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Development of Improved Iron Fischer-Tropsch Catalysts

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I. EXECUTIVE SUMMARY

Two different pretreatment (reduction) procedures were employed in tests of catalyst with nominal composition 100 Fe/ 0.3 Cu/ 0.8 K in a fixed bed reactor, namely reduction with H_2 at 220°C for 1 h (Runs FA-2780 and FB-2800), and reduction with H_2 at 250°C for 2 h (Run FB-3480). After the reduction the catalyst was tested at 250°C, 200 psig, 2 (NL/ g-cat/ h), and H_2 :CO molar feed ratio of about 2:3. The (H_2 + CO) conversion was relatively low, about 33%, in tests FA-2780 and FB-2800 (reduction at 220°C), and it decreased slightly with time on stream. Results (catalyst activity and selectivity) were fairly reproducible in these two tests. Average hydrocarbon product distribution was: 5.8 (CH_4); 19.4 ($C_2 - C_4$), 29.3 ($C_5 - C_{11}$), and 45.5 wt% (C_{12}^+). The catalyst reduced at higher temperature had higher activity, (H_2 + CO) conversion of about 83%, but it produced significantly more low molecular weight hydrocarbons. The average hydrocarbon selectivity during Run FB-3480 was: 10.6 (CH_4); 30.6 ($C_2 - C_4$); 40.2 ($C_5 - C_{11}$) and 18.6 wt% (C_{12}^+).

Three of the silica containing iron catalysts with approximate composition 100 Fe/ 5 Cu/ 4.2 K/ x SiO_2 (where: x = 8, 16, or 40) were characterized by BET surface area, pore size distribution, and by atomic absorption spectroscopy. In addition, the catalyst containing 8 parts of SiO_2 per 100 parts of Fe was analyzed by X-ray powder diffraction (XRPD). Significant differences in the pore size distribution were observed between the catalyst containing 8 SiO_2 and the other two catalysts. Calcined sample of the 100 Fe/ 5 Cu/ 4.2 K/ 8 SiO_2 catalyst did not exhibit crystalline structure, whereas two samples of the same catalyst had developed crystalline phases after exposure to the synthesis gas. Identities of these phases have not been determined yet.

II. OBJECTIVE AND SCOPE OF WORK

The objective of proposed research is development of catalysts with enhanced slurry phase activity and better selectivity to fuel range products, through a more detailed understanding and systematic studies of the effects of pretreatment procedures and promoters/binders (silica) on catalyst performance. In order to accomplish this objective, the work shall be divided into several tasks which are described in the following subsections.

Task 1 – Project Management

Within 60 days of project initiation, the contractor shall prepare and submit to the DOE Project Manager a detailed project work plan covering the entire period of performance of the project. The plan shall present, in detail, all activities that will be performed to successfully complete proposed research and its shall consist of the following: (1) detailed description of the methods and technical approach that shall be used to achieve the objectives of this project; (2) a detailed project schedule for each task or other logical segment of work to be performed; (3) graphs reflecting cumulative estimated costs and person-hours expended by month for each task or other logical segment of work, and for the total project effort; (4) a project work chart showing the key personnel/groups planned to work on each task and percentage of their time devoted to the tasks; and (5) a Work Breakdown Structure (WBS) dictionary to establish the framework for contract execution and to report cost schedule and technical performance.

All project status, milestone schedule, and cost management reports, as well as topical reports, if any, shall be submitted in accordance with the DOE reporting requirements.

Task 2 – Catalyst Pretreatment Research

This task is aimed at developing optimal pretreatment conditions for precipitated unsupported (1 catalyst) and supported (or silica containing; 1-2) iron catalyst, and at providing a better understanding of the role of pretreatment on subsequent catalyst activity, selectivity and longevity during Fischer-Tropsch (F-T) synthesis. This shall be accomplished by examining the effect of various activation conditions on physical and chemical properties of the catalyst as well as on catalytic behavior in fixed and slurry bed reactors. Parameters such as type of reductant (H_2 vs. CO vs. syngas), reductant flow rate, temperature and duration shall be studied. Selected catalysts shall be extensively characterized using a variety of physical, chemical and instrumental techniques with the objective to establish correlations between the physical/chemical properties of the catalysts and their observed catalytic behavior during F-T synthesis.

