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Development of Improved Iron Fischer-Tropsch Catalysts

Quarterly Technical Progress Report
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I. Executive Summary

Three catalyst evaluation tests (one in a fixed bed reactor, and two in a stirred tank slurry reactor) were completed during the reporting period. Also, the progress has been made in the area of characterization of catalysts at various stages of their usage (as prepared, after calcination, reduction or Fischer-Tropsch synthesis).

Pretreatment effect studies in a fixed bed reactor on performance of a precipitated catalyst with nominal composition 100Fe/0.3Cu/0.8K have been continued. This catalyst was evaluated at 250°C, 200 psig, 2 N*l*/g-cat/h and $H_2/CO = 0.66$ after reduction with H_2 at 280°C, 3 N*l*/g-cat/h for 8 h in a test designated FB-3221. Catalyst activity increased gradually between 50 h (50% conversion) and 150 h on stream (57.5% conversion), whereas hydrocarbon product distribution was fairly stable; $(CH_4) = 6.8$, $(C_2–C_4) = 22.4$, $(C_5–C_{11}) = 33.1$ and $C_{12}^+ = 37.7\%$. These trends are consistent with results obtained in our previous studies with this, as well as with other precipitated iron catalysts. Also, this catalyst was characterized by XRD after various pretreatment procedures in a fixed bed reactor. Iron phases in H_2 reduced samples were identified as: either a mixture of Fe_3O_4 and Fe (reductions at 220°C and 280°C) or metallic iron (250°C at high flow rate of H_2). In samples activated with CO or syngas (280°C or 310°C) the main phase present was χ-carbide.

Silica containing precipitated iron catalyst with nominal composition $100Fe/5Cu/8K/24SiO_2$ was evaluated in a slurry reactor test SB-3101 at 260°C, 200 psig, 1.6 N*l*/g-cat/h and $H_2/CO = 0.64$. The (H_2+CO) conversion decreased gradually from about 77% to 60% at 350 h on stream, whereas methane selectivity increased with time from 4.2 to 5.5%.

At the request of DOE's Liquefaction Project Management an iron/silica precipitated catalyst synthesized at United Catalysts Inc. was evaluated in a slurry reactor test SA-3391. After some initial problems with our experimental apparatus, the desired process conditions (265°C, 290 psig, 2.4 N*l*/g-cat/h, $H_2/CO = 0.70$) were established at about 200 h on stream. During 110 h of testing at these conditions the (H_2+CO) conversion varied between 71 and 75%, whereas methane selectivity was between 4.2 and 4.6%. Similar results (activity and methane selectivity) were obtained in a test of the same catalyst conducted at UOP Inc.

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

A fixed bed test was conducted with a precipitated iron catalyst (100Fe/0.3Cu/0.8K) to continue the investigation of pretreatment condition effects on catalyst activity, selectivity and stability. Results from catalyst characterization studies can be found in Section III-3 of this report.

III-1.1 Run FB-3221 with 100Fe/0.3Cu/0.8K Catalyst

Pretreatment conditions employed in this test were: hydrogen reduction at 280°C, 3 Nl/g-cat/h and ambient pressure for 8 h. After reduction, the catalyst was tested at average reaction temperature, pressure, gas space velocity and H_2/CO feed ratio of 250°C, 1.48MPa (200 psig), 2 Nl/g-cat/h and 0.69, respectively. The run was terminated voluntarily after 155 h on stream, and results from three mass balances are summarized in Table 1.

Catalyst Activity and Stability

Catalyst activity, measured by (H_2+CO) conversion and gas volumetric contraction, increased gradually with time-on-stream (Figure 1). For example, the (H_2+CO) conversion at 50 h on stream was 50%, and 57% at 150 h. The water gas shift (WGS) activity of the catalyst was high, and the (H_2/CO) usage ratio varied between 0.58 to 0.66 throughout the test.

Hydrocarbon Selectivity

The average hydrocarbon product distribution (from three mass balances in Table 1) was: 6.8 (CH_4), 22.4 (C_2–C_4), 33.1 (C_5–C_{11}) and 37.6 wt% (C_{12}^+).

A typical carbon number distribution, in the form of Anderson-Shulz-Flory (ASF) plot, is shown in Figure 2. The chain growth parameter for products in C_1–C_{11} range is 0.70. Solid product (wax) collected in a high pressure trap was not analyzed.

Methane and gaseous hydrocarbons selectivities obtained in this test were higher than those obtained in test FB-0021 (Quarterly Report for January – March, 1991) where CO reduction was used (other pretreatment and process conditions were the same as in this test). However, with H_2 reduction the catalyst activity increased with TOS, whereas the opposite trend was observed when CO reduction was employed.

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

III-2.1 Run SB-3101 with 100Fe/5Cu/8K/24SiO_2 Catalyst

This was the first slurry reactor test of this catalyst. Process conditions were: 260°C, 200 psig, 1.6 Nl/g-cat/h and $H_2/CO = 0.64$ throughout the entire test. A feed flowrate upset occurred at about 158 h, but it was corrected immediately by increasing slightly the cylinder delivery pressure. The run was terminated after 354 h on stream. Results from six mass balances made during the test are summarized in Table 2, whereas major events are listed in Table 3.

Catalyst Activity and Selectivity

The catalyst deactivated continuously with time on stream. The (H_2+CO) conversion decreased from initial value of 77% to 60% at 350 h on stream, while volumetric contraction (VC) decreased from 50% to 38% during the same time period. Changes of (H_2+CO) conversion and VC with time on stream are shown in Figure 3. WGS activity of the catalyst was high, and the (H_2/CO) usage ratio varied between 0.56-0.58.

Wax and Catalyst Withdrawals/Inventories

Wax was withdrawn periodically through a porous sintered metal filter with nominal pore size of 0.5 μm. No catalyst was found in the withdrawn wax. The wax production rate decreased from 1.4 to 1.0 g/h as the catalyst deactivated with time.

At the end of the run, 8.5 g of catalyst was recovered from the reactor slurry. Another estimated 2.4 g of catalyst was removed from the reactor during the test with slurry samples for catalyst characterization. Catalyst recovery was about 92%, whereas wax recovery was 101% based on the amounts of catalyst and wax charged into the reactor.

