DOE/PC/89868--8

DE92 016728

Development of Improved Iron Fischer-Tropsch Catalysts

Quarterly Technical Progress Report
for the Period 1 July 1991 – 30 September 1991

Prepared by: Dragomir B. Bukur

Contributors: X. Lang
L. Nowicki
K. Okabe

Texas A&M University
Department of Chemical Engineering
College Station, Texas 77843-3122

October 28, 1991

Prepared for the Pittsburgh Energy Technology Center,
the United States Department of Energy Under Contract No. DE-AC22-89PC89868
V. Udaya Rao, Project Manager (PETC)

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I. Executive Summary

Four catalyst evaluation tests (3 fixed bed reactor, and one slurry reactor) were completed during this period. Also, Ruhrchemie catalyst designated LP 33/81 was characterized by X-ray diffraction (XRD) and BET surface area and pore size distribution after various pretreatment procedures in a fixed bed reactor. Iron phases in H_2 reduced samples were identified as: magnetite Fe_3O_4 (reduction temperatures of 220°C or 280°C), and metallic iron (α -Fe) in samples reduced at 280°C. Samples activated with CO at 280°C, or syngas ($H_2/CO = 2$) at 310°C contained iron carbide(s).

Catalyst with nominal composition 100 Fe/5 Cu/4.2 K/40 SiO_2 was evaluated at different process conditions in two fixed bed tests (Runs FB-1801 and FB-2671) in order to complement our earlier studies with silica containing iron catalysts. Fischer-Tropsch synthesis (FTS) and water-gas-shift (WGS) activities in the first test (FB-1801) were markedly higher than expected, and this was subsequently confirmed in the second test (FB-2671). (H_2+CO) conversion varied between 25 and 54%, whereas methane selectivity was between 4.6 and 6.6% (Run FB-2671). Catalyst with higher SiO_2 content (100 Fe/5 Cu/4.2 K/100 SiO_2) was evaluated at the same process conditions employed in the two tests with 40 SiO_2 catalyst ($T = 220, 235$ and $250^\circ C$, $SV = 2$ and 4 $Nl/g-cat/h$, $P = 200$ and 400 psig; $H_2/CO = 1.06$). Values of (H_2+CO) conversion were lower in comparison to those obtained in test FB-2671 of 40 SiO_2 catalyst, and varied between 13 and 35%, whereas methane selectivity was higher (6.1 – 7%).

A precipitated iron catalyst with silicon oxide as binder was tested in a stirred tank slurry reactor (Run SB-1391) over a period of 700 h. During first 520 h of testing at 260°C, 200 psig, $H_2/CO = 0.66$ and $SV = 2.2 - 4$ $Nl/g-Fe/h$, the (H_2+CO) conversion was between 74 and 83%, and (H_2/CO) usage ratio was about 0.6. Methane selectivity was low, 2.5 – 3.7%, and (C_1+C_2) selectivity was less than 7% up to 450 h on stream, whereas at 500 h (C_1+C_2) selectivity was 8.2%. Catalyst deactivation rate at 260°C was low, but it increased during testing at 265°C (520 – 692 h on stream). For example, at 525 h on stream the (H_2+CO) conversion was 84%, decreasing to 75% at 692 h. Methane selectivity during testing at 265°C was also higher (4.2-4.9%).

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 it 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-hour 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 catalysts, and at providing a better understanding of the role of pretreatment on subsequent catalyst activity, selectivity and longevity

during Fischer-Tropsch synthesis (FTS). 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 FTS.

Task 3 – Improved Iron Silica Catalyst

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

Ruhrchemie catalyst designated LP 33/81 was reduced in a fixed bed reactor. After the reduction (pretreatment) the reactor was emptied in helium atmosphere in a glove box, and catalyst samples were preserved in vials and ampules for future characterization. Approximately 2.5 g of catalyst sieved to 30/60 mesh was used in each of the experiments. Pretreatment conditions employed and preliminary results from X-ray powder diffraction (XRPD) measurements are shown in Table 1.

Crystalline phases found in samples reduced with H_2 were: magnetite (Fe_3O_4) – all three pretreatment procedures, and metallic iron (α -Fe) – for reductions at 280°C only. Low temperature reduction (220°C), recommended by manufacturer, did not result in formation of zero valent iron. Magnetite peaks of the catalyst reduced at 220°C are broad, indicating small crystallite size (Fig. 1b). Upon increasing the reduction temperature to 280°C (Fig. 1c), broad peaks of α -Fe (small crystallites) as well as low intensity peaks of Fe_3O_4 (indicating incomplete reduction) were observed. Reduction at low hydrogen flow rate (125 cm³/min) at 280°C for 8 h (Fig. 1d) results in formation of α -Fe and Fe_3O_4 (both peaks are smaller in comparison to reduction employing high flow rate of hydrogen). It appears that this reduction procedure is less effective, in spite of longer duration, due to higher partial pressure of water. Calcined catalyst (Fig. 1a) shows broad peaks which are tentatively identified as Fe_2O_3 .

