	18.1
C ₂ -C ₄ Hydrocarbons	61.3	60.4	60.5	59.2
C ₅ -C ₁₁ Hydrocarbons	66.3	46.2	60.9	52.8
C ₁₂ + Hydrocarbons	10.7	13.9	16.0	24.5
Wax ^d	9.38	12.2	4.21	19.1
Oxygenates	9.85	6.84	12.2	8.30
Total	168	148	166	163
1 ± 2 Olefins/n-Paraffin Ratio				
C ₂	1.19	.89	1.49	1.80
C ₃	4.24	4.35	4.68	4.82
C ₄	3.38	3.48	3.78	3.97
C ₈	2.87	2.33	3.19	3.46
C ₁₀	2.18	1.91	2.58	3.16

^a Based on unreduced catalyst

^c Based on effective bed volume

^b Maximum axial temperature difference

^d Unanalyzed products collected from hot trap

Table 5 (cont'd). Summary of results for 24 hour H₂ reduction procedures at 250 (FA-25-3237) and 280 °C (FB-25-3227).

Run	FA-25-3237		FB-25-3227	
	250		280	
Reduction Temperature (°C)				
Period	1	2	1	2
Weight % of Hydrocarbons				
CH ₄	12.4	14.7	10.7	11.7
Ethane	5.75	7.38	6.23	4.53
Ethylene	6.40	6.15	8.66	8.28
Propane	2.83	3.10	2.35	2.38
Propylene	11.5	12.9	10.5	10.9
n-Butane	2.67	2.80	2.27	2.23
1+2 Butenes	8.70	9.41	8.28	8.56
C ₄ Isomers	1.06	1.05	.99	.98
n-Pentane	3.20	3.11	2.89	2.89
1+2 Pentenes	7.84	7.71	7.44	9.37
C ₅ Isomers	.74	.67	.70	1.02
n-Hexane	1.63	1.87	1.63	1.50
1+2 Hexenes	5.62	5.51	5.70	5.41
C ₆ Isomers	1.04	1.12	1.44	1.32
n-Heptane	1.93	1.09	1.19	1.04
1+2 Heptenes	3.38	2.93	3.46	3.42
C ₇ Isomers	.62	.62	.97	.86
n-Octane	1.01	.73	.73	.52
1+2 Octenes	2.83	1.67	2.29	1.77
C ₈ Isomers	.45	.35	.39	.23
n-Nonane	1.39	.63	.60	.29
1+2 Nonenes	3.22	1.28	1.88	.96
C ₉ Isomers	.25	.3	.23	.05
n-Decane	1.31	.56	1.01	.40
1+2 Decenes	2.80	1.05	2.58	1.25
C ₁₀ Isomers	.25	.18	.37	.12
n-Undecane	.75	.40	.99	.38
1+2 Undecenes	1.59	.67	2.61	1.19
C ₁₁ Isomers	.17	.12	.46	.18
C ₂ -C ₄	38.9	42.8	39.3	38.3
C ₅ -C ₁₁	42.0	32.7	39.6	34.2
C ₁₂ +	6.76	9.84	10.4	15.8
Wax ^d	5.95	8.66	2.73	12.3

^d Unanalyzed products collected from hot trap

Table 6. Summary of results for fixed bed run FB-25-3377.

Catalyst: 3.30 g^a, 100Fe / 3.0 Cu / 0.2 K
 Catalyst volume: 3.0 cc
 Diluent: 33.9 g, Glass beads
 Diluent Volume: 24.0 cc

Period	1	2
Date	12/06/87	12/08/87
Time on Stream (h)	69.0	115.0
Balance Duration (h)	6.0	6.0
Average Temperature (°C)	250	250
Maximum Δ Temperature (°C) ^b	6.0	6.0
Pressure (MPa)	1.48	1.48
H ₂ /CO Feed Ratio	1.07	1.09
Space Velocity (Nl/g-cat·h) ^a	2.04	2.04
Space Velocity (Nl/g-Fe·h)	2.99	2.99
GHSV (h ⁻¹) ^c	224	224
CO Conversion (%)	76.0	67.2
H ₂ +CO Conversion (%)	64.6	58.4
H ₂ /CO Usage	.76	.81
STY (mols H ₂ +CO/g-cat·h) ^a	.059	.053
$PCO_2 \cdot P_{H_2} / P_{CO} \cdot P_{H_2O}$	5.2	4.6
Weight % of Outlet		
H ₂	3.33	3.64
H ₂ O	8.17	6.62
CO	22.5	30.6
CO ₂	50.1	45.0
Hydrocarbons	11.3	10.1
Oxygenates	.81	.84
Wax ^d	3.74	3.24
Yield (g/Nm ³ H ₂ + CO Converted)		
CH ₄	10.6	9.48
C ₂ -C ₄ Hydrocarbons	45.5	39.4
C ₅ -C ₁₁ Hydrocarbons	47.4	47.7
C ₁₂ + Hydrocarbons	45.8	49.4
Wax ^d	37.1	35.6
Oxygenates	8.02	9.24
Total	158	155
1+2 Olefins/n-Paraffin Ratio		
C ₂	1.47	1.60
C ₃	6.06	6.12
C ₄	5.41	5.33
C ₈	5.36	5.36
C ₁₀	3.81	3.32

^a Based on unreduced catalyst^c Based on effective bed volume^b Maximum axial temperature difference^d Unanalyzed products collected from hot trap

Table 6 (cont'd). Summary of results for fixed bed run FB-25-3377.

Period		1	2
Weight % of Hydrocarbons			
C ₁ H ₄		7.10	6.49
Ethane		3.98	3.66
Ethylene		5.46	5.46
Propane		1.66	1.40
Propylene		9.61	8.17
n-Butane		1.43	1.23
1+2 Butenes		7.50	6.32
C ₄ Isomers		.84	.71
n-Pentane		2.01	1.72
1+2 Pentenes		6.62	5.84
C ₅ Isomers		.57	.52
n-Hexane		.98	1.35
1+2 Hexenes		3.94	3.75
C ₆ Isomers		.83	.81
n-Heptane		.65	.97
1+2 Heptenes		2.44	2.51
C ₇ Isomers		.52	.53
n-Octane		.50	.47
1+2 Octenes		2.64	2.46
C ₈ Isomers		.36	.20
n-Nonane		.54	.78
1+2 Nonenes		2.59	2.79
C ₉ Isomers		.21	.23
n-Decane		.68	.87
1+2 Decenes		2.55	2.84
C ₁₀ Isomers		.21	.43
n-Undecane		.61	.82
1+2 Undecenes		2.10	2.40
C ₁₁ Isomers		.23	.39
C ₂ -C ₄		30.5	27.0
C ₅ -C ₁₁		31.8	32.7
C ₁₂ +		30.7	33.9
Wax ^d		24.9	24.3

^d Unanalyzed products collected from hot trap

Table 7. Summary of results for fixed bed run FA-99-3357.