Task 3 – Improved Iron/Silica Catalysts

The objective of this task is to determine optimal concentrations of silica and K_2O in a catalyst with composition $100 Fe/ x Cu/ y K_2O/ z SiO_2$ (in parts per weight). The effect of SiO_2 and K_2O on catalytic activity, selectivity and stability shall be determined to arrive at promoter/binder concentrations for an improved catalyst performance. The screening tests shall be conducted in fixed bed reactors to obtain preliminary indication of F-T activity and selectivity at different process conditions. Catalysts which show enhanced activity and/or selectivity towards transportation fuels shall be tested in slurry reactors up to 30 days on stream. Selected catalysts shall be extensively characterized, to determine relations between the physico-chemical properties of catalyst and their catalytic behavior during F-T synthesis.

III. DETAILED DESCRIPTION OF TECHNICAL PROGRESS

III-1. Task 2. Catalyst Pretreatment Research

Three fixed bed reactor tests were conducted with a precipitated iron catalyst with nominal composition 100 Fe/ 0.3 Cu/ 0.8 K to investigate effects of pretreatment conditions on catalyst activity and stability. Only two different pretreatment procedures were employed, since the same pretreatment conditions were used in two of the three tests. Results from these three tests are described in detail in subsections III-1.1 through III-1.3.

III-1.1 Run FA-2780 with 100Fe/0.3Cu/0.8K Catalyst

Before reduction the catalyst was inadvertently exposed to 200 - 240°C, with no gas flow through the bed, for a period of about 20 h. Following this the catalyst was reduced in-situ with hydrogen at 220°C for 1 h at superficial gas velocity of 1.5 m/s. Throughout the test average reaction temperature, pressure, gas space velocity and H₂/CO feed ratio were maintained at 250°C, 200 psig, 2 NI/g-cat/h, and 0.69, respectively. The run was terminated voluntarily after 120 h on stream, and no operational problems were encountered during this period. The results from two mass balances are summarized in Table 1.

Catalyst Activity and Stability

Catalyst activity, measured by volumetric gas contraction and (H₂ + CO) conversion, decreased somewhat with time on stream (Figs. 1 and 2). The water gas shift (WGS) activity of the catalyst was high, and H₂ to CO usage ratio was less than the feed ratio throughout the test.

Hydrocarbon Selectivity

The average hydrocarbon product distribution (from two mass balances in Table 1) was: 5.4 (CH₄); 21.2 (C₂ - C₄); 26.3 (C₅-C₁₁), and 47.1 wt% (C₁₂+).

III-1.2 Run FB-2800 with 100Fe/0.3Cu/0.8K Catalyst

In this test the same pretreatment and process conditions were employed as in Run FA-2780. The purpose of the test was to check whether inadvertent exposure of catalyst to temperature of 200-240°C, prior to reduction, in the previous test had any adverse effect on the catalyst performance. This test was terminated voluntarily after 175 h on stream. Results from three mass balances are summarized in Table 2.

Catalyst Activity and Stability

After initial increase in catalyst activity (30-50 h on stream), the activity decreased with time on stream as shown in Figures 3 and 4. The ($H_2 + CO$) conversions in balances 1 and 2 (67 and 124 h) were similar to those obtained in Run FA-2780 in mass balances 1 and 2 at 68 and 114 h on stream, respectively. The usage ratio in this test was between 0.70 and 0.81, whereas values of the usage ratio were between 0.58 and 0.70 in Run FA-2780. Overall, the catalyst activity was similar in both tests, but somewhat faster deactivation was observed in the Run FB-2800.