Figure 2 shows XRD patterns of Ruhrchemie catalyst reduced with (a) CO at 280°C for 12 h, and (b) syngas with $H_2/CO = 2$ at 310°C for 6 h. Peaks were identified as iron carbides in both cases. The peaks are relatively broad and unresolved, preventing more precise identification. All samples will be submitted for Mössbauer Effect Spectroscopy analysis, which will provide more detailed information about phases present and their relative amounts.

Surface areas and pore volumes of two reduced samples were measured by physical adsorption of N_2 at 77 K, and values obtained are listed in Table 2. Surface area (SA) and pore volume (V_p) of Ruhrchemie catalyst samples decreased by reduction with CO or H_2 at 280°C for 8

h, and the changes were more profound with CO reduction than with H₂ reduction. The changes in SA and V_p with CO reduction were from 289 to 118 m²/g and from 0.62 to 0.34 ml/g respectively, and those with H₂ reduction were to 160 m²/g and to 0.49 ml/g, respectively. However, the mean pore diameter ($\bar{d}_p$), which is defined by the following equation,

$$\bar{d}_p = 4 \times V_p / SA$$

was almost the same for these two reduced catalysts (115 and 121 Å, respectively).

Figure 3 shows differential pore volume distribution of calcined and reduced Ruhrchemie catalyst samples. Each sample showed bi-modal distribution. Although the peak position of large pore diameter (≈ 190 Å) hardly changed by reduction, the relative intensity of the peak maximum apparently increased more by CO reduction than by H₂ reduction. This result implies that the large pores were actually unchanged by the reduction, but that the amount of small pores decreased more during CO reduction than during H₂ reduction.

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

Four tests (3 screening tests in a fixed bed reactor, and a slurry reactor test) were completed during the reporting period. Two of the fixed bed tests were made using catalyst with nominal composition 100 Fe/5 Cu/4.2 K/40 SiO₂ (Runs FB-2801 and FB-2671), and one test was made using catalyst with nominal composition 100 Fe/5 Cu/4.2 K/100 SiO₂. These tests were made to either complement or verify results obtained in our earlier studies with catalysts of nominal composition 100 Fe/5 Cu/4.2 K/z SiO₂, where: z = 0, 8, 16, 24 and 100 (Final Report for Contract DE-AC22-PC80011 for catalysts with z = 0, 8, 24 and 100, and Technical Progress Report April 1 – June 30, 1991 for catalyst with z = 16 – Run FB-1431). Results from all four tests are described in detail in Sections III-2.1 – III.2-3, and Appendix I (Run SB-1931).

III-2.1 Run FB-1801 with 100Fe/5Cu/4K/40SiO₂ Catalyst

This was the first test of this catalyst, after the standard pretreatment procedure (CO at 280°C for 12 h). Six mass balances were made during the test which lasted 175 h, and results are

summarized in Table 3. Total mass balance closures were rather low and varied between 88.1% (balance 6) and 94% (balance 5). Synthesis gas with nominal feed composition of $H_2/CO = 1$ was employed throughout the test, and reaction pressure was 200 psig except in balance 6 where the pressure was 400 psig.

The (H_2+CO) conversion increased with reaction temperature while maintaining other process conditions constant ($P = 200$ psig, $SV = 2$ Nl/g-cat/h). At 220°C (balance 4) the conversion was 39.6%, increasing to 62.4 and 71% at 235°C (balance 1) and 250°C (balance 3), respectively. Some deactivation was observed between 48 and 143 h on stream, as (H_2+CO) conversion decreased from 62.4% in balance 1 to 57.8% in balance 5. Catalyst deactivated markedly after exposure to high pressure in balance 6. The (H_2+CO) conversion in balance 6 was 40.4%, which is significantly lower than that in balance 5 (57.6%). The values of (H_2+CO) conversion were significantly higher whereas usage ratios were lower, than the corresponding values obtained in test of catalyst with nominal composition 100 Fe/5 Cu/4.2 K/24 SiO_2 (Run FA-66-0548, Final Report for DOE Contract DE-AC22-85PC80011). These results are inconsistent with our previous findings that both FTS and WGS activity decrease with increasing silica content. The reasons for this discrepancy in results are not known at the present time. A new test (Run FB-2671) was made in attempt to clarify these results (see Sec. III-2.2).

Due to low mass balance closures and unexpectedly high values of conversion, a complete analysis of aqueous and organic phase products collected was done for two mass balances (1 and 4) only. Hydrocarbon selectivities are shown in Table 3. Methane selectivity was 2.9% at 220°C (balance 4), and 4.0% at 235°C (balance 1). These values are consistent with those obtained previously with silica containing catalysts.