Catalyst: 3.50 g^a, Ruhchemie LP 33/81
Catalyst volume: 3.00 cc

Diluent: 34.1 g, Glass beads
Diluent Volume: 22.0 cc

Period	1	2	3	4	5
Date	12/04/87	12/06/87	12/07/87	12/08/87	12/09/87
Time on Stream (h)	64.5	109.5	134.0	158.0	182.0
Balance Duration (h)	7.0	6.0	6.0	6.0	7.5
Average Temperature (°C)	220	235	250	251	250
Maximum Δ Temperature (°C) ^b	2.0	2.5	4.0	3.2	3.2
Pressure (MPa)	1.48	1.48	1.48	1.48	1.48
H ₂ /CO Feed Ratio	1.09	1.09	1.10	1.10	1.10
Space Velocity (NI/g cat-h) ^a	2.00	2.00	2.00	4.00	.75
GHSV (h ⁻¹) ^c	233	233	233	466	87
CO Conversion (%)	20.9	44.2	69.5	55.4	90.4
H ₂ + CO Conversion (%)	25.3	45.0	61.7	53.8	77.6
H ₂ /CO Usage	1.53	1.12	.95	1.04	.80
STY (mols H ₂ + CO/g cat-h) ^a	.023	.040	.058	.096	.026
$P_{CO_2} \cdot P_{H_2} / P_{CO} \cdot P_{H_2O}$	.5	1.3	3.4	2.0	16.9
Weight % of Outlet					
H ₂	5.17	3.88	2.85	3.55	2.42
H ₂ O	6.75	8.14	7.43	7.89	5.79
CO	73.9	50.8	27.7	42.1	8.63
CO ₂	8.72	23.8	42.6	32.6	61.1
Hydrocarbons	2.68	6.48	12.2	8.41	16.7
Oxygenates	.78	.80	.72	.88	.64
Wax ^d	1.98	6.00	6.53	4.55	4.73
Yield (g/Nm ³ H ₂ + CO Converted)					
CH ₄	10.5	12.3	15.0	13.9	20.1
C ₂ C ₄ Hydrocarbons	28.4	32.3	37.5	35.8	51.0
C ₅ C ₁₁ Hydrocarbons	24.8	36.0	49.2	35.9	57.6
C ₁₂ + Hydrocarbons	54.1	102	88.2	66.3	53.9
Wax ^d	50.2	87.6	66.3	53.3	40.3
Oxygenates	19.9	11.7	7.3	10.3	5.46
Total	138	194	197	162	188
1 + 2 Olefins/n-Paraffin Ratio					
C ₂	1.19	1.00	.56	.82	.26
C ₃	3.82	4.10	4.10	4.75	3.15
C ₄	2.95	3.20	3.26	3.81	2.56
C ₅	2.02	2.88	1.54	2.44	.99
C ₁₀	2.06	1.67	1.12	1.66	.68

^a Based on unreacted catalyst

^c Based on effective bed volume

^b Maximum axial temperature difference

^d Unanalyzed products collected from hot trap

Table 7 (cont'd). Summary of results for fixed bed run FA-99-3357.

Period	6	7	8	9
Date	12/10/87	12/11/87	12/12/87	12/13/87
Time on Stream (h)	206.0	230.0	254.0	277.5
Balance Duration (h)	7.5	7.5	6.0	6.0
Average Temperature (°C)	265	235	250	235
Maximum Δ Temperature (°C) ^b	1.6	3.0	4.0	4.0
Pressure (MPa)	1.48	1.48	2.17	1.48
H ₂ /CO Feed Ratio	1.10	1.10	1.10	1.10
Space Velocity (Nl/g-cat·h) ^a	.75	.75	3.00	2.00
GHSV (h ⁻¹) ^c	87	87	350	233
CO Conversion (%)	95.6	52.5	58.1	31.4
H ₂ +CO Conversion (%)	81.1	53.7	59.1	36.5
H ₂ /CO Usage	.78	1.14	1.13	1.44
STY (mols H ₂ +CO/g-cat·h) ^a	.027	.018	.079	.033
$P_{CO_2} \cdot P_{H_2} / P_{CO} \cdot P_{H_2O}$	61.3	1.5	1.6	.6
Weight % of Outlet				
H ₂	2.30	3.24	3.03	4.27
H ₂ O	3.48	8.12	8.34	8.79
CO	4.02	43.1	40.3	63.1
CO ₂	65.6	27.9	30.8	14.1
Hydrocarbons	22.0	11.7	11.5	6.00
Oxygenates	.49	1.02	.76	1.01
Wax ^d	2.17	4.95	5.33	2.70
Yield (g/Nm ³ H ₂ + CO Converted)				
CH ₄	26.3	13.2	14.3	12.8
C ₂ -C ₄ Hydrocarbons	57.2	44.5	42.7	38.9
C ₅ -C ₁₁ Hydrocarbons	70.8	55.1	50.1	42.2
C ₁₂ + Hydrocarbons	40.4	90.4	70.1	60.5
Wax ^d	17.5	60.6	56.0	48.0
Oxygenates	3.97	12.5	7.97	18.0
Total	198	216	185	172
1+2 Olefins/n-Paraffin Ratio				
C ₂	.14	1.13	.94	1.87
C ₃	2.53	4.83	4.53	4.82
C ₄	2.20	3.78	3.60	3.82
C ₈	.82	2.24	2.16	2.58
C ₁₀	.58	2.34	1.77	2.34

^a Based on unreduced catalyst^c Based on effective bed volume^b Maximum axial temperature difference^d Unanalyzed products collected from hot trap

Table 7 (cont'd). Summary of results for fixed bed run FA-99-3357.

Period		1	2	3	4	5
Weight % of Hydrocarbons						
CH ₄		8.85	6.73	7.88	9.16	11.0
Ethane		3.57	3.11	4.06	4.36	6.58
Ethylene		4.95	2.89	2.13	3.34	1.59
Propane		1.76	1.24	1.44	1.47	2.55
Propylene		6.42	4.84	5.62	6.67	7.66
n Butane		1.80	1.30	1.47	1.55	2.60
i + 2 Butenes		5.11	4.01	4.63	5.71	6.42
C ₄ Isomers		.45	.33	.38	.43	.52
n Pentane		2.02	1.51	1.72	2.17	2.80
i + 2 Pentenes		5.43	4.16	4.26	5.86	5.03
C ₅ Isomers		.22	.32	.45	.50	.75
n Hexane		1.56	1.00	1.26	1.27	1.92
i + 2 Hexenes		3.60	2.87	2.94	3.25	2.76
C ₆ Isomers		.72	.41	.41	.53	.43
n Heptane		.99	.66	1.10	.69	1.65
i + 2 Heptenes		2.19	1.71	1.94	1.99	1.90
C ₇ Isomers		.32	.22	.28	.30	.23
n Octane		.46	.48	1.18	.59	1.96
i + 2 Octenes		.91	1.37	1.79	1.42	1.91
C ₈ Isomers		.18	.15	.14	.08	.09
n Nonane		.17	.46	1.23	.53	2.07
i + 2 Nonenes		.36	1.00	1.61	1.01	1.69
C ₉ Isomers		.02	.03	.08	.03	.09
n Decane		.26	.68	1.35	.64	2.02
i + 2 Decenes		.53	1.12	1.49	1.04	1.35
C ₁₀ Isomers		.21	.02	.08	.05	.10
n Undecane		.29	.67	1.33	.67	1.77
i + 2 Undecenes		.55	.93	1.22	.97	.95
C ₁₁ Isomers		.03	.02	.07	.08	.08
C ₂ C ₄		24.1	17.7	19.7	23.5	27.9
C ₅ C ₁₁		21.0	19.8	25.9	23.6	31.6
C ₁₂ l		46.1	55.8	46.5	43.6	29.5
Wax ^d		42.5	48.1	34.9	35.1	22.1

^d Unanalyzed products collected from hot trap

Table 7 (cont'd). Summary of results for fixed bed run FA-99-3357.