Hydrocarbon Selectivity

Hydrocarbon distribution in the first mass balance was markedly different than in the other two balances (See Table 2). In particular, (C_5-C_{11}) fraction in balance 1 was markedly lower, whereas $C_{12}+$ fraction was markedly higher than in the other two balances, which may be due to errors in product collection. The hydrocarbon distribution from balances 2 and 3 was: 6.2 (CH_4); 17.6 (C_2-C_4), 32.3 (C_5-C_{11}) and 43.9 wt% ($C_{12}+$). This is similar to the distribution obtained in the Run FA-2780.

In summary, reproducibility of results from two tests (FA-2780 and FB-2800) was fairly good, and it may be concluded that inadvertent exposure of the catalyst to elevated temperature in Run FA-2780 did not have marked effect on its performance.

III-1.3 Run FB-3480 with 100Fe/0.3Cu/0.8K Catalyst

In this test the catalyst was reduced in-situ with hydrogen at 250°C and superficial gas velocity of 1.5 m/s for 2 h. The use of higher reduction temperature and longer duration, in comparison to Runs FA-2790 and FB-2800, is expected to enhance reduction of iron and result in higher activity. The test was terminated after 200 h on stream, and the catalyst was tested at: 250°C, 200 psig, 2 NI/ g-cat/ h and $H_2/CO = 0.65$. Results from three mass balances are summarized in Table 3.

Catalyst Activity and Stability

The activity of the catalyst was high (volumetric contraction about 50%, and $(H_2 + CO)$ conversion ca. 83%), and it increased slightly during the test. The WGS activity was also high, and the usage ratio was about 0.60.

Hydrocarbon Selectivity

Hydrocarbon distribution was fairly stable in all three mass balances (Table 3), and average values for methane and lumped hydrocarbons were: 10.6 (CH_4); 30.6 (C_2-C_4), 40.2 (C_5-C_{11}) and 18.6 wt% ($C_{12}+$).

In summary, the catalyst reduced with H_2 at 250°C for 2 h (Run FB-3480) had markedly higher activity and methane selectivity, than the catalyst reduced at 220°C for 1 h (Runs FA-2780 and FB-2800).

III-2. Task 3. Improved Iron/Silica Catalysts

III-2.1 Catalyst Characterization

Some of precipitated iron catalysts containing silica as a binder have been characterized by BET surface area (SA), pore size distribution (PSD), atomic absorption spectroscopy (AA), and X-ray powder diffraction (XRPD). Results are described in the following subsections. Also, several

samples of used catalysts have been submitted to University of Kentucky for characterization by Mössbauer spectroscopy, but no results have been received yet.

Surface Area and Pore Size Distribution

Three silica containing catalyst with nominal compositions 100 Fe/ 5 Cu/ 4.2 K/ 8 SiO₂ (two preparations) and 100 Fe/ 5 Cu/ 4.2 K/ 16 SiO₂ were analyzed by AA (bulk phase composition) and BET surface area and pore size distribution. Results of these measurements are summarized in Table 4.

The actual composition, as determined by AA, was close to the expected (nominal) composition for two of the three catalysts. However, the AA analysis of the second catalyst with nominal composition 100 Fe/ 5 Cu/ 4.2 K/ 8 SiO₂, had revealed that the catalyst contains about five times more silica than the intended amount. Both of the catalysts with intended composition 100 Fe/ 5 Cu/ 4.2 K/ 8 SiO₂, were synthesized by Chemistry Department at TAMU during the previous DOE Contract (DE-AC22-85 PC 80011). In view of this we plan to verify the actual composition of the first batch of the catalyst containing 8 g of SiO₂ per 100 g of Fe (intended composition). The catalyst with nominal composition 100 Fe/ 5 Cu/ 4.2 K/ 16 SiO₂ was synthesized in our laboratory during the current DOE contract, and its composition determined by AA spectroscopy is close to the intended one. Results of AA analysis made in our Laboratory, are in good agreement with those obtained at Sandia National Laboratory.