III-2.2 Run FB-2671 with 100Fe/5Cu/4.2K/40SiO₂ Catalyst

This test was conducted with objective to check results obtained in Run FB-1801 with the same catalyst. Pretreatment and process conditions were the same in both tests. Results from six mass balances are summarized in Table 4.

The ($\text{H}_2 + \text{CO}$) conversion increased with reaction temperature, while keeping pressure and gas-space velocity constant (200 psig, and 2 Nl/g-cat/h). At 220°C the conversion was 25.2%, and it increased to 43.7 and 54.3%, at 235°C (balance 1) and 250°C (balance 3), respectively. Conversions in balances 5 (144 h) and 1 (48 h) at 235°C, 200 psig and 2 Nl/g-cat/h, were approximately equal indicating no loss of activity during 100 h of testing. Upon increasing pressure to 400 psig (balance 6), while keeping (P/SV) constant, the ($\text{H}_2 + \text{CO}$) conversion decreased to 40%, from 43.2% in balance 5. Values of ($\text{H}_2 + \text{CO}$) conversion obtained in this test were lower, whereas values of ($\text{H}_2 + \text{CO}$) usage ratio were higher than those obtained in Run FB-1801. Results from Run FB-2671 are consistent with those obtained previously with catalysts containing 24 parts of SiO_2 per 100 parts of iron (Run FA-66-0548), and 100 parts of SiO_2 (Run FA-69-0668 and FB-2391, see below). This test confirms that results obtained in Run FB-1801 are not correct.

Weight percent of methane in hydrocarbon products varied between 4.6 and 6.7 throughout the test. Hydrocarbon selectivity was not affected markedly with changes in gas space velocity (2 vs. 4 Nl/g-cat/h) at 235°C (balances 1 and 2), and reaction pressure (1.5 vs. 3 MPa) at space velocity of 4 Nl/g-cat/h (balances 2 and 6). Methane and ($\text{C}_2 - \text{C}_4$) fraction increased with increasing temperature (235°C vs. 250°C), however data at 220°C (balance 4) do not follow the expected trend, i.e. CH_4 and ($\text{C}_2 - \text{C}_4$) selectivities are greater than those obtained at 235°C. The latter is due to errors in product collection, handling and analysis.

Carbon number product distribution for mass balance five, in the form of Anderson-Shulz-Flory (ASF) plot, is shown in Figure 4. Solid product (wax) collected in a high pressure trap was not analyzed. Data in $\text{C}_1 - \text{C}_{11}$ carbon number range are well represented by a straight line with slope of 0.68 (chain growth probability).

III-2.3 Run FB-2391 with 100Fe/5Cu/4.2K/100SiO₂ Catalyst

The objective of this test was to check results obtained previously in Run FA-69-0668 (Final Report for DOE Contract DE-AC22-85PC80011). Approximately 3.5 g of calcined catalyst

was ground and sieved to 30/60 mesh size range, mixed with glass beads of the same size range and then loaded into the reactor. Catalyst pretreatment was performed in-situ with CO at 280°C for 12 h and space velocity of 3 Nl/g-cat/h. The test was terminated voluntarily after 175 h on stream. Process conditions were the same as those used in tests FB-1801 and FB-2071. Results from six mass balances are summarized in Table 5. We have not collected any organic phase products in balances 1 and 6. Therefore, product selectivities are reported for the remaining four balances only (balances 2 to 5).

The FTS activity (measured by H_2+CO conversion) and the WGS activity (measured by H_2/CO usage ratio) of the catalysts in this test were very similar to those found in the previous test of this catalyst. The activity was stable with time-on-stream and at high reaction pressure. The (H_2+CO) conversions obtained at 200 psig, 235°C and 2 Nl/g-cat/h at 48 h (balance 1) and 143 h (balance 5) on stream were 25.5 and 26.7%, respectively, whereas the (H_2+CO) conversion during balance 6 (400 psig and 4 Nl/g-cat/h) at 168 h was 27.1%.

Methane selectivity varied between 6.1 and 7%, and these values are higher than those obtained in Run FA-60-0668 (4.6 to 5.9%). On the other hand gaseous hydrocarbon (C_2-C_4) selectivities in this test were lower than those in the previous test. However, in view of difficulties associated with obtaining accurate hydrocarbon selectivities in laboratory reactors, one may consider that the agreement between two tests is satisfactory.

Carbon number product distribution for mass balance three is shown in Figure 5 (Wax was not analyzed). Methane selectivity is above the ASF line corresponding to $\alpha_1 = 0.70$.

III-2.4 Run SB-1931

Results from this test contain potentially patentable information and are presented in a separate section of this report (Appendix I), which is not intended for publication/distribution.

III-3 Catalyst Characterization

During the current reporting period, we prepared three catalysts and their composition was determined by atomic absorption (AA). Also, we have continued our characterization studies of catalysts from fixed bed reactor tests by X-ray diffraction (XRD) analysis. The following sections contain detailed descriptions of progress in each of these areas.