Period		6	7	8	9
Weight % of Hydrocarbons					
CH ₄		13.5	5.51	8.09	8.28
Ethane		7.17	3.16	3.72	2.50
Ethylene		.91	3.32	3.27	4.35
Propane		3.24	1.41	1.64	1.67
Propylene		7.81	6.48	7.09	7.67
n-Butane		3.10	1.52	1.76	1.82
1+2 Butenes		6.57	5.53	6.11	6.73
C ₄ Isomers		.56	.46	.49	.47
n-Pentane		3.40	1.79	2.02	2.12
1+2 Pentenes		4.93	5.12	6.00	6.55
C ₅ Isomers		1.09	.37	.50	.33
n-Hexane		2.65	.94	1.21	1.38
1+2 Hexenes		2.62	3.00	3.79	4.23
C ₆ Isomers		.43	.48	.51	.56
n-Heptane		2.39	1.15	1.06	.95
1+2 Heptenes		2.08	1.39	2.19	2.47
C ₇ Isomers		.31	.28	.30	.34
n-Octane		2.67	.69	1.13	.75
1+2 Octenes		2.14	1.51	2.40	1.89
C ₈ Isomers		.17	.12	.18	.07
n-Nonane		2.59	.85	.77	.47
1+2 Nonenes		1.76	2.10	1.54	1.16
C ₉ Isomers		.21	.18	.08	.10
n-Decane		2.35	1.05	.83	.58
1+2 Decenes		1.33	2.43	1.45	1.35
C ₁₀ Isomers		.20	.25	.16	.14
n-Undecane		1.96	1.02	.81	.56
1+2 Undecenes		.92	2.17	1.20	1.20
C ₁₁ Isomers		.17	.25	.13	.14
C ₂ -C ₄		29.4	21.9	24.1	25.2
C ₅ -C ₁₁		36.4	27.1	28.3	27.3
C ₁₂ +		20.8	44.5	39.6	39.2
Wax ^d		9.00	29.8	31.6	31.1

^d Unanalyzed products collected from hot trap

Table 8. Summary of results for fixed bed run FB-99-3477, using standard reduction conditions.

Catalyst: 3.50 g^a, Ruhchemie LP 33/81

Diluent: 33.4 g, Glass beads

Catalyst volume: 3.0 cc

Diluent Volume: 22.0 cc

Period	1	2	3	4	5	6
Date	12/15/87	12/16/87	12/17/87	12/18/87	12/19/87	12/20/87
Time on Stream (h)	38.0	63.0	87.0	111.0	134.5	158.5
Balance Duration (h)	6.0	6.0	6.0	6.0	7.0	7.0
Average Temperature (°C)	220	235	235	249	250	235
Maximum Δ Temperature (°C) ^b	5.0	2.0	3.0	3.0	3.0	1.0
Pressure (MPa)	1.18	1.48	1.48	1.48	1.48	1.58
H ₂ /CO Feed Ratio	1.10	1.10	1.10	1.10	1.10	1.10
Space Velocity (NI/g cat-h) ^a	2.00	2.00	4.00	2.00	.75	.75
Space Velocity (NI/g Fe-h)	3.57	3.57	7.13	3.57	1.34	1.34
GHSV (h ⁻¹) ^c	233	233	466	233	87	87
CO Conversion (%)	37.8	39.6	28.6	64.4	86.1	62.2
H ₂ + CO Conversion (%)	37.9	43.7	33.7	60.6	75.5	61.8
H ₂ /CO Usage	1.10	1.31	1.47	.97	.84	1.08
STY (mols H ₂ + CO/g cat-h) ^a	.034	.039	.060	.054	.025	.021
$P_{CO_2} : P_{H_2} / P_{CO} : P_{H_2O}$	2.1	.4	.6	2.8	13.8	3.9
Weight % of Outlet						
H ₂	4.54	3.80	4.66	3.26	2.59	2.96
H ₂ O	4.91	14.1	7.46	7.25	4.64	4.50
CO	57.7	55.2	68.3	34.3	13.4	36.8
CO ₂	23.0	15.3	11.0	37.9	58.2	38.2
Hydrocarbons	5.41	7.46	6.18	12.1	15.1	12.2
Oxygenates	.55	1.67	.78	.67	.69	.59
Wax ^d	3.94	2.52	1.58	4.48	5.42	4.80
Yield (g/Nm ³ H ₂ + CO Converted)						
CH ₄	7.83	11.9	11.8	12.9	14.1	12.4
C ₂ C ₄ Hydrocarbons	32.9	54.2	53.8	54.2	52.8	51.4
C ₅ C ₁₁ Hydrocarbons	30.3	39.1	40.0	47.5	49.4	47.5
C ₁₂ + Hydrocarbons	87.8	43.8	37.8	54.8	52.5	56.7
Wax ^d	67.0	37.6	29.2	45.7	44.6	47.6
Oxygenates	9.26	24.9	14.5	6.86	5.65	5.87
Total	168	174	158	176	174	174
1 + 2 Olefins/n Paraffin Ratio						
C ₂	1.71	1.42	1.42	.95	.20	1.42
C ₃	5.26	5.72	5.69	5.77	3.57	5.83
C ₄	4.25	4.61	4.61	4.55	2.63	4.51
C ₅	3.65	2.36	2.42	2.11	.93	2.20
C ₁₀	4.13	2.33	2.16	1.33	.80	1.56

^a Based on unreacted catalyst^b Maximum axial temperature difference^c Based on effective bed volume^d Unanalyzed products collected from hot trap

Table 8 (cont'd). Summary of results for fixed bed run FB-99-3477, using standard reduction conditions.