Hydrocarbon Selectivity

Hydrocarbon product distribution shifted gradually toward lower molecular weight products with time on stream. For example, at 40 h on stream, hydrocarbon selectivity was $(CH_4) = 4.2$, $(C_2–C_4) = 14.6$, $(C_5–C_{11}) = 25$ and $C_{12}^+ = 56.2$ wt%, while at 340 h, it became $(CH_4) = 5.5\%$, $(C_2–C_4) = 16.5$, $(C_5–C_{11}) = 23$ and $C_{12}^+ = 55$ wt%.

A typical carbon number product distribution is shown in Figure 4 in the form of ASF plot. This plot is based on products collected overhead (i.e. the wax from the reactor was not analyzed).

III-2.2 Run SA-3391 with UCI Iron/Silica Catalyst

This test was conducted as part of DOE/PETC coordinated program for evaluating one of iron/silica catalysts synthesized by United Catalysts Inc. (UCI). The nominal composition of this catalyst is $100Fe/4.3Cu/8K/17SiO_2$. The same catalyst was tested in a stirred tank slurry reactor at UOP.

About 25g of this catalyst was loaded as received (without calcination), and 330g of ETHYLFLO^{TM} 164 oil was employed as the initial slurry medium. After sealing of the reactor nitrogen was introduced at 153 psig and stirring was initiated at 1100 rpm. Then the slurry temperature was raised linearly to 280°C in 3 hours under nitrogen flow. When 280°C was reached, the nitrogen flow was replaced with synthesis gas ($H_2/CO = 0.7$), and the catalyst was pretreated at 280°C, 153 psig, 2.0 N*l*/g-Fe/h for 12 h. After the pretreatment the catalyst was tested at 265°C (it was found later that the actual temperature was 270°C), 290 psig, 3.0 N*l*/g-Fe/h and $H_2CO = 0.70$ for the first 100 h (mass balances 1 & 2). At about 103 h on stream, the gas space velocity was lowered from 3.0 to 2.4 N*l*/g-Fe/h (mass balance 3). After the third balance, the temperatures of the reactor head and the exit line were decreased by 30-40°C while the process conditions were unchanged (mass balance 4). At 193h on stream, the reactor temperature was lowered to actual 265°C (mass balance 5). The feed was switched to premixed synthesis gas ($H_2/CO = 0.67$) at 287 h (mass balance 6), and the test was terminated voluntarily after 310 h on stream. Results from six mass balances made during the test are summarized in Table 4, whereas major events are listed in Table 5.

Catalyst Activity and Stability

Changes in (H_2+CO) conversion and VC with time-on-stream at various process conditions are shown in Figure 5. After reaching the initial process conditions of 265°C (270°C actual), 290 psig, 3.0 Nl/g-Fe/h, the (H_2+CO) conversion increased gradually from 76% at 3 h to 80% at 24 h, then it remained stable during the next 80 h of testing. At about 103 h, gas flow rate was decreased (SV = 2.4 Nl/g-Fe/h) in order to test the catalyst under the same conditions as those employed at UOP. Consequently, the (H_2+CO) conversion increased to 82-83% and was stable during the next 60 h on stream. Since our values of the (H_2+CO) conversion (83%) and methane selectivity (~8%) were significantly greater than those obtained at UOP (70% and 4.0%, respectively) we suspected that there may be some problems with our apparatus. The (H_2+CO) conversion decreased to 79%, when temperature of the reactor head was decreased from 270 to 230°C and that of the exit line from 250 to 210°C at 170 h on stream, whereas the slurry temperature was maintained at 265°C (i.e. 270°C). An error in the temperature readout device was confirmed at this time. At 196 h, the reactor temperature was corrected from 270 to 265°C, and the (H_2+CO) conversion decreased further to 75%. During remaining 110 h of testing (196 to 310 h), the catalyst activity decreased slowly with time. For example, the (H_2+CO) conversion was about 71.5% at 310 h. These conversions are similar to those obtained at UOP.

WGS activity of the catalyst was high and stable throughout the entire test. The usage ratio varied between 0.56 to 0.61.

Wax and Catalyst Withdrawals/Inventories

The withdrawals were made daily through a porous metal filter at an initial pressure drop across the filter of 15 psig during the first 2-3 days of testing. However, after four days on stream the pressure drop had to be increased to 80 psig in order to facilitate wax withdrawal. No catalyst was found in the withdrawn wax. During the test, three slurry samples were withdrawn for future catalyst characterization.

At the end of the run, about 268g of wax was recovered from the reactor, whereas the initial amount (after the slurry sample and wax withdrawals following the pretreatment) was estimated to be 235g. This discrepancy is partly due to different gas hold-up in the slurry at the beginning and at the end of the test (different feed flow rate and slurry temperature).

Hydrocarbon Selectivity

The initial methane selectivity was about 4.2 wt% (at 3 h on stream). Then it increased continuously with time during the next 150 h. For example, at 140 h (270°C, 290 psig, 2.4 Nl/g-Fe/h) hydrocarbon selectivity was $(CH_4) = 8.2$, $(C_2\text{–}C_4) = 17.5$, $(C_5\text{–}C_{11}) = 20.0$ and $C_{12}^+ = 45.6$ wt%. However, methane selectivity immediately dropped to 5.3 wt% when temperatures of the reactor head and exit line were decreased by 30-40°C (after 173 h). It seems that a hot spot existed along the exit line which either caused cracking of hydrocarbon products to methane, or catalyzed FT synthesis reaction (but mainly forming C1-C2 products because of short contact time). After correcting the reactor temperature to 265°C, methane selectivity decreased further. The average hydrocarbon product distribution from the last two mass balances made at 265°C, 290 psig, 2.4 Nl/g-Fe/h, $H_2/CO = 0.70\text{-}0.67$ was: $(CH_4) = 4.4$ $(C_2\text{–}C_4) = 16.5$, $(C_5\text{–}C_{11}) = 23.6$ and $C_{12}^+ = 55.5$ wt%. As stated earlier, methane selectivity of about 4.0% was obtained during testing of this catalyst at UOP.