Preparation and Elemental Analysis of Catalysts

By incipient wetness method, KHCO_3 was added to 100 Fe/5 Cu/16 SiO_2 catalyst, which was synthesized previously, to form 100 Fe/5 Cu/8 K/16 SiO_2 catalyst (26 g). Catalysts with nominal compositions of 100 Fe/1 Cu/0.8 K and 100 Fe/5 Cu/100 SiO_2 were prepared (140 g and 125 g, respectively), using the controlled-pH continuous precipitation method. The actual compositions of these catalysts were determined by atomic absorption (AA), and are summarized in Table 6. Values for copper and potassium levels (x and y) in each catalyst are reported in part by weight of metals relative to 100 parts by weight of iron; whereas the value for silicon (z), in part by weight of silicon oxide relative to 100 parts by weight of iron. The analyzed copper contents of the catalysts are very close to the nominal values. Potassium analyses are generally higher than predicted. Significantly excessive amount of potassium was detected in 100 Fe/5 Cu/100 SiO_2 sample, which is considered to be due to incomplete washing of the catalyst after the incorporation of potassium silicate. The silica contents fluctuated from the expected values, because of relatively large experimental errors associated with determination of SiO_2 .

X-Ray Diffraction (XRD) Results

During the current reporting period, the phases of used Ruhrchemie catalysts after different pretreatment conditions and of used catalysts with different silica contents were identified by X-ray diffraction.

Figure 6 shows XRD patterns of used Ruhrchemie catalysts after different pretreatment conditions. The XRD peaks of used catalysts reduced with H_2 at 220°C and 280°C were identified

as Fe_3O_4 and Fe-carbide(s) both in top and bottom parts of the reactor (a - c). On the contrary, the XRD patterns of the used catalyst reduced with $(\text{H}_2/\text{CO}) = 2$ at 310°C showed that the top part of the reactor (d) contained mainly Fe-carbide(s) whereas in the bottom part (e) Fe_3O_4 is the only phase that was identified. A simple correlation between the iron phases found and reaction results could not be obtained.

Figure 7 shows XRD patterns of used 100 Fe/3 Cu/4 K/z SiO_2 catalysts ($z = 8, 16$) reduced with H_2 at $220 - 240^\circ\text{C}$ for 2 h. The peaks of the catalyst with 8 SiO_2 (Fig. 7a) were identified as Fe_3O_4 and Fe-carbide(s), whereas those with 16 SiO_2 (Fig. 7b) were identified as Fe-carbide(s) only. This fact suggests that carburization of the catalyst was more pronounced with catalyst having higher SiO_2 content. However, the catalyst performance was similar in both tests (January - March, 1991 Quarterly Report).

Figure 8 shows XRD patterns of used 100 Fe/5 Cu/4.2 K/z SiO_2 catalysts ($z = 16, 40, 100$) from top and bottom parts of the reactor. Except for catalyst in test FB-1801 (8c and 8d), the XRD patterns of samples from the top and the bottom parts were similar, and the peaks were identified as Fe_3O_4 (magnetite), indicating that the iron phase was uniform throughout the reactor. The peaks of the catalyst from the top part of reactor in Run FB-1801 were identified as Fe-carbide(s) (Fig. 8c) whereas those from the bottom part (Fig. 8d) were identified as Fe_3O_4 . Catalyst activities (FTS and WGS) varied significantly in these four tests, however product distributions (selectivities) were similar in all tests (see sections III-2.1 to III-2.3 of this report, and Quarterly Report for period April - June, 1991 for Run FB-1431).

Table 1. X-Ray Diffraction Analysis of Reduced Ruhrchemie Catalyst (LP 33/81)

Gas	Reduction Conditions			Phase
	Flow rate (ml/min)	Temp. (°C)	Duration (h)	
H ₂	3350	220	1	Fe ₃ O ₄ (broad)
H ₂	3160	280	1	Fe + Fe ₃ O ₄
H ₂	125	280	8	Fe + Fe ₃ O ₄
CO	125	280	12	Fe _x C
(H ₂ /CO) - 2	1200	310	6	Fe _x C

Table 2. BET and PSD Result of Ruhrchemie Catalyst

	Gas	Pretreatment Conditions			SA ^{a)} (m ² /g)	V _p ^{b)} (cc/g)	$\bar{d}_p$ ^{c)} (Å)
		Temp.	Duration	Flow rate			
Calcined	Air	300°C	5 h	3 Nl/g/h	289±1	0.62	86
Reduced	CO	280°C	8 h	3 Nl/g/h	118±1	0.34	115
Reduced	H ₂	280°C	8 h	3 Nl/g/h	160±1	0.49	121

a) Surface area.

b) Pore Volume.

c) Mean pore diameter ($\bar{d}_p = 4 \times V_p / SA$).