Surface areas of catalysts before and after calcination in air at 300°C for 5 h, were not affected by differences in the amount of silica present in the catalyst (8-40 g of SiO₂ per 100 g of Fe). Loss in surface area upon calcination was relatively small (10 to 20%) for all three catalyst. The total pore volume of the catalyst containing 8 parts of SiO₂ (0.4 cc/g), was significantly smaller than that of the other two catalysts, (0.78 cc/g for the catalyst containing 40 parts of SiO₂, and 0.71 cc/g for the catalyst containing 18 parts of SiO₂).

Physical properties of the catalyst containing 8 SiO₂, were markedly different than those of

the catalysts containing larger amounts of SiO_2 , as shown in Figures 7-9. Complete adsorption/desorption isotherms for the three catalysts (after calcination) are shown in Fig. 7. All three materials exhibited desorption hysteresis. The latter was more pronounced with the catalyst containing 8 SiO_2 / 100 Fe, whereas the isotherms for the other two catalysts had a similar shape. The shape of isotherms for the catalysts containing 18 and 40 SiO_2 , is indicative of cylindrical pores with nearly constant cross sectional area.

Pore size distribution was obtained by application of the Kelvin equation to the desorption branch of the isotherm, and results are shown in Fig. 8 (differential pore volume vs. average pore diameter). The catalyst containing 8 SiO_2 exhibits a bimodal distribution, with a principal maximum at about 60 Å and the second one at about 18 Å. About 75% of all pore volume (see Fig. 9a) and 90% of all surface area comes from pores with the average pore diameter less than 100 Å. The catalysts containing 40 and 16 SiO_2 have broader PSD as shown in Figs. 8b, 9b and 8c, 9c, respectively. Both catalysts exhibit two maxima in their differential pore volume distribution, one at about 20 Å, and the second one at 200 Å (40 SiO_2) or at 30 Å (16 SiO_2). The fraction of pores smaller than 100 Å is much smaller in these two catalysts, than in the catalyst containing 8 SiO_2 . The fractions of total pore volume and surface area which may be attributed to pores smaller than 100 Å are: 20% and 60%, respectively for the catalyst containing 40 SiO_2 ; whereas for the catalyst containing 18 SiO_2 they are 30% and 65%, respectively.

As stated earlier calcination in air, at 300°C for 5 h, had a small effect on the total surface area and the pore volume for all three catalysts (Table 1). The effect of calcination on PSD was also rather small as shown in Fig. 10 for the catalyst containing 18 SiO_2 .

Preliminary X-Ray Powder Diffraction (XRPD) Analysis Results

X-ray patterns of the 100 Fe/ 5 Cu/ 4.2 K/ 8 SiO_2 catalyst, after calcination, and of two used catalyst samples at the end of fixed bed reactor runs FA-3448 and FA-0418 are shown in Figure 11. The calcined sample gave no discernible diffraction peaks (Fig. 11a), indicating that

the material was either amorphous or had micro-crystalline structure (crystallites less than 40 Å). On the other hand, the two used catalyst samples had discernible diffraction peaks (Figs. 11b and 11c). The identity of crystalline phases is not known at this point. We plan to analyze these data and report results in future reports.

III-3. Other Activities

We have experienced problems with three of our gas chromatographs during the reporting period. Two Carle 400 AGC series chromatographs, used for off-line analysis of gaseous products (C_1 - C_5 hydrocarbons, CO, CO_2 and H_2) were not working properly. After considerable troubleshooting, including consultations with the manufacturer, we replaced hydrogen transfer tube in the older GC and it has worked satisfactorily since then. The new Carle GC (purchased in August of 1990) was sent to manufacturer for repair under the warranty in November. We were notified that the GC had been repaired late in December, and expect to receive it in early part of January.