Carbon number distribution obtained from balance 5 is given in Figure 6, in the form of ASF plot. Wax withdrawn from the reactor was not analyzed, which explains the rapid decrease in concentration of C_{17}^+ products shown on the plot.

III-3 Catalyst Characterization

During the current reporting period, residual amounts of potassium in the newly prepared catalysts were determined by atomic absorption (AA). Some of the previously prepared fresh catalysts were characterized by surface area/pore size distribution measurement (BET/PSD), and X-ray diffraction (XRD). Also, we have continued our characterization studies of reduced and catalyst samples by XRD. The following sections contain detailed descriptions of progress in each of these areas.

Preparation and Elemental Analysis of Catalysts

Previously prepared 100Fe/5Cu/100SiO$_2$ catalyst was washed with distilled water again to remove excessive amount of potassium on it, and the composition was determined by AA. In order to check reproducibility of experimental results some other catalyst samples were also measured, and results are summarized in Table 6. By washing the 100Fe/5Cu/100SiO$_2$ for another week, the residual amount of potassium decreased from 4.6 parts by weight (S5000-1) to 2.1 parts by weight (S5000-2). By further washing, the potassium content decreased to 1.1 parts by weight (S5000-4), although contents of copper and silica were almost unchanged.

Reproducibility of measurements made at TAMU was quite satisfactory, however the potassium content in sample S-5000-1 measured at Galbraith Laboratories Inc. (by ICP) was significantly lower than that obtain at TAMU (2.7 vs. 4.5).

Surface Area and Pore Size Distribution

Surface areas and pore volumes were measured by physical adsorption of N$_2$ at 77 K, and values obtained are listed in Table 7, whereas differential pore volume distributions are shown in Fig. 7 Surface area (SA) of calcined 100Fe/0.3Cu/0.8K catalyst sample (C0308-1) was slightly larger than that of another batch with the same composition (C0308-3), and pore volume (v$_p$) was slightly smaller, resulting in smaller average pore diameter (d$_p$). A smaller surface area (~150 m^2/g) was obtained for calcined 100Fe/5Cu/4.2K/100SiO$_2$ catalyst sample than for other calcined 100Fe/5Cu/4.2K/zSiO$_2$ catalyst samples in this series (z = 0, 8, 16, 24, 40). For these catalysts the surface areas were between 180 and 260 m^2/g, and the value obtained with z = 100 is believed to be in error. The pore volume of 0.83 cm^3/g was higher than that obtained with catalysts containing less silica, which is as expected.

X-Ray Diffraction of Fresh Catalysts

As-prepared and calcined catalysts with nominal composition of 100Fe/0.3Cu/0.8K, as well as commercial catalysts (Ruhrchemie and UCI), were characterized by XRD. X-ray diffraction patterns depicted in Figure 8 show that the main phase in each of catalyst samples is Fe_2O_3. The differences on peak intensity and width indicate differences in crystallite sizes. The crystallite sizes were estimated by the line broadening method and summarized in Table 8. The peaks of as-prepared 100Fe/0.3Cu/0.8 catalyst sample (C0308-1) and of the Ruhrchemie catalyst samples were too broad and unresolved to determine the crystallite sizes. It is presumed that these crystallite sizes were less than 50 Å. The average crystallite size of as-prepared C0308-3 catalyst was almost the same as of the calcined one, but was significantly greater than that of C0308-1 catalyst. After calcination the difference in crystallite sizes of these two catalyst batches becomes smaller. The larger crystallite size coincides with large pore diameter, as mentioned above. Although the preparation procedure and the chemical compositions of these catalysts were almost the same, as reported previously, there are some differences in their physical properties.

X-Ray Diffraction of Reduced Catalysts

During the present reporting period, catalyst with nominal composition of 100Fe/0.3Cu/0.8K (C-0308-3) was reduced under various conditions, and the pretreatment effects on the initial phases of reduced catalysts were investigated by XRD. Results are summarized in Table 9 and Figures 9 and 10.

Figure 9 shows XRD patterns of the 100Fe/0.3Cu/0.8K catalyst after calcination, and reduction with H_2 under various conditions. Calcined catalyst showed a typical pattern of Fe_2O_3. After reduction with H_2 at 220°C for 1 h, this phase changed into Fe_3O_4 mainly. At a higher reduction temperature (250°C) with the same flow rate and duration, the XRD pattern was typical of metallic iron with very sharp peaks, indicating large crystallite size. On the other hand, reduction at even higher temperature (280°C) and of longer duration (8 h), but at lower flow rate, resulted in formation of metallic iron and magnetite (Fig. 9d). These results imply that high flow rate of H_2 is needed for complete reduction of iron in the catalyst.

Figure 10 shows the XRD patterns of the 100Fe/0.3Cu/0.8K catalyst reduced with (a) CO at 280°C for 8 h, (b) $H_2/CO = 2$ at 310°C for 6 h, and (c) $H_2/CO = 0.67$ at 280°C for 8 h. In all three cases χ-carbide (Fe_5C_2) was identified as the dominant phase.

X-Ray Diffraction of Used Catalysts from Fixed Bed Reactor

Figure 11 shows XRD patterns of used catalysts from top and bottom parts of a fixed bed reactor. Nominal catalyst composition and reduction conditions are listed in Table 10. No significant difference in the patterns was found between catalyst samples from top and bottom parts, indicating that phases were uniform throughout the reactor. With H_2 reductions, the main phase in used catalysts was always iron carbide(s), as shown in Fig. 11 (a) and (b). A small peak of metallic iron was found in a sample from Run FB-3221 from top part of the reactor (a-1). On the other hand, in the case of CO reduction (Fig. 11 (c) and (d)), magnetite was identified as the main phase in used catalysts. With increasing silica content, the peak intensity decreased, probably because of smaller crystallite sizes of the original iron phases.

Mössbauer Effect Spectroscopy (MES)

We have sent 39 catalyst samples to the University of Kentucky (CFFLS) for characterization by MES, but have not received any results yet.

Table 1. Summary of results for .ed bed run FB-3221 .