Table 3. Summary of results for ed bed run FB-1801 .

Catalyst: 3.50 g^a, 100Fe/5Cu/4.2K/40SiO₂
 Catalyst volume: 5.00 cc
 Diluent: 30.93 g, Glass beads
 Diluent Volume: 20.00 cc

Period	1	2	3	4	5	6
Date	07/02/91	07/03/91	07/04/91	07/05/91	07/06/91	07/07/91
Time on Stream (h)	48.0	72.0	92.0	119.0	143.0	169.0
Balance Duration (h)	6.8	7.0	7.0	7.2	6.5	6.0
Average Temperature (°C)	235.	235.	250.	220.	235.	235.
Maximum Δ Temperature (°C) ^b	5.00	2.00	3.00	3.00	2.00	2.00
Pressure (MPa)	1.48	1.48	1.48	1.48	1.48	2.96
H ₂ /CO Feed Ratio	1.06	1.06	1.06	1.06	1.06	1.06
Space Velocity (Nl/g-cat·h) ^a	2.00	4.00	2.00	2.00	2.00	4.00
Space Velocity (Nl/g-Fe·h)	3.35	6.69	3.35	3.35	3.35	6.69
GHSV (h ⁻¹) ^c	280.	560.	280.	280.	280.	560.
CO Conversion (%)	70.3	40.4	85.4	40.1	65.7	38.7
H ₂ +CO Conversion (%)	62.4	38.9	71.1	39.6	57.8	40.5
H ₂ /CO Usage	.829	.986	.717	1.04	.817	1.16
STY (mols H ₂ +CO/g-cat·h) ^a	.056	.069	.063	.035	.052	.072
P _{CO₂} · P _{H₂} / P _{CO} · P _{H₂O}	4.32	1.70	11.2	1.43	3.29	1.50
Weight % of Outlet						
H ₂	3.50	4.70	3.25	4.64	3.70	4.63
H ₂ O	6.55	5.48	6.11	6.12	7.26	4.56
CO	30.2	58.7	14.7	59.9	33.6	64.4
CO ₂	42.9	20.4	54.5	19.8	38.2	16.7
Hydrocarbons	7.25			3.47		
Oxygenates	.537			.434		
Wax ^d	9.08	6.42	11.1	5.59	10.1	5.12
Yield (g/Nm ³ H ₂ + CO Converted)						
CH ₄	6.21	5.54	7.34	4.03	5.62	4.31
C ₂ -C ₄ Hydrocarbons	29.1	25.7	31.0	22.6	28.9	24.3
C ₅ -C ₁₁ Hydrocarbons	31.5			24.2		
C ₁₂ + Hydrocarbons	89.3			87.8		
Wax ^d	86.8	101.	93.9	85.5	109.	72.9
Oxygenates	5.14			6.63		
Total	161.	170.	182.	145.	185.	137.
1+2 Olefins/n-Paraffin Ratio						
C ₂	2.89	3.79	2.04	4.78	3.57	3.96
C ₃	5.73	5.69	6.18	5.16	5.92	4.21
C ₄	5.14	5.07	5.56	4.58	5.31	3.81
C ₈	3.99			3.39		
C ₁₀	3.37			3.15		

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

Table 3 (cont'd). Summary of results for fixed bed run FB-1801.

Period	1	2	3	4	5	6
Weight % of Hydrocarbons						
CH ₄	3.98			2.91		
Ethane	1.36			.786		
Ethylene	3.66			3.51		
Propane	1.18			1.12		
Propylene	6.43			5.51		
n-Butane	.992			.964		
1+2 Butenes	4.92			4.26		
C ₄ Isomers	.132			.173		
n-Pentane	.868			.866		
1+2 Pentenes	3.96			3.45		
C ₅ Isomers	1.91			1.70		
n-Hexane	.719			.602		
1+2 Hexenes	2.76			2.24		
C ₆ Isomers	.818			.791		
n-Heptane	.484			.477		
1+2 Heptenes	1.75			1.74		
C ₇ Isomers	.659			.653		
n-Octane	.307			.352		
1+2 Octenes	1.20			1.17		
C ₈ Isomers	.525			.486		
n-Nonane	.348			.235		
1+2 Nonenes	.919			.808		
C ₉ Isomers	.189			.095		
n-Decane	.285			.218		
1+2 Decenes	.947			.678		
C ₁₀ Isomers	.257			.151		
n-Undecane	.249			.144		
1+2 Undecenes	.751			.412		
C ₁₁ Isomers	.236			.161		
C ₂ -C ₄	18.7			16.3		
C ₅ -C ₁₁	20.2			17.4		
C ₁₂ +	57.2			63.3		
Wax ^d	55.6			61.7		

^d Unanalyzed products collected from hot trap

Table 4. Summary of results for ed bed run FB-2671.