Also, the Perkin-Elmer Sigma 1 gas chromatograph used for organic phase product analysis (C_5 - C_{30} hydrocarbons, and C_3 - C_{11} oxygenates) was not performing well. A new capillary column was installed, and carrier flow rates were adjusted, but separation of n-alkanes and 1- and 2-alkenes needs to be improved. We plan to continue working on this problem as the time permits. This GC is very old and has been used heavily, and we'll investigate possibility of using one of our Varian 3400 GC series chromatographs for the organic phase analysis.

Table 1. Summary of results for fixed bed run FA-2780 .

Catalyst: 3.50 g^a, 100Fe/0.3Cu/0.8K
 Catalyst volume: 3.11 cc
 Diluent: 35.04 g, Glass beads
 Diluent Volume: 24.00 cc

Period	1	2
Date	10/09/90	10/11/90
Time on Stream (h)	68.0	114.0
Balance Duration (h)	12.0	12.0
Average Temperature (°C)	250.	250.
Maximum Δ Temperature (°C) ^b	7.00	5.00
Pressure (MPa)	1.48	1.48
H ₂ /CO Feed Ratio	.686	.686
Space Velocity (Nl/g-cat·h) ^c	2.01	2.01
Space Velocity (Nl/g-Fe·h)	2.91	2.91
GHSV (h ⁻¹) ^c	259.	259.
CO Conversion (%)	37.1	34.1
H ₂ +CO Conversion (%)	36.1	32.0
H ₂ /CO Usage	.640	.583
STY (mols H ₂ +CO/g-cat·h) ^a	.032	.029
P _{CO₂} · P _{H₂} /P _{CO} · P _{H₂O}	10.7	11.3
Weight % of Outlet		
H ₂	3.14	3.44
H ₂ O	.723	.618
CO	61.1	64.6
CO ₂	26.5	23.0
Hydrocarbons	4.21	4.59
Oxygenates	.406	.578
Wax ^d	3.91	3.19
Yield (g/Nm ³ H ₂ + CO Converted)		
CH ₄	9.37	9.89
C ₂ -C ₄ Hydrocarbons	36.2	39.1
C ₅ -C ₁₁ Hydrocarbons	39.1	54.6
C ₁₂ + Hydrocarbons	87.1	79.8
Wax ^d	82.6	75.2
Oxygenates	8.60	13.6
Total	180.	197.
1+2 Olefins/n-Paraffin Ratio		
C ₂	3.10	2.79
C ₃	6.29	6.18
C ₄	5.65	5.56
C ₅	3.07	3.54
C ₁₀	.988	2.58

^a Based on unreduced catalyst

^c Based on reactor volume

^b Maximum axial temperature difference

^d Unanalyzed products collected from hot trap

Table 1 (cont'd). Summary of results for fixed bed run FA-2780 .

Weight % of Hydrocarbons	Period	
	1	2
CH ₄	5.46	5.40
Ethane	1.42	1.58
Ethylene	4.11	4.12
Propane	1.18	1.23
Propylene	7.09	7.28
n-Butane	1.11	1.10
1+2 Butenes	6.05	5.90
C ₄ Isomers	.107	.126
n-Pentane	.0962	1.18
1+2 Pentenes	.329	4.19
C ₅ Isomers	2.94	3.26
n-Hexane	.696	.776
1+2 Hexenes	2.82	2.97
C ₆ Isomers	1.23	1.37
n-Heptane	.519	.627
1+2 Heptenes	2.04	2.55
C ₇ Isomers	.781	.663
n-Octane	.534	.656
1+2 Octenes	1.61	2.28
C ₈ Isomers	.916	.774
n-Nonane	.734	.633
1+2 Nonenes	1.81	2.28
C ₉ Isomers	.923	.140
n-Decane	1.00	.933
1+2 Decenes	.976	2.37
C ₁₀ Isomers	.614	.197
n-Undecane	.843	.344
1+2 Undecenes	.912	1.33
C ₁₁ Isomers	.441	.230
C ₂ -C ₄	21.1	21.3
C ₅ -C ₁₁	22.8	29.8
C ₁₂ +	50.7	43.5
Wax ^d	48.1	41.0

^d Unanalyzed products collected from hot trap

Table 2. Summary of results for fixed bed run FB-2800 .