Period	7	8
Date	12/21/87	12/22/87
Time on Stream (h)	183.0	206.0
Balance Duration (h)	6.0	6.5
Average Temperature (°C)	235	235
Maximum Δ Temperature (°C) ^b	1.0	3.0
Pressure (MPa)	1.48	2.96
H ₂ /CO Feed Ratio	1.10	1.10
Space Velocity (NL/g cat-h) ^a	2.00	3.94
Space Velocity (NL/g Fe-h)	3.57	7.04
GHSV (h ⁻¹) ^c	233	460
CO Conversion (%)	37.7	36.2
H ₂ + CO Conversion (%)	42.9	42.0
H ₂ /CO Usage	1.39	1.43
STY (mol% H ₂ + CO/g cat-h) ^a	0.38	0.74
$P_{CO_2} \cdot P_{H_2} / P_{CO} \cdot P_{H_2O}$	7	6
Weight % of Outlet		
H ₂	3.95	3.98
H ₂ O	8.39	8.71
CO	59.6	61.2
CO ₂	16.1	13.4
Hydrocarbons	8.40	7.63
Oxygenates	.77	.73
Wax ^d	2.72	4.41
Yield (g/Nm ³ H ₂ + CO Converted)		
CH ₄	11.3	8.36
C ₂ C ₄ Hydrocarbons	50.7	45.6
C ₅ C ₁₁ Hydrocarbons	48.7	46.4
C ₁₂ + Hydrocarbons	50.8	78.0
Wax ^d	39.6	65.3
Oxygenates	11.2	10.8
Total	173	189
1 + 2 Olefins/ π Paraffin Ratio		
C ₂	1.61	1.78
C ₃	5.91	4.40
C ₄	4.73	3.54
C ₅	2.65	2.55
C ₁₀	2.35	2.50

^a Based on unreacted catalyst

^b Maximum axial temperature difference

^c Based on effective bed volume

^d Unanalyzed products collected from hot trap

Table 8 (cont'd). Summary of results for fixed bed run PB-99-3477, using standard reduction conditions.

Period	1	2	3	4	5	6
Weight % of Hydrocarbons						
C ₁₁ H ₄	4.93	7.98	8.24	7.60	8.34	7.40
Ethane	2.88	5.08	5.46	5.02	7.73	3.80
Ethylene	4.60	6.75	7.22	4.46	1.42	5.02
Propane	1.14	2.04	2.03	1.84	2.75	1.82
Propylene	5.70	11.1	11.0	10.1	9.35	10.1
n-Butane	1.17	1.92	1.99	1.80	2.63	1.69
1+2 Butenes	4.79	8.53	8.86	7.90	6.67	7.37
C ₄ Isomers	.47	.92	.89	.81	.74	.77
n-Pentane	1.47	2.46	2.46	2.33	2.98	2.30
1+2 Pentenes	4.58	7.30	7.60	6.65	5.41	7.00
C ₅ Isomers	.29	.60	.60	.61	.89	.75
n-Hexane	1.07	1.45	1.27	.86	2.02	1.19
1+2 Hexenes	3.39	4.33	3.66	2.94	3.06	3.56
C ₆ Isomers	.61	.93	.86	.59	.60	.73
n-Heptane	.60	.89	.72	.64	1.67	.66
1+2 Heptenes	1.77	2.26	1.88	1.67	1.79	1.75
C ₇ Isomers	.36	.59	.54	.32	.36	.43
n-Octane	.22	.50	.53	.89	1.79	.75
1+2 Octenes	.80	1.16	1.27	1.85	1.64	1.62
C ₈ Isomers	.08	.24	.23	.24	.35	.35
n-Nonane	.12	.29	.48	1.13	1.69	.94
1+2 Nonenes	.85	.72	1.13	1.84	1.38	1.87
C ₉ Isomers	.07	.10	.17	.25	.34	.32
n-Decane	.24	.31	.64	1.18	1.09	.90
1+2 Decenes	.97	.72	1.35	1.55	.85	1.39
C ₁₀ Isomers	.10	.29	.32	.30	.25	.33
n-Undecane	.29	.28	.65	.98	.54	.65
1+2 Undecenes	1.01	.59	1.21	1.02	.46	.61
C ₁₁ Isomers	.15	.24	.33	.23	.12	.15
C ₁₂ C ₄	20.8	36.4	37.5	32.0	31.3	30.6
C ₅ C ₁₁	19.1	26.3	27.9	28.1	29.3	28.3
C ₁₂ I	55.3	29.4	26.4	32.4	31.1	33.8
Wax ^d	42.2	25.3	20.4	27.0	26.5	28.3

^d Unanalyzed products collected from hot trap

Table 8 (cont'd). Summary of results for fixed bed run FB-99-3477, using standard reduction conditions.

Period		7	8
Weight % of Hydrocarbons			
CH ₄			
Ethane		6.98	4.69
Ethylene		4.34	3.11
Propane		6.53	5.18
Propylene		1.67	1.74
<i>n</i> Butane		9.42	7.29
<i>i</i> Butane		1.57	1.71
<i>i</i> 2 Butenes		7.17	5.85
C ₄ Isomers		.71	.68
<i>n</i> Pentane		1.95	2.01
<i>i</i> 2 Pentenes		6.08	5.25
C ₅ Isomers		.45	.45
<i>n</i> Hexane		1.18	1.32
<i>i</i> 2 Hexenes		4.49	3.97
C ₆ Isomers		.87	.72
<i>n</i> Heptane		.87	.92
<i>i</i> 2 Heptenes		2.53	2.39
C ₇ Isomers		.55	.57
<i>n</i> Octane		.70	.60
<i>i</i> 2 Octenes		1.82	1.49
C ₈ Isomers		.32	.23
<i>n</i> Nonane		.61	.46
<i>i</i> 2 Nonenes		1.71	1.21
C ₉ Isomers		.33	.37
<i>n</i> Decane		.77	.51
<i>i</i> 2 Decenes		1.79	1.27
C ₁₀ Isomers		.51	.38
<i>n</i> Undecane		.76	.47
<i>i</i> 2 Undecenes		1.46	1.09
C ₁₁ Isomers		.38	.31
C ₁₂ C ₁₄		31.1	25.6
C ₁₅ C ₁₇		30.2	26.0
C ₁₈ C ₂₀		31.4	43.8
Wax ^d		24.5	36.6

^d Unanalyzed products collected from hot trap

Table 9. Comparison of Ruhrchemie LP 33/81 catalyst with 100Fe/3Cu/0.2K precipitated catalyst. Run

FA-99-3357: LP 33/81 using manufacturer's recommended reduction¹; Run FB-99-3477: LP 33/81 using standard CO reduction²; Run FA-25-2447³: 100Fe/3Cu/0.2K using standard CO reduction². 1.48 MPa, 2 NL/g-cat·h, (H₂/CO) = 1.

Run	FA-99-3357			FB-99-3477			FA-25-2447 ³		
T(°C)	220	235	250	220	235 ⁴	250	220	235	250
% (H ₂ +CO) Conversion	25.3	45.0	64.7	37.9	43.7	60.6	42.9	54.4	72.2
% CO Conversion	20.9	44.2	69.5	37.8	39.6	64.4	41.2	54.5	81.7
Weight % of Hydrocarbons									
CH ₄	8.85	6.73	7.88	4.93	7.98	7.60	4.31	7.80	10.3
C ₂ -C ₄	24.1	17.7	19.7	20.8	36.4	32.0	19.9	37.3	36.8
C ₅ -C ₁₁	21.0	19.8	25.9	19.1	26.3	28.1	20.2	29.6	32.8
C ₁₂ +	46.1	55.8	46.5	55.3	29.4	32.4	55.6	25.3	20.
(1+2)-olefins/n-paraffin									
C ₂	1.49	1.00	.56	1.71	1.42	.95	.84	1.06	.38
C ₃	3.82	4.10	4.10	5.26	5.72	5.77	4.39	5.04	3.61
C ₄	2.95	3.20	3.26	4.25	4.61	4.55	3.94	4.61	3.77
C ₈	2.02	2.88	1.58	3.65	2.36	2.11	1.86	2.57	1.79
C ₁₀	2.06	1.67	1.12	4.13	2.33	1.33	2.15	2.09	1.55

¹ H₂, 220 °C, 1 h, 60 NL/g-cat·h.