Catalyst: 3.50 g, 100Fe/5Cu/4.2K/40SiO₂
 Catalyst volume: 5.20 cc
 Diluent: 32.50 g, Glass beads
 Diluent Volume: 21.00 cc

Period	1	2	3	4	5	6
Date	09/26/91	09/27/91	09/28/91	09/29/91	09/30/91	10/01/91
Time on Stream (h)	47.5	71.5	96.0	119.5	144.0	168.0
Balance Duration (h)	7.0	6.2	6.2	8.0	6.5	6.5
Average Temperature (°C)	234.	235.	250.	220.	235.	235.
Maximum Δ Temperature (°C) ^b	3.00	4.00	3.00	2.00	2.00	3.00
Pressure (MPa)	1.48	1.48	1.48	1.48	1.48	2.93
H ₂ /CO Feed Ratio	1.06	1.06	1.06	1.06	1.06	1.06
Space Velocity (NI/g-cat·h) ^a	2.01	4.01	2.00	2.00	2.00	3.99
Space Velocity (NI/g-Fe·h)	4.01	8.02	3.99	3.99	4.00	7.99
GHSV (h ⁻¹) ^c	265.	530.	264.	264.	264.	528.
CO Conversion (%)	40.9	25.0	57.8	21.7	39.5	35.5
H ₂ +CO Conversion (%)	43.7	29.5	54.3	25.2	43.2	40.0
H ₂ /CO Usage	1.20	1.43	.934	1.39	1.26	1.32
STY (mols H ₂ +CO/g-cat·h) ^a	.039	.053	.048	.022	.039	.071
P _{CO₂} · P _{H₂} / P _{CO} · P _{H₂O}	.756	.490	2.04	.471	.792	.444
Weight % of Outlet						
H ₂	3.84	4.68	3.49	5.09	3.81	4.00
H ₂ O	8.98	7.08	7.92	6.17	8.16	10.1
CO	55.4	69.2	39.2	72.9	56.7	60.6
CO ₂	17.2	9.03	31.9	7.32	16.9	11.9
Hydrocarbons	7.05	4.40	9.19	4.15	6.36	5.93
Oxygenates	1.24	.887	1.19	.825	.990	1.20
Wax ^d	6.31	4.74	7.10	3.50	7.08	6.26
Yield (g/Nm ³ H ₂ + CO Converted)						
CH ₄	9.05	9.80	12.4	13.2	10.5	9.05
C ₂ -C ₄ Hydrocarbons	33.6	34.7	42.0	40.6	37.1	32.0
C ₅ -C ₁₁ Hydrocarbons	48.4	44.0	47.8	44.3	41.6	40.5
C ₁₂ + Hydrocarbons	106.	115.	93.5	99.6	112.	115.
Wax ^d	93.2	106.	85.3	90.4	106.	101.
Oxygenates	18.4	19.8	14.3	21.3	14.8	19.3
Total	216.	224.	210.	219.	216.	216.
1+2 Olefins/n-Paraffin Ratio						
C ₂	2.43	2.71	1.84	2.59	2.49	2.01
C ₃	5.93	5.83	6.50	5.11	5.89	3.78
C ₄	5.51	5.23	6.02	4.37	5.49	3.60
C ₈	3.54	3.55	3.42	3.20	3.46	2.69
C ₁₀	2.45	2.35	2.77	2.59	3.07	2.53

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

Table 4 (cont'd). Summary of results for fixed bed run FB-2671.

Weight % of Hydrocarbons	Period					
	1	2	3	4	5	6
CH ₄	4.58	4.81	6.34	6.66	5.23	4.59
Ethane	1.31	1.24	2.08	1.64	1.44	1.48
Ethylene	2.96	3.14	3.57	3.95	3.35	2.78
Propane	1.03	1.05	1.21	1.41	1.13	1.43
Propylene	5.80	5.83	7.50	6.89	6.38	5.16
n-Butane	.908	.928	1.03	1.17	.949	1.15
1+2 Butenes	4.83	4.69	5.96	4.94	5.03	3.99
C ₄ Isomers	.185	.141	.124	.538	.158	.266
n-Pentane	.853	.747	.902	.978	.830	.955
1+2 Pentenes	3.95	3.85	5.04	4.05	3.98	3.13
C ₅ Isomers	1.50	1.52	1.73	1.67	1.57	1.39
n-Hexane	.736	.713	.675	.731	.627	.760
1+2 Hexenes	2.97	2.78	3.04	2.59	2.57	2.12
C ₆ Isomers	.850	.812	.598	.971	.812	.747
n-Heptane	.745	.620	.530	.715	.548	.664
1+2 Heptenes	2.68	2.28	1.85	2.16	2.01	1.73
C ₇ Isomers	.616	.620	.454	.703	.575	.583
n-Octane	.626	.529	.456	.585	.437	.541
1+2 Octenes	2.18	1.84	1.53	1.84	1.49	1.43
C ₈ Isomers	.492	.515	.456	.262	.421	.399
n-Nonane	.438	.350	.526	.395	.456	.476
1+2 Nonenes	1.44	1.20	1.70	1.22	1.21	1.28
C ₉ Isomers	.233	.110	.379	.143	.193	.277
n-Decane	.552	.436	.571	.406	.334	.505
1+2 Decenes	1.33	1.01	1.56	1.04	1.01	1.26
C ₁₀ Isomers	.279	.168	.389	.216	.238	.336
n-Undecane	.497	.371	.491	.426	.316	.467
1+2 Undecenes	1.15	.958	1.24	1.03	.843	1.16
C ₁₁ Isomers	.400	.191	.337	.265	.214	.337
C ₂ -C ₄	17.0	17.0	21.5	20.5	18.4	16.3
C ₅ -C ₁₁	24.5	21.6	24.4	22.4	20.7	20.5
C ₁₂ +	53.9	56.6	47.8	50.4	55.6	58.6
Wax ^d	47.2	51.9	43.6	45.7	52.7	51.4