Catalyst: 3.50 g^a, 100Fe/0.3Cu/0.8K
Catalyst volume: 3.60 *cc*

Diluent: 33.67 *g*, Glass beads
Diluent Volume: 22.50 *cc*

Period	1	2	3
Date	11/21/91	11/23/91	11/24/91
Time on Stream (*h*)	72.5	120.5	149.0
Balance Duration (*h*)	7.5	6.5	6.5
Average Temperature (°C)	250.	250.	250.
Maximum Δ Temperature (°C)[b]	4.00	5.00	5.00
Pressure (*MPa*)	1.48	1.48	1.48
H_2/CO Feed Ratio	.667	.686	.686
Space Velocity (*Nl*/*g*–cat·*h*)[a]	2.01	2.00	2.00
Space Velocity (*Nl*/*g*–Fe·*h*)	2.91	2.91	2.91
GHSV (h^{-1})[c]	268.	267.	267.
CO Conversion (%)	56.0	56.4	60.9
H_2+CO Conversion (%)	54.1	54.2	58.2
H_2/CO Usage	.609	.620	.612
STY (*mols* H_2+CO/*g*–cat·*h*)[a]	.048	.048	.052
$P_{CO_2} \cdot P_{H_2} / P_{CO} \cdot P_{H_2O}$	46.5	42.0	48.4
Weight % of Outlet			
H_2	2.24	2.31	2.15
H_2O	.272	.309	.305
CO	42.0	41.5	37.3
CO_2	41.8	41.0	44.9
Hydrocarbons	9.09	9.13	8.83
Oxygenates	.968	1.08	1.23
Wax[d]	3.63	4.67	5.31
Yield (g/Nm^3 H_2 + CO *Converted*)			
CH_4	12.6	13.5	12.8
C_2–C_4 Hydrocarbons	42.4	43.3	42.3
C_5–C_{11} Hydrocarbons	69.9	62.1	57.0
C_{12}+ Hydrocarbons	59.8	78.8	76.7
Wax[d]	52.7	66.9	70.9
Oxygenates	14.0	15.5	16.4
Total	199.	213.	205.
1+2 Olefins/*n*–Paraffin Ratio			
C_2	2.81	2.53	2.57
C_3	4.21	4.30	4.28
C_4	3.48	3.62	3.18
C_8	1.93	2.06	2.12
C_{10}	2.60	2.55	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 FB-3221 .

Period	1	2	3
Weight % of Hydrocarbons			
CH4	6.81	6.82	6.80
Ethane	1.76	1.84	1.86
Ethylene	4.63	4.34	4.45
Propane	1.79	1.68	1.72
Propylene	7.20	6.89	7.03
n–Butane	1.71	1.57	1.62
1+2 Butenes	5.75	5.50	4.98
C_4 Isomers	.125	.103	.746
n–Pentane	1.85	1.73	1.68
1+2 Pentenes	5.10	4.75	4.83
C_5 Isomers	4.28	3.89	.990
n–Hexane	1.48	1.27	1.29
1+2 Hexenes	3.74	3.20	3.23
C_6 Isomers	1.59	1.47	1.47
n–Heptane	1.68	1.35	1.36
1+2 Heptenes	3.25	2.74	2.80
C_7 Isomers	1.16	.891	.880
n–Octane	1.46	.974	1.04
1+2 Octenes	2.75	1.97	2.18
C_8 Isomers	.974	.578	.764
n–Nonane	.778	.583	.668
1+2 Nonenes	1.98	1.47	1.71
C_9 Isomers	.439	.312	.417
n–Decane	.693	.553	.650
1+2 Decenes	1.78	1.39	1.65
C_{10} Isomers	.483	.324	.462
n–Undecane	.564	.483	.522
1+2 Undecenes	1.40	1.18	1.29
C_{11} Isomers	.405	.302	.320
C_2–C_4	23.0	21.9	22.4
C_5–C_{11}	37.8	31.4	30.2
C_{12}+	32.4	39.9	40.6
Wax[d]	28.5	33.8	37.6

[d] Unanalyzed products collected from hot trap

Table 2. Summary of results slurry run SB-3101 .

Catalyst: 11.70 g^a, 100Fe/5Cu/8K/24SiO_2 Slurry liquid: 290.0 g, n-C28

Reactor volume: 430. cc^b

Period	1	2	3	4	5	6
Date	11/08/91	11/10/91	11/13/91	11/16/91	11/19/91	11/21/91
Time on Stream (h)	39.0	86.0	171.0	243.0	302.0	339.5
Balance Duration (h)	8.0	6.5	11.0	12.0	6.5	11.0
Average Temperature (°C)	260.	260.	260.	260.	260.	260.
Pressure (MPa)	1.48	1.48	1.48	1.48	1.48	1.48
H_2/CO Feed Ratio	.645	.645	.650	.650	.650	.639
Space Velocity (Nl/g-cat·h)[a]	1.62	1.62	1.62	1.60	1.63	1.63
Space Velocity (Nl/g-Fe·h)	3.11	3.11	3.11	3.08	3.14	3.14
GHSV (h^{-1})[b]	44.0	44.0	44.0	40.2	40.9	40.9
CO Conversion (%)	78.6	75.2	70.5	67.1	65.0	62.8
H_2+CO Conversion (%)	74.4	72.3	67.7	64.1	61.3	60.1
H_2/CO Usage	.557	.581	.586	.577	.556	.570
STY ($mols$ H_2+CO/g-cat·h)[a]	.054	.052	.049	.046	.044	.044
$P_{CO_2} \cdot P_{H_2} / P_{CO} \cdot P_{H_2O}$	50.5	42.6	26.3	26.1	28.2	32.1
Weight % of Outlet						
H_2	1.42	1.43	1.62	1.80	2.00	1.91
H_2O	.463	.456	.668	.633	.565	.447
CO	20.4	23.6	28.0	31.3	33.7	35.1
CO_2	59.0	56.6	53.3	50.4	47.2	46.3
Hydrocarbons	9.52	9.69	9.61	9.53	9.10	8.75
Oxygenates	.177	.201	.155	.129	.568	.465
Wax[c]	8.96	7.96	6.63	6.18	6.93	7.04
Yield (g/Nm^3 $H_2 + CO$ *Converted*)						
CH_4	8.37	8.95	9.49	10.7	10.8	11.7
C_2–C_4 Hydrocarbons	29.0	29.0	30.4	33.7	33.1	35.1
C_5–C_{11} Hydrocarbons	49.6	50.1	51.9	51.5	47.9	48.0
C_{12}+ Hydrocarbons	111.	107.	99.7	99.1	114.	117.
Wax[c]	96.1	87.8	78.2	76.7	89.2	94.6
Oxygenates	1.90	2.22	1.82	1.60	7.31	6.24
Total	200.	197.	193.	197.	214.	218.
1+2 Olefins/n-Paraffin Ratio						
C_2	3.34	2.99	2.86	2.74	2.63	2.49
C_3	6.21	6.22	5.86	5.80	5.75	5.63
C_4	4.91	5.41	4.86	4.54	4.59	4.44
C_8	3.18	3.23	2.74	2.58	2.30	2.44
C_{10}	1.46	2.99	2.92	2.90	3.00	2.40