² CO, 280 °C, 8 h, 3 NL/g-cat·h.

³ Reported in the Technical Progress Report for the period 1 July - 30 September 1987.

⁴ Balance 2 results.

Table 10. Comparison of Ruhrchemie LP 33/81 catalyst with United Catalyst, Inc. C-73 fused iron.

Run FA-99-3357: LP 33/81 using manufacturer's recommended reduction¹; Run FB-99-3477: LP

33/81 using standard CO reduction²; Run FA-01-1537: UCI C-73 using H₂ reduction³. 1.48

MPa, 0.75 NQ/g-cat·h, (H₂/CO) = 1.

Run	FA-99-3357			FB-99-3477		FA-25-2447 ³		
T (°C)	235 ⁴	250	265	235	250	235	250	265
% (H ₂ +CO) Conversion	53.7	77.6	81.1	61.8	75.5	52.2	77.4	86.3
% CO Conversion	52.5	90.4	95.6	62.2	86.1	60.4	90.7	97.9
Weight % of Hydrocarbons								
CH ₄	6.51	11.0	13.5	7.40	8.34	8.99	11.1	11.2
C ₂ -C ₄	21.9	27.9	29.4	30.6	31.3	40.5	36.6	34.4
C ₅ +	71.6	61.1	57.2	62.1	60.4	50.5	52.3	54.4
(1+2)-olefins/n-paraffin								
C ₂	1.13	.26	.14	1.42	.20	1.52	0.89	0.92
C ₃	4.83	3.15	2.53	5.83	3.57	4.32	4.57	5.21
C ₄	3.78	2.56	2.20	4.51	2.63	3.55	3.99	4.63
C ₈	2.24	.99	.82	2.20	.93	4.25	3.29	3.19
C ₁₀	2.34	.68	.58	1.56	.80	2.71	2.49	2.66

¹ H₂, 220 °C, 1 h, 60 NQ/g-cat·h.

² CO, 280 °C, 8 h, 3 NQ/g-cat·h.

³ Reported in the Technical Progress Report for the period 1 April - 30 June 1987.

⁴ Data obtained after partial catalyst deactivation.

Table 11. Summary of results for slurry run SA-05-2957.

Catalyst: 25.9 g^a, 100 Fe/0.3 Cu/0.2 K

Slurry liquid: 295 g, PTF-300

Reactor volume: 442 cc^b

Period	1	2	3	4	5	6
Date	10/26/87	10/27/87	10/29/87	10/30/87	10/31/87	11/01/87
Time on Stream (h)	33.0	56.5	106.0	129.0	153.0	177.0
Balance Duration (h)	6.0	6.0	6.0	6.0	6.0	6.0
Average Temperature (°C)	220	235	250	250	250	264
Pressure (MPa)	1.48	1.48	1.48	1.48	1.48	1.48
H ₂ /CO Feed Ratio	1.02	1.02	1.02	1.02	1.02	1.02
Space Velocity (NL/g cat·h) ^a	2.00	2.00	2.00	4.00	1.01	2.00
Space Velocity (NL/g Fe·h)	2.87	2.87	2.87	5.75	1.45	2.87
Space Velocity (h ⁻¹) ^b	117	117	117	234	59	117
CO Conversion (%)	18.4	37.1	66.9	46.0	87.0	85.9
H ₂ + CO Conversion (%)	22.4	36.2	55.6	40.9	68.8	70.3
H ₂ /CO Usage	1.45	.97	.68	.79	.60	.65
STY (mols H ₂ + CO/g cat·h) ^a	.020	.032	.050	.073	.031	.063
P _{CO₂} · P _{H₂} / P _{CO} · P _{H₂O}	.9	2.0	5.0	6.0	45.9	37.9
Weight % of Outlet						
H ₂	5.06	4.44	3.68	4.38	3.29	3.03
H ₂ O	3.51	4.58	6.00	2.63	2.17	2.19
CO	76.2	58.8	29.8	50.1	11.9	12.9
CO ₂	8.80	21.2	42.6	31.5	63.5	62.2
Hydrocarbons	2.72	6.63	17.3	7.09	18.5	18.3
Oxygenates	.30	.31	.57	.21	.38	.32
Wax ^c	3.36	4.01	.00	4.08	.30	1.02
Yield (g/Nm ³ H ₂ + CO Converted)						
CH ₄	8.82	8.03	12.1	7.84	22.3	22.5
C ₂ C ₄ Hydrocarbons	31.8	27.4	39.4	28.8	57.8	58.0
C ₅ C ₁₁ Hydrocarbons	33.4	50.5	79.3	45.2	69.9	60.9
C ₁₂ + Hydrocarbons	103	109	83.0	100	35.1	45.1
Wax ^c	99.3	73.3	.0	66.5	2.97	9.85
Oxygenates	8.95	5.63	6.99	3.49	3.75	3.06
Total	189	200	221	185	189	190
1 + 2 Olefins/ ^a Paraffin Ratio						
C ₂	1.54	2.55	.87	2.78	.26	.24
C ₃	4.80	5.10	4.04	4.93	2.20	2.39
C ₄	4.10	4.33	3.28	3.83	2.17	2.44
C ₅	2.38	3.18	2.03	2.14	1.00	.98
C ₁₀	1.58	3.51	1.12	2.11	.95	.87

^a Based on unreduced catalyst^b Based on static slurry volume^c Calculated wax produced during balance

Table 11 (cont'd). Summary of results for slurry run SA-05-2957.

Period	7	8	9	10	11	12
Date	11/02/87	11/04/87	11/05/87	11/06/87	11/07/87	11/08/87
Time on Stream (h)	201.0	248.5	272.5	297.0	321.0	345.0
Balance Duration (h)	6.0	6.0	6.0	6.0	6.0	6.0
Average Temperature ($^{\circ}\text{C}$)	250	220	235	250	250	250
Pressure (MPa)	.79	1.48	1.48	1.48	1.48	1.48
H_2/CO Feed Ratio	1.02	.67	.69	.71	.72	.65
Space Velocity ($\text{NL/g cat}\cdot\text{h}$) ^a	1.05	2.00	2.11	2.03	4.07	1.02
GHSV (h^{-1}) ^b	62	117	117	113	225	56
CO Conversion (%)	79.0	21.3	42.8	76.2	50.2	73.0
H_2/CO Conversion (%)	61.1	20.5	40.6	70.2	49.4	80.8
H_2/CO Usage	.56	.60	.61	.58	.69	.83
STY ($\text{mols H}_2/\text{CO/g cat}\cdot\text{h}$) ^a	.029	.018	.038	.064	.090	.037
$P_{\text{CO}_2} \cdot P_{\text{H}_2}/P_{\text{CO}} \cdot P_{\text{H}_2\text{O}}$	45.6	3.5	5.6	18.8	9.7	5.2
Weight % of Outlet						
H_2	3.81	3.79	2.97	1.86	2.49	.33
H_2O	1.38	1.03	1.69	1.37	1.15	.80
CO	19.4	77.08	54.4	22.7	46.5	25.8
CO_2	56.1	12.7	30.2	55.1	36.5	57.7
Hydrocarbons	16.4	2.24	3.59	11.5	4.20	9.19
Oxygenates	.18	.05	.22	.19	.14	.15
Wax ^c	2.68	3.18	6.85	7.26	9.06	6.03
Yield ($\text{g/Nm}^3 \text{ H}_2 + \text{CO Converted}$)						
C_{11}	23.1	2.93	3.25	4.90	3.31	3.38
$\text{C}_2\text{-C}_4$ Hydrocarbons	55.7	14.6	14.4	18.5	13.4	20.7
$\text{C}_5\text{-C}_{11}$ Hydrocarbons	12.0	27.2	23.8	42.3	25.0	37.3
$\text{C}_{12} + \text{Hydrocarbons}$	68.5	158	158	140	168	87.7
Wax ^c	29.2	119	131	79.4	143	59.1
Oxygenates	1.95	1.95	4.18	2.10	2.26	1.47
Total	211	205	203	207	211	151
$\text{H}_2/\text{C}_{12}\text{-fins}/n$ Paraffin Ratio						
C_2	.26	1.16	2.66	1.64	3.36	1.14
C_3	2.26	4.16	4.89	5.59	5.95	5.76
C_4	2.46	3.20	3.77	4.47	4.46	4.63
C_5	.63	2.08	2.29	2.78	2.39	2.51
C_{10}	.62	1.29	2.70	2.43	2.43	2.38