^d Unanalyzed products collected from hot trap

Table 5. Summary of results for ed bed run FB-2391 .

Catalyst: 3.50 g^a, 100Fe/5Cu/4.2K/100SiO₂
 Diluent: 33.50 g, Glass beads
 Catalyst volume: 7.40 cc Diluent Volume: 22.00 cc

Period	1	2	3	4	5	6
Date	08/30/91	08/31/91	09/01/91	09/02/91	09/03/91	09/04/91
Time on Stream (h)	48.5	71.0	96.0	119.5	143.5	167.5
Balance Duration (h)	7.5	6.5	7.0	8.0	7.0	6.5
Average Temperature (°C)	235.	235.	250.	220.	235.	235.
Maximum Δ Temperature (°C) ^b	2.00	3.00	6.00	2.00	3.00	7.00
Pressure (MPa)	1.48	1.48	1.48	1.48	1.48	2.93
H ₂ /CO Feed Ratio	1.06	1.06	1.06	1.06	1.06	1.06
Space Velocity (NI/g-cat·h) ^a	2.00	4.00	2.00	2.00	2.00	3.96
Space Velocity (NI/g-Fe·h)	5.08	10.2	5.09	5.09	5.09	10.1
GHSV (h ⁻¹) ^c	253.	508.	254.	254.	254.	502.
CO Conversion (%)	22.0	15.0	29.8	13.4	21.2	22.3
H ₂ +CO Conversion (%)	25.8	18.1	34.6	17.0	26.1	27.3
H ₂ /CO Usage	1.42	1.49	1.39	1.61	1.54	1.52
STY (mols H ₂ +CO/g-cat·h) ^a	.023	.032	.031	.015	.023	.048
P _{CO₂} · P _{H₂} / P _{CO} · P _{H₂O}	.465	.249	.508	.298	.336	.267
Weight % of Outlet						
H ₂	5.34	5.68	4.31	5.65	4.95	5.03
H ₂ O	4.78	5.19	8.15	4.64	6.68	5.96
CO	77.1	80.1	65.1	80.4	73.7	75.2
CO ₂	5.64	3.20	11.0	3.45	5.86	4.18
Hydrocarbons		2.38	6.15	2.40	4.38	
Oxygenates		.472	1.03	.462	.742	
Wax ^d	3.58	3.02	4.33	3.01	3.73	6.21
Yield (g/Nm ³ H ₂ + CO Converted)						
CH ₄	11.6	11.7	13.8	14.3	12.6	10.7
C ₂ -C ₄ Hydrocarbons	28.8	26.6	32.9	29.2	28.0	28.2
C ₅ -C ₁₁ Hydrocarbons		41.0	51.3	34.1	38.1	
C ₁₂ + Hydrocarbons		113.	99.9	130.	122.	
Wax ^d	85.2	108.	81.7	116.	92.5	143.
Oxygenates		16.8	19.4	17.7	18.4	
Total		209.	217.	225.	220.	
1+2 Olefins/n-Paraffin Ratio						
C ₂	1.66	2.05	1.34	1.39	1.43	1.38
C ₃	5.13	5.36	5.42	4.37	4.69	3.25
C ₄	4.71	4.95	5.18	4.29	4.54	3.09
C ₈		3.44	3.48	2.93	3.12	
C ₁₀		2.14	2.64	2.75	2.63	

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

Table 5 (cont'd). Summary of results for fixed bed run FB-2391.