Catalyst: 3.50 g^a, 100Fe/0.3Cu/0.8K
 Catalyst volume: 3.20 cc
 Diluent: 36.00 g, Glass beads
 Diluent Volume: 25.00 cc

Period	1	2	3
Date	10/26/90	10/29/90	10/30/90
Time on Stream (h)	67.0	124.0	159.0
Balance Duration (h)	12.2	12.0	14.9
Average Temperature (°C)	250.	250.	250.
Maximum Δ Temperature (°C) ^b	3.00	2.00	2.00
Pressure (MPa)	1.48	1.48	1.48
H ₂ /CO Feed Ratio	.678	.678	.678
Space Velocity (NI/g-cat.h) ^a	2.03	2.03	2.03
Space Velocity (NI/g-Fe.h)	2.95	2.95	2.95
GHSV (h ⁻¹) ^c	252.	252.	252.
CO Conversion (%)	33.8	29.8	26.7
H ₂ +CO Conversion (%)	34.3	32.2	27.3
H ₂ /CO Usage	.702	.814	.715
STY (mols H ₂ +CO/g-cat.h) ^a	.031	.029	.025
$P_{CO_2} \cdot P_{H_2}/P_{CO} \cdot P_{H_2O}$	4.92	2.35	4.89
Weight % of Outlet			
H ₂	3.10	3.02	3.44
H ₂ O	1.17	1.96	.926
CO	64.7	67.7	71.9
CO ₂	21.2	18.2	16.7
Hydrocarbons	3.85	6.04	5.54
Oxygenates	.229	.506	.167
Wax ^d	5.77	2.56	1.36
Yield (g/Nm ³ H ₂ + CO Converted)			
CH ₄	10.2	11.1	13.5
C ₂ -C ₄ Hydrocarbons	29.7	32.6	37.2
C ₅ -C ₁₁ Hydrocarbons	36.4	65.5	63.2
C ₁₂ + Hydrocarbons	138.	97.1	78.3
Wax ^d	128.	61.4	37.8
Oxygenates	5.08	12.1	4.67
Total	219.	219.	197.
1+2 Olefins/n-Paraffin Ratio			
C ₂	1.48	1.38	1.22
C ₃	5.19	5.17	4.79
C ₄	5.61	5.59	5.26
C ₅	2.56	1.96	2.97
C ₁₀	2.28	3.88	2.55

^a Based on unreduced catalyst

^c Based on reactor volume

^b Maximum axial temperature difference

^d Unanalyzed products collected from hot trap

Table 2 (cont'd). Summary of results for fixed bed run FB-2800 .

Weight % of Hydrocarbons	Period		
	1	2	3
CH ₄	4.79	5.39	7.00
Ethane	1.49	1.74	2.32
Ethylene	2.07	2.25	2.63
Propane	.948	1.08	1.45
Propylene	4.69	5.31	6.63
n-Butane	.723	.841	1.03
1+2 Butenes	3.92	4.54	5.21
C ₄ Isomers	.0456	.0520	.0767
n-Pentane	.909	1.06	1.04
1+2 Pentenes	2.97	3.34	3.88
C ₅ Isomers	.207	1.23	1.53
n-Hexane	.420	.562	.615
1+2 Hexenes	1.83	2.42	2.62
C ₆ Isomers	.586	.683	.854
n-Heptane	.340	.405	.547
1+2 Heptenes	1.56	1.64	2.07
C ₇ Isomers	.454	.469	.648
n-Octane	.430	.440	.857
1+2 Octenes	1.08	.846	2.50
C ₈ Isomers	.552	.337	.912
n-Nonane	.392	.819	.853
1+2 Nonenes	1.28	3.20	3.04
C ₉ Isomers	.0213	.0847	.00000
n-Decane	.707	1.67	1.15
1+2 Decenes	1.59	6.38	2.89
C ₁₀ Isomers	.0460	.183	.0896
n-Undecane	.234	.930	1.92
1+2 Undecenes	1.57	4.92	4.47
C ₁₁ Isomers	.0347	.138	.418
C ₂ -C ₄	13.9	15.8	19.3
C ₅ -C ₁₁	17.0	31.7	32.9
C ₁₂ +	64.3	47.1	40.8
Wax ^d	60.0	29.8	19.7

^d Unanalyzed products collected from hot trap

Table 3. Summary of results for fixed bed run FB-3480 .