[a] Based on unreduced catalyst

[b] Based on static slurry volume

[c] Unanalyzed wax withdrawn from reactor

Table 2 (cont'd). Summary of results for slurry run SB-3101 .

Period	1	2	3	4	5	6
Weight % of Hydrocarbons						
CH4	4.22	4.60	4.96	5.49	5.22	5.52
Ethane	1.09	1.10	1.17	1.31	1.24	1.33
Ethylene	3.40	3.08	3.13	3.34	3.06	3.10
Propane	.805	.838	945	1.04	.975	1.02
Propylene	4.77	4.97	5.28	5.74	5.35	5.48
n–Butane	.709	.773	.887	1.00	.924	.959
1+2 Butenes	3.36	4.04	4.16	4.40	4.09	4.11
C_4 Isomers	.514	.114	.300	.455	.423	.547
n–Pentane	.722	.771	.926	.973	.960	.937
1+2 Pentenes	3.15	3.37	3.63	3.76	3.52	3.54
C_5 Isomers	.720	2.43	2.27	2.35	2.13	2.26
n–Hexane	.855	.935	.989	.882	.911	.910
1+2 Hexenes	2.41	2.62	2.62	2.56	2.47	2.60
C_6 Isomers	.869	1.10	1.05	1.17	1.12	1.16
n–Heptane	.587	.667	.800	.809	.845	.814
1+2 Heptenes	1.80	2.03	2.07	2.08	1.93	1.94
C_7 Isomers	.612	.885	.819	.794	.663	.724
n–Octane	.550	.578	.749	.756	.746	.656
1+2 Octenes	1.72	1.84	2.02	1.91	1.69	1.57
C_8 Isomers	.513	.841	.503	.403	.471	.427
n–Nonane	.619	.453	.568	.538	.544	.459
1+2 Nonenes	1.54	1.50	1.77	1.63	1.26	1.09
C_9 Isomers	.471	.289	.334	.333	.278	.236
n–Decane	1.18	.568	.626	.570	.381	.393
1+2 Decenes	1.70	1.67	1.80	1.63	1.12	.929
C_{10} Isomers	1.27	.501	.450	.444	.363	.305
n–Undecane	.674	.549	.638	.600	.349	.335
1+2 Undecenes	1.71	1.81	2.00	1.83	1.09	1.06
C_{11} Isomers	1.37	.323	.459	.390	.387	.309
C_2–C_4	14.6	14.9	15.9	17.3	16.1	16.5
C_5–C_{11}	25.0	25.7	27.1	26.4	23.2	22.7
C_{12}+	56.1	54.7	52.1	50.8	55.5	55.3
Wax[c]	48.5	45.1	40.8	39.3	43.2	44.6

[c] Unanalyzed wax withdrawn from reactor

Table 3. Major events in Run SB-3101

TOS (h)	Event
	Slurry loading: 310 g n-octacosane, 12.5 g catalyst (particle size <270 mesh)
	Catalyst pretreatment: H_2 at 250°C
	Slurry sample withdrawal: 20.4 g wax, 0.8 g catalyst
	Wax withdrawal through filter: 6.31 g of wax
0	Initiate synthesis gas flow
1	Achieved process conditions: T=260°C, P=1.48 MPa, SV= 1.6 Nl/g-cat/h, (H_2/CO=0.64)
158	Discovered decrease in feed flow rate and restored to desired flow rate
182	Slurry sample withdrawal: 24.5 g wax, 0.9 g catalyst
352	Slurry sample withdrawal: 49.3 g wax, 1.4 g catalyst
354	End of run: 287 g wax, 8.5 g catalyst recovered from reactor
	Wax/catalyst removed during the run: 400 g of wax, 2.3 g of catalyst
	Catalyst recovery: 92.3%; Wax recovery: 101%

Table 4. Summary of results slurry run SA-3391 .