Period	1	2	3	4	5	6
Weight % of Hydrocarbons						
CH ₄		6.06	6.99	6.89	6.27	
Ethane		1.23	1.88	1.75	1.63	
Ethylene		2.35	2.35	2.27	2.17	
Propane		.895	1.03	1.04	.977	
Propylene		4.57	5.35	4.32	4.38	
n-Butane		.789	.923	.793	.817	
1+2 Butenes		3.77	4.61	3.28	3.58	
C ₄ Isomers		.214	.463	.619	.362	
n-Pentane		.728	.957	.592	.765	
1+2 Pentenes		3.33	4.40	2.87	3.16	
C ₅ Isomers		1.18	1.05	.773	.761	
n-Hexane		.780	.762	.602	.598	
1+2 Hexenes		3.11	3.25	1.95	2.15	
C ₆ Isomers		.695	.670	.528	.312	
n-Heptane		.789	.735	.572	.494	
1+2 Heptenes		2.79	2.73	1.68	1.60	
C ₇ Isomers		.463	.473	.115	.0486	
n-Octane		.768	.654	.608	.372	
1+2 Octenes		2.59	2.23	1.75	1.14	
C ₈ Isomers		.222	.224	.300	.0359	
n-Nonane		.558	.724	.255	.449	
1+2 Nonenes		1.63	2.02	.726	1.21	
C ₉ Isomers		.0190	.130	.0381	.0879	
n-Decane		.300	.655	.346	.648	
1+2 Decenes		.633	1.71	.940	1.68	
C ₁₀ Isomers		.0440	.180	.0893	.187	
n-Undecane		.184	.662	.455	.909	
1+2 Undecenes		.448	1.46	1.11	2.06	
C ₁₁ Isomers		.0533	.254	.136	.273	
C ₂ -C ₄		13.8	16.6	14.1	13.9	
C ₅ -C ₁₁		21.3	25.9	16.4	18.9	
C ₁₂ +		58.8	50.5	62.6	60.9	
Wax ^d		56.0	41.3	55.6	46.0	

^d Unanalyzed products collected from hot trap

Table 6. Catalyst Composition Determined by Atomic Absorption

Nominal Composition 100Fe/xCu/yK/zSiO ₂	Sample Code	x	Actual Composition y	z ^{*)}
100Fe/5Cu/8K/16SiO ₂	S5816	5.5 ± 0.5	10.8 ± 1.3	12.3 ± 7.7
100Fe/1Cu/0.8K	C1008	0.88 ± 0.08	1.08 ± 0.13	
100Fe/5Cu/100SiO ₂	S5000	5.0 ± 0.4	4.4 ± 0.5	111.9 ± 7.8

*) Estimated by calculation, by determining contents of Fe, Cu and K, and by assuming that the remainder is SiO₂.

Fig. 1 XRD Pattern of Ruhrchemie Catalyst.

(a) calcined, (b) reduced with H_2 (3350 ml/min) at 220°C for 1 h, (c) reduced with H_2 (3160 ml/min) at 280°C for 1 h, and (d) reduced with H_2 (125 ml/min) at 280°C for 8 h.

Fig. 2 XRD Pattern of Ruhrchemie Catalyst Reduced with
(a) CO (125 ml/min) at 280°C for 12 h, and
(b) $\text{H}_2/\text{CO} = 2$ (1200 ml/min) at 310°C for 6 h.

Fig. 3 Differential Pore Volume Distribution of Ruhrchemie Catalyst.
 (a) calcined, (b) reduced with CO at 280°C for 8 h,
 (c) reduced with H₂ at 280°C for 8 h.

Figure 4. Anderson-Schulz-Flory plot for run FB-2671, balance 5.

Figure 5. Anderson-Schulz-Flory plot for run FB-2391, balance 3.

Fig. 6 XRD Pattern of Used Ruhrchemie Catalyst

- (a) reduced with H_2 at $220^\circ C$ for 1 h, TOS = 1170 h;
- (b) reduced with H_2 at $280^\circ C$ for 1 h (top part), TOS = 330 h;
- (c) reduced with H_2 at $280^\circ C$ for 1 h (bottom part), TOS = 330 h;
- (d) reduced with H_2/CO (=2) at $310^\circ C$ for 6 h (top part), TOS = 160 h;
- (e) reduced with H_2/CO (=2) at $310^\circ C$ for 6 h (bottom part), TOS = 160 h.

Fig. 7 XRD Pattern of Used 100Fe/3Cu/4K/zSiO₂ Catalyst
 Reduced with H₂ for 2 h.
 (a) $z = 8$ (reduction temp. = 220°C, TOS = 161 h);
 (b) $z = 16$ (reduction temp. = 240°C, TOS = 169 h).

Fig. 8 XRD Pattern of Used 100Fe/5Cu/4.2K/zSiO₂ Catalyst Reduced with CO at 280°C for 12 h.

(a) z = 16, TOS = 173 h, top part; (b) z = 16, TOS = 173 h, bottom part; (c) z = 40, TOS = 174 h, top part;
 (d) z = 40, TOS = 174 h, middle part; (e) z = 40, TOS = 175 h, top part; (f) z = 40, TOS = 175 h, bottom part;
 (g) z = 100, TOS = 175 h, top part; (h) z = 100, TOS = 175 h, bottom part.

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