Catalyst: 3.50 g^a, 100Fe/0.3Cu/0.8K
 Catalyst volume: 3.20 cc
 Diluent: 36.22 g, Glass beads
 Diluent Volume: 25.20 cc

Period	1	2	3
Date	12/18/90	12/20/90	12/22/90
Time on Stream (h)	87.0	140.2	185.5
Balance Duration (h)	7.0	16.7	12.1
Average Temperature (°C)	250.	250.	250.
Maximum Δ Temperature (°C) ^b	11.0	11.0	9.00
Pressure (MPa)	1.48	1.48	1.48
H ₂ /CO Feed Ratio	.647	.647	.647
Space Velocity (NI/g-cat·h) ^a	2.03	2.03	2.03
Space Velocity (NI/g-Fe·h)	2.95	2.95	2.95
GHSV (h ⁻¹) ^c	259.	259.	259.
CO Conversion (%)	86.5	85.8	88.4
H ₂ +CO Conversion (%)	82.8	82.1	84.3
H ₂ /CO Usage	.577	.577	.572
STY (mole H ₂ +CO/g-cat·h) ^a	.075	.074	.076
$P_{CO_2} \cdot P_{H_2} / P_{CO} \cdot P_{H_2O}$	795.	775.	926.
Weight % of Outlet			
H ₂	1.04	1.07	.985
H ₂ O	.0363	.0364	.0356
CO	13.2	13.8	11.2
CO ₂	64.1	64.0	66.1
Hydrocarbons	15.9	15.9	16.9
Oxygenates	2.71	3.12	2.64
Wax ^d	3.05	2.05	2.12
Yield (g/Nm ³ H ₂ + CO Converted)			
CH ₄	18.4	18.1	19.7
C ₂ -C ₄ Hydrocarbons	52.3	52.5	55.0
C ₅ -C ₁₁ Hydrocarbons	69.3	69.1	73.6
C ₁₂ + Hydrocarbons	38.7	31.6	28.9
Wax ^d	28.7	19.6	19.8
Oxygenates	25.6	29.7	24.6
Total	204.	201.	202.
1+2 Olefins/n-Paraffin Ratio			
C ₂	1.58	1.60	1.54
C ₃	4.05	3.72	3.78
C ₄	3.68	3.17	3.28
C ₈	2.11	1.85	1.95
C ₁₀	2.32	2.18	2.15

^a Based on unreduced catalyst

^b Maximum axial temperature difference

Table 3 (cont'd). Summary of results for fixed bed run FB-3480 .