^a Based on unreduced catalyst^b Calculated wax produced during balance^c Based on static slurry volume

Table 11 (cont'd). Summary of results for slurry run SA-05-2957.

Period	13	14	15	16	17	18
Date	11/10/87	11/11/87	11/12/87	11/14/87	11/15/87	11/16/87
Time on Stream (h)	393.0	115.5	445.0	494.0	517.0	541.0
Balance Duration (h)	6.0	6.0	6.0	6.0	6.0	6.0
Average Temperature (°C)	265	250	250	250	250	250
Pressure (MPa)	1.48	.79	1.18	1.48	2.24	2.96
H ₂ /CO Feed Ratio	.71	.67	.68	1.06	1.03	1.03
Space Velocity (NI/g cat·h) ^a	2.24	1.12	1.00	2.00	3.00	4.00
GLSV (h ⁻¹) ^b	113	56	50	100	151	201
CO Conversion (%)	83.6	57.9	84.7	82.0	80.8	78.8
H ₂ +CO Conversion (%)	76.8	58.9	84.7	67.1	68.8	66.1
H ₂ /CO Usage	.57	.70	.68	.69	.72	.70
STY (mols H ₂ +CO/g-cat·h) ^a	.077	.029	.038	.060	.092	.118
P _{CO} : P _{H₂} : P _{CO} : P _{H₂O}	23.5	25.2	94.6	63.0	27.2	17.1
Weight % of Outlet						
H ₂	1.64	1.77	.73	3.37	3.08	3.37
H ₂ O	1.59	.43	.18	1.07	1.96	2.94
CO	16.1	39.5	15.0	16.9	18.6	21.0
CO ₂	64.5	42.8	59.7	59.6	56.7	55.0
Hydrocarbons	15.4	7.87	13.3	18.7	16.5	15.2
Oxygenates	.25	.07	.12	.36	.46	.76
Wax ^c	.45	7.58	10.9	0.0	2.67	1.77
1:2 Olefins/n Paraffin Ratio						
C ₂	.35	.97	.57	.23	.30	.51
C ₃	3.38	5.53	4.34	2.26	2.52	2.81
C ₄	3.04	4.28	3.63	2.07	2.25	2.29
C ₈	1.34	1.72	1.74	.70	.70	1.23
C ₁₀	1.00	1.25	1.25	.55	.67	.88
Yield (g/Nm ³ H ₂ + CO Converted)						
CH ₄	16.8	11.5	8.36	22.3	16.5	12.6
C ₂ C ₄ Hydrocarbons	41.9	33.7	23.9	54.6	45.0	37.3
C ₃ C ₁₁ Hydrocarbons	62.1	43.9	53.8	69.4	59.2	61.3
C ₁₂ + Hydrocarbons	30.3	121	132	33.4	57.0	49.3
Wax ^c	4.36	103	98.1	0.0	24.7	16.7
Oxygenates	2.39	.94	1.12	3.50	4.23	7.15
Total	157	211	219	183	182	168

^a Based on unreduced catalyst

^b Based on static slurry volume

^c Calculated wax produced during balance

Table 11 (cont'd). Summary of results for slurry run SA-05-2957.

Period	1	2	3	4	5	6
Weight % of Hydrocarbons						
CH ₄	4.91	4.12	5.66	4.31	12.0	12.1
Ethane	2.93	1.22	2.54	1.11	6.74	6.51
Ethylene	4.21	2.90	2.05	2.89	1.66	1.48
Propane	1.12	.84	1.44	1.03	3.85	3.63
Propylene	5.13	4.32	5.56	4.85	8.09	8.28
n-Butane	1.10	.85	1.54	1.18	3.29	3.13
1+2 Butenes	4.34	3.53	4.87	4.37	6.90	7.36
C ₄ Isomers	.52	.41	.41	.39	.71	.67
n-Pentane	1.53	1.13	1.91	1.56	3.50	3.37
1+2 Pentenes	4.44	5.69	5.20	4.32	7.44	6.49
C ₅ Isomers	.48	.31	.64	.29	2.30	2.03
n-Hexane	1.39	.98	1.25	1.11	2.85	2.11
1+2 Hexenes	3.51	2.61	3.15	3.17	3.06	2.76
C ₆ Isomers	.00	1.43	.68	.59	.60	.44
n-Heptane	1.22	.90	.85	.79	1.92	1.61
1+2 Heptenes	2.36	1.80	1.85	2.33	1.87	1.67
C ₇ Isomers	.04	.95	.38	.49	.54	.39
n-Octane	.55	.41	.63	.81	1.69	1.47
1+2 Octenes	1.29	1.29	1.26	1.70	1.65	1.42
C ₈ Isomers	.05	.21	.24	.32	.46	.20
n-Nonane	.19	.36	1.89	.51	1.51	1.36
1+2 Nonenes	.36	1.55	2.32	1.25	1.45	1.25
C ₉ Isomers	.07	.09	.18	.12	.52	.23
n-Decane	.19	.62	3.09	.77	1.49	1.45
1+2 Decenes	.30	2.13	3.41	1.60	1.40	1.24
C ₁₀ Isomers	.08	.12	.22	.22	.41	.27
n-Undecane	.19	.82	3.75	.91	1.41	1.47
1+2 Undecenes	.24	2.38	3.77	1.70	1.28	1.14
C ₁₁ Isomers	.09	.16	.42	.28	.44	.29
C ₂ -C ₄	19.4	14.1	18.4	15.8	31.2	31.1
C ₅ -C ₁₁	18.6	26.0	37.1	24.9	37.8	32.7
C ₁₂ +	57.2	55.9	38.8	55.0	19.0	24.2
Wax ^c	55.2	37.7	.00	36.5	1.61	5.28

^c Calculated wax produced during balance

Table 11 (cont'd). Summary of results for slurry run SA-05-2957.