Catalyst: 23.60 g^a, 100Fe/4.3Cu/8K/17SiO_2 Slurry liquid: 240.0 g, C30

Reactor volume: 400. cc^b

Period	1	2	3	4	5	6
Date	12/08/91	12/10/91	12/12/91	12/14/91	12/16/91	12/19/91
Time on Stream (h)	43.0	91.0	139.0	187.0	235.0	297.0
Balance Duration (h)	7.0	6.0	6.0	6.0	6.0	10.0
Average Temperature (°C)	270.	270.	270.	270.	265.	265.
Pressure (MPa)	2.10	2.10	2.10	2.10	2.10	2.10
H_2/CO Feed Ratio	.698	.698	.698	.698	.698	.669
Space Velocity (Nl/g-cat·h)[a]	1.71	1.71	1.37	1.37	1.37	1.37
Space Velocity (Nl/g-Fe·h)	2.99	2.99	2.39	2.39	2.39	2.40
GHSV (h^{-1})[b]	101.	101.	74.2	74.2	74.2	67.5
CO Conversion (%)	85.5	85.9	87.3	84.6	79.2	73.9
H_2+CO Conversion (%)	79.9	81.1	82.8	79.3	74.4	71.7
H_2/CO Usage	.587	.604	.612	.592	.595	.620
STY ($mols$ H_2+CO/g-cat·h)[a]	.061	.062	.051	.048	.045	.044
$P_{CO_2} \cdot P_{H_2} / P_{CO} \cdot P_{H_2O}$	21.4	22.5	21.6	22.3	18.8	13.8
Weight % of Outlet						
H_2	1.37	1.23	1.11	1.36	1.56	1.45
H_2O	1.60	1.45	1.53	1.46	1.37	1.28
CO	14.1	13.6	12.0	14.8	19.9	25.0
CO_2	61.9	62.9	62.7	62.1	57.9	53.2
Hydrocarbons	10.0	10.9	12.1	10.9	9.63	10.1
Oxygenates	.218	.294	.368	.368	.413	.409
Wax[c]	10.7	9.72	10.2	9.07	9.27	8.56
Yield (g/Nm^3 $H_2 +$ CO *Converted*)						
CH_4	12.2	14.9	17.2	10.3	8.91	8.45
C_2–C_4 Hydrocarbons	30.6	32.6	36.7	34.8	33.8	32.0
C_5–C_{11} Hydrocarbons	34.3	38.2	42.1	44.8	42.3	52.0
C_{12}+ Hydrocarbons	119.	109.	114.	104.	110.	111.
Wax[c]	101.	92.1	95.9	87.9	95.8	93.5
Oxygenates	2.06	2.78	3.47	3.56	4.27	4.47
Total	198.	198.	214.	197.	200.	208.
1+2 Olefins/n–Paraffin Ratio						
C_2	1.41	1.14	.871	1.59	2.38	2.50
C_3	6.13	5.61	5.19	6.19	6.11	6.22
C_4	5.41	5.01	4.78	5.57	5.61	5.48
C_8	2.91	2.85	2.57	3.44	3.70	3.29
C_{10}	2.28	2.08	2.25	2.69	2.96	2.68

[a] Based on unreduced catalyst

[b] Based on static slurry volume

[c] Unanalyzed wax withdrawn from reactor

Table 4 (cont'd). Summary of resı for slurry run SA-3391 .

Period	1	2	3	4	5	6
Weight % of Hydrocarbons						
CH4	6.20	7.64	8.19	5.30	4.56	4.15
Ethane	2.05	2.51	3.02	2.18	1.57	1.38
Ethylene	2.71	2.68	2.45	3.23	3.49	3.21
Propane	.915	1.04	1.15	1.04	1.01	.898
Propylene	5.35	5.57	5.70	6.14	5.89	5.33
n–Butane	.722	.832	.902	.829	.819	.762
1+2 Butenes	3.77	4.02	4.16	4.46	4.43	4.03
C_4 Isomers	.0614	.0689	.0716	.0825	.0897	.0857
n–Pentane	.621	.767	.846	.732	.728	.707
1+2 Pentenes	2.98	3.17	3.26	3.62	3.69	3.37
C_5 Isomers	.642	.693	.792	.837	.845	2.35
n–Hexane	.603	.703	.790	.729	.677	.820
1+2 Hexenes	2.10	2.18	2.34	2.76	2.50	2.82
C_6 Isomers	.793	.824	.880	1.06	.927	1.04
n–Heptane	.510	.625	.680	.666	.587	.636
1+2 Heptenes	1.72	1.93	1.95	2.38	2.26	2.34
C_7 Isomers	.680	.667	.686	.770	.559	.744
n–Octane	.452	.536	.577	.544	.470	.547
1+2 Octenes	1.29	1.50	1.45	1.84	1.71	1.77
C_8 Isomers	.527	.726	.442	.622	.386	.588
n–Nonane	.350	.436	.464	.443	.402	.475
1+2 Nonenes	.907	1.02	1.07	1.32	1.26	1.40
C_9 Isomers	.214	.294	.304	.418	.348	.503
n–Decane	.379	.476	.442	.490	.433	.527
1+2 Decenes	.852	.978	.981	1.30	1.26	1.39
C_{10} Isomers	.293	.375	.380	.492	.510	.789
n–Undecane	.383	.410	.422	.475	.419	.495
1+2 Undecenes	.859	.937	.918	1.20	1.22	1.43
C_{11} Isomers	.324	.331	.341	.437	.470	.784
C_2–C_4	15.6	16.7	17.5	18.0	17.3	15.7
C_5–C_{11}	17.5	19.6	20.0	23.1	21.7	25.5
C_{12}+	60.7	56.1	54.3	53.6	56.5	54.6
Wax[c]	51.6	47.3	45.6	45.4	49.0	45.9

[c] Unanalyzed wax withdrawn from reactor

Table 5. Major events in Run SA-3391

TOS (h)	Event
	Slurry loading: 335 g ethylflo 164 (C30) liquid, 25.0 g catalyst (particle size <270 mesh)
	Catalyst pretreatment: $H_2/CO=0.70$, T=285°C, P=1.14 MPa, SV=2.0 N*l*/g-Fe/h, for 12 h
	Slurry sample withdrawal: 18.7 g wax, 1.4 g catalyst, temperature was lowered from 285 to 270°C over 3 h
	Wax withdrawal through filter: 81.0 g of wax
0	Achieved process conditions: T=270°C, P=2.10 MPa, SV= 3.0 N*l*/g-Fe/h, feed $(H_2/CO)=0.70$
98	Slurry sample withdrawal: 25 g wax, 1.9 g catalyst
101	Space velocity change from 3.0 to 2.4 N*l*/g-Fe/h
173	Lowered reactor head (270 → 230°C) and exit line temperature (250 → 210°C)
196	Slurry temperature was lowered from 270°C to 265°C
265	Slurry sample withdrawal: 25 g wax, 2.0 g catalyst
287	Feed gas changed to $(H_2/CO)=0.67$
310	End of run: 288 g slurry recovered from the reactor
	Wax/catalyst removed during the run: 726 g of wax/3.9 g of catalyst