Weight % of Hydrocarbons	Period		
	1	2	3
CH ₄	10.3	10.6	11.1
Ethane	4.19	3.45	3.60
Ethylene	6.17	5.16	5.17
Propane	2.22	2.66	2.65
Propylene	8.58	9.46	9.58
n-Butane	1.76	2.24	2.21
1+2 Butenes	6.23	6.84	6.99
C ₄ Isomers	.137	.829	.832
n-Pentane	.823	1.94	3.27
1+2 Pentenes	4.30	5.12	9.02
C ₅ Isomers	.818	1.24	1.27
n-Hexane	1.38	1.14	1.28
1+2 Hexenes	3.88	2.82	2.04
C ₆ Isomers	1.89	1.82	.886
n-Heptane	2.39	1.56	3.79
1+2 Heptenes	3.31	2.08	.797
C ₇ Isomers	2.69	.529	1.29
n-Octane	1.73	1.66	1.58
1+2 Octenes	3.58	3.03	3.03
C ₈ Isomers	2.00	1.51	1.31
n-Nonane	1.34	1.67	1.38
1+2 Nonenes	2.82	3.12	2.68
C ₉ Isomers	.390	1.79	.665
n-Decane	.963	1.38	1.14
1+2 Decenes	2.20	2.96	2.41
C ₁₀ Isomers	.360	.840	.539
n-Undecane	.475	1.11	.849
1+2 Undecenes	1.22	2.45	1.88
C ₁₁ Isomers	.198	.615	.423
C ₂ -C ₄	29.3	30.6	31.0
C ₅ -C ₁₁	38.8	40.4	41.5
C ₁₂ +	21.6	18.4	16.3
Wax ^d	16.1	11.4	11.2

^d Unanalyzed products collected from hot trap

Table 4. Composition and Physical Properties of Iron/Silica Catalysts

Nominal Composition (parts by weight)	Analyzed Composition (a) (parts by weight)		Surface Area (m ² /g)	Pore Volume (cm ³ /g)
100 Fe/ 5 Cu/ 4.2 K/ 8 SiO ₂	100 Fe/ 5.1 Cu/ 4 K/ 7.8 SiO ₂ (1)	uncalc. calcined	313 250	0.41 0.38
100 Fe/ 5 Cu/ 4.2 K/ 8 SiO ₂	100 Fe/ 5 Cu/ 5.5 K/ 39 SiO ₂ (2) 100 Fe/ 4.2 Cu/ 6.2 K/ 40.3 SiO ₂ (3)	uncalc. calcined	287 238	0.78 0.73
100 Fe/ 5 Cu/ 4.2 K/ 16 SiO ₂	100 Fe/ 5 Cu/ 4.3 K/ 18 SiO ₂ (2) 100 Fe/ 4.5 Cu/ 4.8 K/ 17.9 SiO ₂ (3)	uncalc. calcined	285 257	0.71 0.70

(a) Composition determined by atomic absorption spectroscopy at: (1) Chemistry Department - TAMU; (2) Sandia National Laboratory; (3) our laboratory.

Figure 1. Volumetric contraction versus time on stream for run FA-2780

Figure 2. Stability plot, (H₂+CO) conversion versus time on stream, for run FA-2780

Figure 3. Volumetric contraction versus time on stream for run FB-2800

Figure 4. Stability plot, (H₂+CO) conversion versus time on stream, for run FA-2800

Figure 5. Volumetric contraction versus time on stream for run FB-3480

Figure 6. Stability plot, (H₂+CO) conversion versus time on stream, for run FB-3480

Figure 7. Adsorption/desorption isotherms for N₂ at -196 C on calcined catalysts (300 C for 5h in air):

- (a) 100Fe/5Cu/4.2K/8S10₂
- (b) 100Fe/5Cu/4.2K/40S10₂
- (c) 100Fe/5Cu/4.2K/18S10₂

Figure 8. Differential pore volume distribution of calcined iron catalysts:
 (a) 100Fe/5Cu/4.2K/8SiO₂
 (b) 100Fe/5Cu/4.2K/40SiO₂
 (c) 100Fe/5Cu/4.2K/18SiO₂

Figure 9. Cumulative pore volume plot for calcined iron catalysts:

(a) 100Fe/5Cu/4.2K/8SiO₂

(b) 100Fe/5Cu/4.2K/40SiO₂

(c) 100Fe/5Cu/4.2K/18SiO₂

Figure 10. Differential pore volume distribution of uncalcined (a) and calcined (b) 100Fe/5Cu/4.2K/18SiO₂ catalyst.

Figure 11. XRPD patterns of 100Fe/5Cu/4.2K/8SiO₂ catalyst ((a) After calcination in air; (b) After synthesis: Run FA-3448; (c) After synthesis: Run FA-0418).

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