Period	7	8	9	10	11	12
Weight % of Hydrocarbons						
CH ₄	11.1	1.44	1.63	2.39	1.58	2.26
Ethane	5.81	1.22	.70	1.06	.41	2.55
Ethylene	1.42	1.67	1.75	1.61	1.30	2.71
Propane	3.15	.44	.43	.52	.36	.68
Propylene	6.79	1.74	2.02	2.79	2.04	3.74
n Butane	2.68	.47	.46	.53	.40	.72
1+2 Butenes	6.37	1.46	1.68	2.27	1.72	3.21
C ₄ Isomers	.48	.17	.17	.22	.16	.29
n-Pentane	3.02	.64	.63	.69	.57	.96
1+2 Pentenes	4.41	2.60	1.66	2.68	1.71	2.80
C ₅ Isomers	1.63	.12	.12	.32	.10	.22
n Hexane	3.05	.84	.93	.65	.54	1.24
1+2 Hexenes	2.65	1.98	1.81	1.56	1.51	3.11
C ₆ Isomers	.52	.67	.77	.25	.29	.51
n Heptane	2.03	.75	.60	.69	.54	1.57
1+2 Heptenes	1.30	1.74	1.22	1.50	1.25	3.78
C ₇ Isomers	.34	.50	.34	.28	.27	.68
n-Octane	1.53	.39	.33	.73	.42	.81
1+2 Octenes	.95	.79	.75	1.98	.99	1.99
C ₈ Isomers	.12	.04	.16	.27	.13	.28
n Nonane	1.41	.19	.17	.74	.30	.54
1+2 Nonenes	.88	.23	.49	1.91	.77	1.30
C ₉ Isomers	.08	.05	.07	.22	.09	.20
n-Decane	1.61	.33	.22	.82	.33	.61
1+2 Decenes	.99	.42	.59	1.97	.79	1.44
C ₁₀ Isomers	.13	.08	.11	.23	.09	.25
n-Undecane	1.68	.40	.26	.91	.37	.68
1+2 Undecenes	.94	.52	.65	1.95	.79	1.64
C ₁₁ Isomers	.16	.12	.08	.25	.10	.36
C ₁₂ C ₁	26.7	7.17	7.22	9.00	6.38	13.9
C ₅ C ₁₁	29.4	13.4	12.0	20.6	11.9	25.0
C ₁₂ I	32.8	78.0	79.3	68.0	80.1	58.9
Wax ^c	14.0	58.7	65.6	38.7	68.3	39.6

^c Calculated wax produced during balance

Table 11 (cont'd). Summary of results for slurry run SA-05-2957.

Period		13	14	15	16	17	18
Weight % of Hydrocarbons							
CH ₄		10.9	5.46	3.84	12.4	9.28	7.88
Ethane		6.01	2.65	1.78	6.92	5.45	4.22
Ethylene		1.96	2.39	.94	1.50	1.54	2.02
Propane		2.56	.88	.81	3.65	2.89	2.41
Propylene		8.26	4.66	3.37	7.87	6.97	6.47
n-Butane		2.47	1.02	.86	3.26	2.50	2.35
1+2 Butenes		7.24	4.20	3.01	6.53	5.42	5.20
C ₄ Isomers		.56	.26	.18	.67	.57	.55
n-Pentane		2.86	1.36	1.00	3.47	2.62	2.46
1+2 Pentenes		5.93	4.22	2.87	6.11	5.04	5.21
C ₅ Isomers		.87	.30	.30	.63	.56	.59
n-Hexane		2.75	1.25	1.08	3.25	2.30	2.11
1+2 Hexenes		4.61	3.32	3.04	3.47	3.34	3.50
C ₆ Isomers		.69	.59	.78	.57	.44	.40
n-Heptane		1.84	.88	1.11	2.87	1.99	2.09
1+2 Heptenes		2.50	1.95	1.78	2.17	2.09	2.47
C ₇ Isomers		1.09	.42	.31	.47	.44	.60
n-Octane		1.73	.73	1.20	2.47	1.88	2.15
1+2 Octenes		2.28	1.23	2.04	1.71	1.29	2.60
C ₈ Isomers		.25	.22	.17	.25	.23	.38
n-Nonane		2.11	.55	1.23	2.29	1.99	2.13
1+2 Nonenes		2.33	.75	1.74	1.39	1.50	2.13
C ₉ Isomers		.16	.09	.19	.21	.14	.34
n-Decane		2.16	.65	1.30	2.41	2.18	2.30
1+2 Decenes		2.13	.80	1.61	1.32	1.43	1.99
C ₁₀ Isomers		.18	.11	.14	.18	.20	.35
n-Undecane		2.04	.68	1.28	2.24	2.16	2.34
1+2 Undecenes		1.73	.72	1.38	1.02	1.23	1.73
C ₁₁ Isomers		.16	.12	.15	.20	.25	.30
C ₇ C ₄		29.1	16.1	11.0	30.4	25.3	23.2
C ₅ C ₁₁		40.4	20.9	24.7	38.6	33.3	38.2
C ₁₂ l		19.6	57.6	60.5	18.6	32.1	30.7
Wax ^a		2.82	49.1	45.0	0.0	13.9	10.4

^a Calculated wax produced during balance

Figure 1. Comparison of activity and stability for CO reduction procedures, ($H_2 + CO$) conversion versus time at testing conditions.

Figure 2. Comparison of weight percent hydrocarbon distribution and selected (1+2)-olefins/n-paraffin ratios for the CO reduction procedures.

Figure 3. Effect of time on stream for CO reduction procedures on weight percent hydrocarbon distribution and selected (1-2)-olefins/n-paraffin ratios.

Figure 1. Comparison of activity and stability for ambient and high (1.48 MPa) pressure CO reductions, (H₂+CO) conversion versus time at testing conditions.

Figure 5. Comparison of weight percent hydrocarbon distribution and selected (1+2)-olefins/n-paraffin ratios for the ambient and high (1.48 MPa) pressure CO reductions.

Figure 6. Comparison of activity and stability for H₂ reduction procedures, (H₂+CO) conversion versus time at testing conditions.

Figure 7. Comparison of weight percent hydrocarbon distribution and selected (1-2)-olefins *n*-paraffin ratios for the H₂ reduction procedures.

Figure 8. Effect of time on stream for H_2 reduction procedures on the weight percent hydrocarbon distribution and selected (1-2)-olefins/n-paraffin ratios.

Figure 9. Comparison of activity and stability for H_2 and CO reductants, (H_2+CO) conversion versus time at testing conditions.

Figure 10. Comparison of weight percent hydrocarbon distribution and selected (1-2)-olefins *n*-paraffin ratios for the H₂ and CO reduction procedures.

Figure 11. Comparison of activity and stability for CO and (H₂+CO) = 0.68 reductions, (H₂+CO) conversion versus time at testing conditions.

Figure 12. Comparison of weight percent hydrocarbon distribution and selected (1+2)-olefins/*n*-paraffin ratios for H₂, (H₂/CO) = 0.68, and CO reduced catalyst.