Table 6. Catalyst Composition Determined by Atomic Absorption

Nominal Composition $100Fe/xCu/yK/zSiO_2$	ID #	Actual Composition x	y	$z^{*)}$
$100Fe/5Cu/4.2K/40SiO_2$	#63.2	5.6±0.5	6.7±0.5	38±9
		(5.1±0.5	6.6±0.8	39±5)
$100Fe/5Cu/100SiO_2$	S5000-1	5.4±0.5	4.6±0.5	112±10
		(5.0±0.4	4.4±0.5	112±8)
		[4.6	2.7	100]
$100Fe/5Cu/100SiO_2$	S5000-2	5.3±0.5	2.1±0.3	105±10
$100Fe/5Cu/100SiO_2$	S5000-4	5.2±0.5	1.1±0.1	104±10
$100Fe/5Cu/4.2K/100SiO_2$	#69	5.0±0.4	9.4±1.1	95±10
		(4.6±0.4	8.0±1.0	95±8)
Ruhrchemie catalyst	#99	5.6±0.5	5.1±0.6	31±9
		(5.3±0.5	5.6±0.7	30±8)

*) Estimated by calculation, by determining contents of Fe, Cu and K, and by assuming that the remainder is SiO_2.

( ) Previous results.

[ ] Determined by Galbraith Lab. Inc.

Table 7. BET and PSD Result of Calcined Catalyst Samples

Catalyst composition	Catalyst Code	$SA^{a)}$ (m^2/g)	$V_p^{b)}$ (cc/g)	$\bar{d}_p^{c)}$ (Å)
100Fe/0.3Cu/0.8K	C0308-1	151.5±1.1	0.26	69
100Fe/0.3Cu/0.8K	C0308-3d)	129.6±1.5	0.33	101
$100Fe/5Cu/4.2K/100SiO_2$	#69	149.7±0.2	0.83	222

a) Surface area.
b) Pore Volume.
c) $\bar{d}_p = 4 \times V_p / SA$.
d) Reported in Quarterly Report #7 (April – June, 1991).

Table 8. X-ray Diffraction Analysis of Fresh Catalysts

Catalyst	Composition	Gas Temperature	Phase	Crystallite size (Å)
C-0308-1	100Fe/0.3Cu/0.8K	as-prepared	Fe_2O_3 (?)	*
C-0308-1	100Fe/0.3Cu/0.8K	calcined	Fe_2O_3	160 – 190
C-0308-3	100Fe/0.3Cu/0.8K	as-prepared	Fe_2O_3	240 – 270
C0308-3**)	100Fe/0.3Cu/0.8K	calcined	Fe_2O_3	220 – 370
Ruhrchemie LP33/81		as-prepared	Fe_2O_3	*
Ruhrchemie LP33/81		calcined	Fe_2O_3	*
UCI		as-prepared	Fe_2O_3	470

*) The peaks were too broad to determine the crystallite size.
**) Reported in Quarterly Report #7 (April – June, 1991).

Table 9. X-Ray Diffraction Analysis of Reduced 100Fe/0.3Cu/0.8K Catalyst

Reduction Conditions				
Gas	Flow rate (ml/min)	Temp. (°C)	Duration (h)	Phase
H_2	3350	220	1	Fe_3O_4 (+ Fe)
H_2	3350	250	2	Fe
H_2	85	280	8	Fe_3O_4 + Fe
CO	85	280	8	χ-$Fe_{2.5}C$ (Fe_5C_2)
(H_2/CO) = 2	1200	310	6	χ-$Fe_{2.5}C$ (Fe_5C_2)
(H_2/CO) = 0.67	85	280	8	χ-$Fe_{2.5}C$ (Fe_5C_2)

Table 10. X-Ray Diffraction Analysis of Used Catalysts from Fixed Bed Reactor

			Reduction Condition			
Run #	Location	Catalyst Composition	Gas	T(°C)	t(h)	Phase
FB-3221	(top)	100Fe/0.3Cu/0.8K	H_2	280	8	Fe_2C Fe
FB-3221	(bottom)	↑	↑	↑	↑	Fe_2C
FA-0959		100Fe/5Cu/4.2K/16SiO_2	H_2	220	8	Fe_xC
FB-2671	(top)	100Fe/5Cu/4.2K/40SiO_2	CO	280	12	Fe_3O_4
FB-2671	(bottom)	↑	↑	↑	↑	Fe_3O_4
FB-2391	(top)	100Fe/5Cu/4.2K/100SiO_2	CO	280	12	Fe_3O_4
FB-2391	(bottom)	↑	↑	↑	↑	Fe_3O_4