Figure 13. $(H_2 + CO)$ conversion as a function of gas space velocity, $250^\circ C$, $1.48 MPa$, $(H_2/CO) = 0.67$ and 1.0 (nominal).

Figure 14. Space time yield as a function of pressure at constant P/SV , 250 °C, $(H_2/CO) = 0.67$ and 1.0 (nominal).

Figure 15. Effect of SiO₂ content on surface area of 100 Fe/5 Cu precipitate, following calcination for 5 h at 300 °C and subsequent reduction in CO for 5 h at 300 °C.

Figure 16. Pore volume distribution for 100 Fe/5 Cu/8 SiO₂ precipitate determined by mercury porosimetry, following calcination for 5 h at 300 °C and subsequent reduction in CO for 5 h at 300 °C.

Figure 17. Pore volume distribution for 100 Fe/5 Cu/25 SiO₂ precipitate determined by mercury porosimetry, following calcination for 5 h at 300 °C and subsequent reduction in CO for 5 h at 300 °C.

Figure 18. Pore volume distribution for 100 Fe/5 Cu/100 SiO₂ precipitate determined by mercury porosimetry, following calcination for 5 h at 300 °C and subsequent reduction in CO for 5 h at 300 °C.

Figure 19. Pore volume distribution for 100 Fe/3 Cu precipitate determined by mercury porosimetry, following calcination for 5 h at 300 °C and subsequent reduction in CO for 5 h at 300 °C.

Figure 20. Pore volume distribution for 100 Fe/3 Cu precipitate determined by mercury porosimetry, following calcination for 5 h at 300 °C and subsequent reduction in H₂ for 5 h at 300 °C.

Figure 21. XPS spectra of unpromoted 100 Fe precipitate in Fe 2p region. (a) following calcination for 5 h at 300 °C; (b) following subsequent exposure to H₂ for 5 h at 300 °C.

Figure 22. XPS spectra of unpromoted 100 Fe precipitate in Fe 2p region. (a) following calcination for 5 h at 300 °C and subsequent reduction in CO for 5 h at 300 °C; (b) following subsequent exposure to (H₂ : CO) = 2 mixture at 250 °C.

Figure 23. XPS spectra of 100 Fe/3 Cu/0.2 K precipitate in Fe 2p region. (a) untreated; (b) following calcination for 5 h at 300 °C.

Figure 24. XPS spectra of 100 Fe/3 Cu/0.2 K precipitate in K 2p and C 1s region. (a) untreated; (b) following calcination for 5 h at 300 °C.

Figure 25. XPS spectra of 100 Fe/3 Cu/0.2 K precipitate in Cu 2p region. (a) untreated; (b) following calcination for 5 h at 300 °C.

Figure 26. XPS spectra of 100 Fe/3 Cu/0.2 K precipitate in O 1s region. (a) untreated; (b) following calcination for 5 h at 300 °C.

Figure 27. XPS spectra of 100 Fe/3 Cu/0.2 K precipitate in Fe 2p region. (a) following reduction in CO for 5 h at 300 °C; (b) following subsequent exposure to (H₂/CO) = 2 mixture at 250 °C.

Figure 28. XPS spectra of 100 Fe/3 Cu/0.2 K precipitate in Cu 2p region. (a) following reduction in CO for 5 h at 300 °C; (b) following subsequent exposure to (H₂/CO) = 2 mixture at 250 °C.

Figure 29. XPS spectra of 100 Fe/3 Cu/0.2 K precipitate in K 2p and C 1s region. (a) following reduction in CO for 5 h at 300 °C; (b) following subsequent exposure to (H₂/CO) = 2 mixture at 250 °C.

Figure 30. XPS spectra of 100 Fe/3 Cu 0.2 K precipitate in O 1s region. (a) following reduction in CO for 5 h at 300 °C; (b) following subsequent exposure to (H₂/CO) = 2 mixture at 250 °C.

Figure 31. XPS spectra of 100 Fe/3 Cu/0.2 K precipitate in Fe 2p region. (a) following reduction in H_2 for 5 h at 300 °C; (b) following subsequent exposure to $(\text{H}_2 : \text{CO}) = 2$ mixture at 250 °C.

Figure 32. XPS spectra of 100 Fe-3 Cu-0.2 K precipitate in Cu 2p region. (a) following reduction in H_2 for 5 h at 300 °C; (b) following subsequent exposure to $(H_2 : CO) = 2$ mixture at 250 °C.

Figure 33. XPS spectra of 100 Fe 3 Cu 0.2 K precipitate in K 2p and C 1s region. (a) following reduction in H₂ for 5 h at 300 °C; (b) following subsequent exposure to (H₂:CO) = 2 mixture at 250 °C.

Figure 35. XPS spectra of 100 Fe 5 Cu 100 SiO₂ precipitate in Fe 2p region. (a) following reduction in H₂ for 5 h at 300 °C; (b) following subsequent exposure to (H₂ : CO) = 2 mixture at 250 °C.

Figure 34. XPS spectra of 100 Fe/3 Cu/0.2 K precipitate in O 1s region. (a) following reduction in H₂ for 5 h at 300 °C; (b) following subsequent exposure to (H₂/CO) = 2 mixture at 250 °C.

Figure 36. XPS spectra of 100 Fe/5 Cu/100 SiO₂ precipitate in Cu 2p region. (a) following reduction in H₂ for 5 h at 300 °C; (b) following subsequent exposure to (H₂/CO) = 2 mixture at 250 °C.

Figure 37. XPS spectra of 100 Fe/5 Cu/100 SiO₂ precipitate in K 2p and C 1s region. (a) following reduction in H₂ for 5 h at 300 °C; (b) following subsequent exposure to (H₂/CO) = 2 mixture at 250 °C.

Figure 38. XPS spectra of 100 Fe:5 Cu:100 SiO₂ precipitate in O 1s region. (a) following reduction in H₂ for 5 h at 300 °C; (b) following subsequent exposure to (H₂/CO) = 2 mixture at 250 °C.

Figure 39. XPS spectra of 100 Fe/5 Cu/100 SiO₂ precipitate in Si 2p region. (a) following reduction in H₂ for 5 h at 300 °C; (b) following subsequent exposure to (H₂/CO) = 2 mixture at 250 °C.

Figure 40. FT-IR spectra of adsorbed NO at 25 °C on calcined 25 wt % Fe, SiO_2 . (a) following reduction in H_2 for 16 h at 300 °C; (b) following reduction in CO for 16 h at 300 °C.

Figure 41. FT-IR spectra of adsorbed NO at 25 °C on calcined 25 wt % Fe/SiO₂ catalysts, following pre-adsorption of H₂ at 25 °C. (a) unpromoted; (b) containing 1 wt % Cu promoter; (c) containing 1 wt % K₂O promoter.

Figure 42. FT-IR spectra of adsorbed NO at 25 °C on calcined Fe-SiO₂. (a) 25 wt % Fe-SiO₂ containing 1 wt % Cu promoter, following reduction in (H₂-CO)=2 mixture for 16 h at 300 °C; (b) 25 wt % Fe-SiO₂, following reduction in CO for 16 h at 300 °C.

Appendix I. Preparation of Silica-supported Iron Catalysts

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