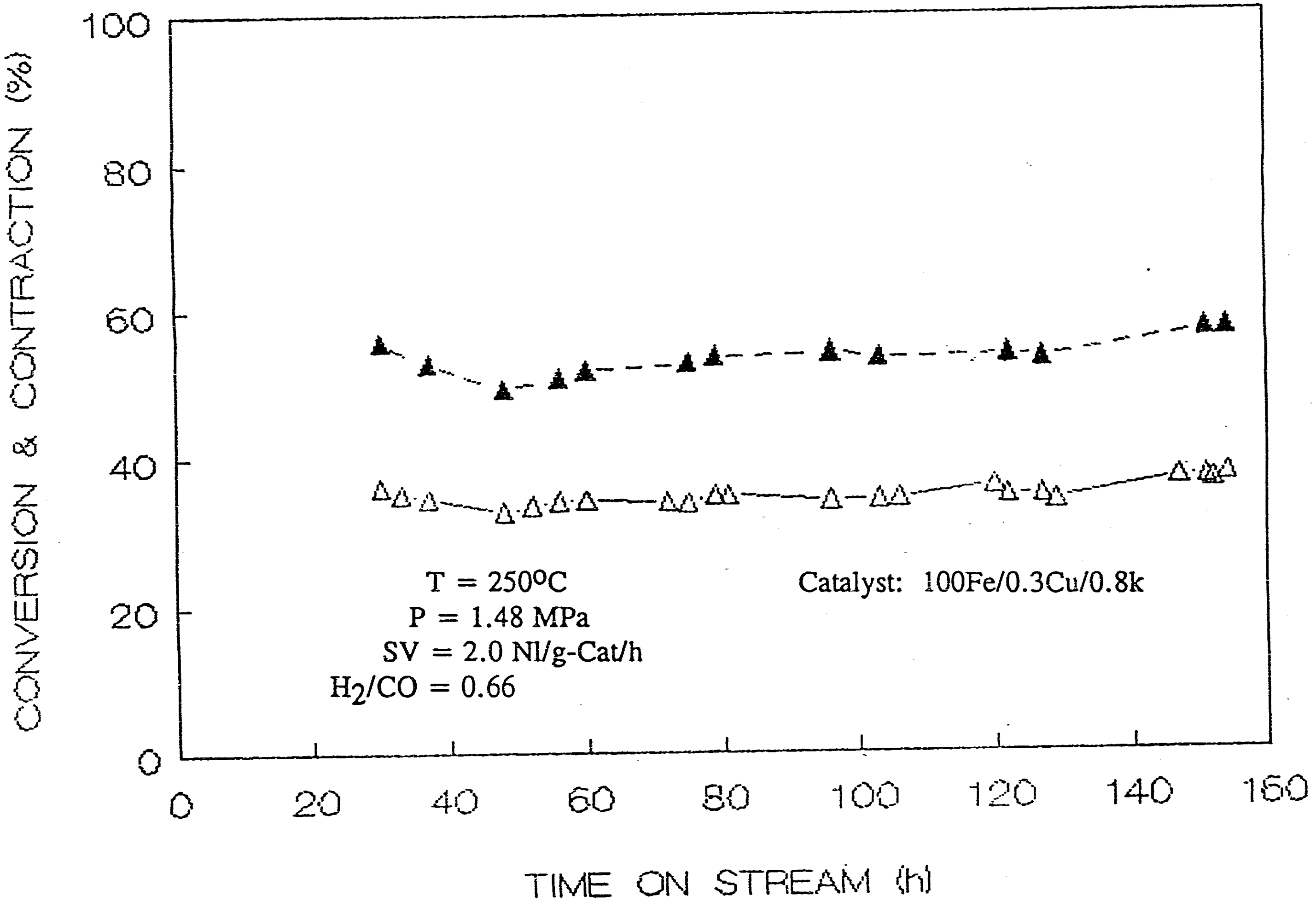


Figure 1. (H_2+CO) conversion (solid symbols) and volumetric contraction (open symbols) versus time on stream for run FB-3221.

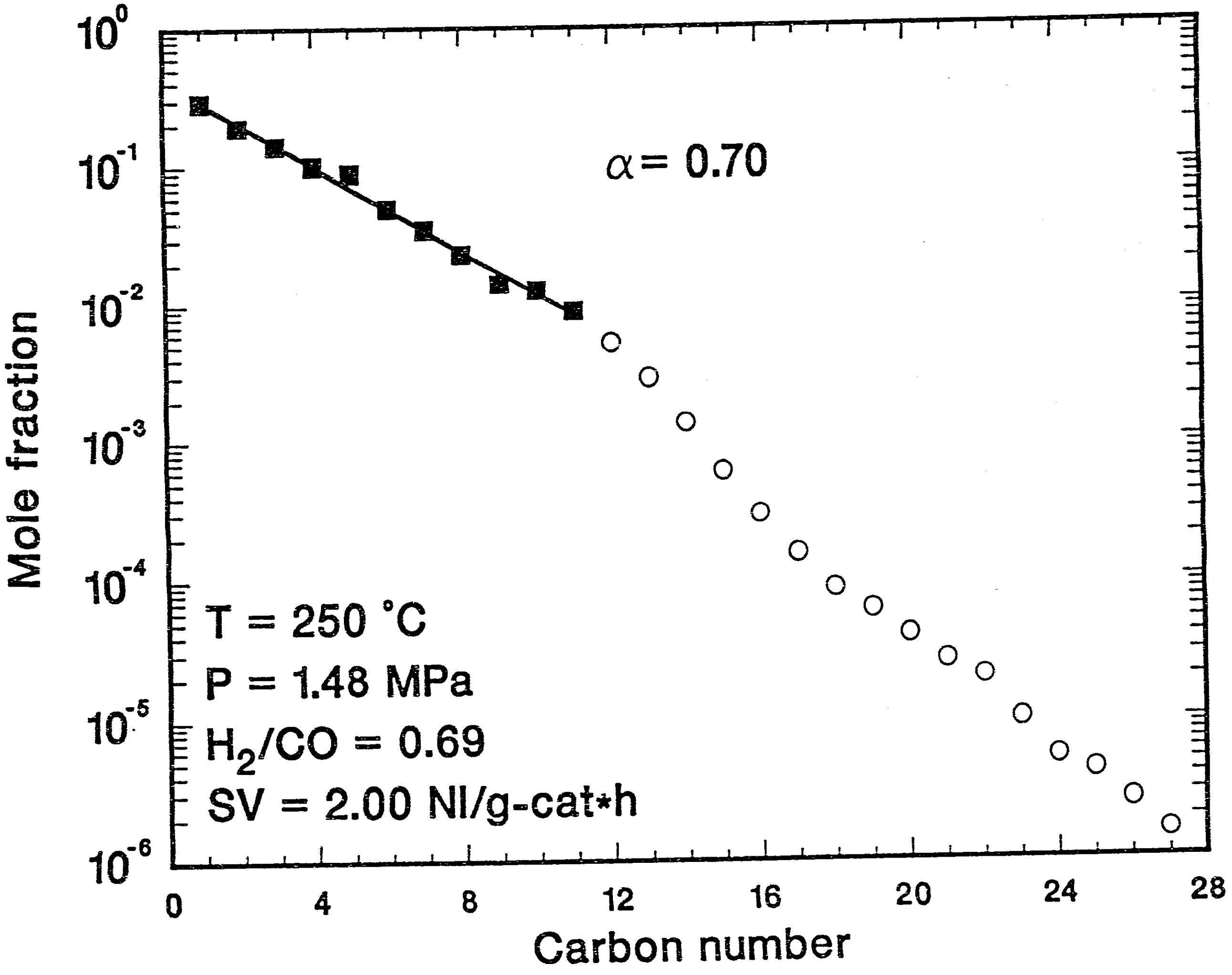


Figure 2. Anderson-Schulz-Flory plot for run FB-3221, balance 3, total products excluding wax.

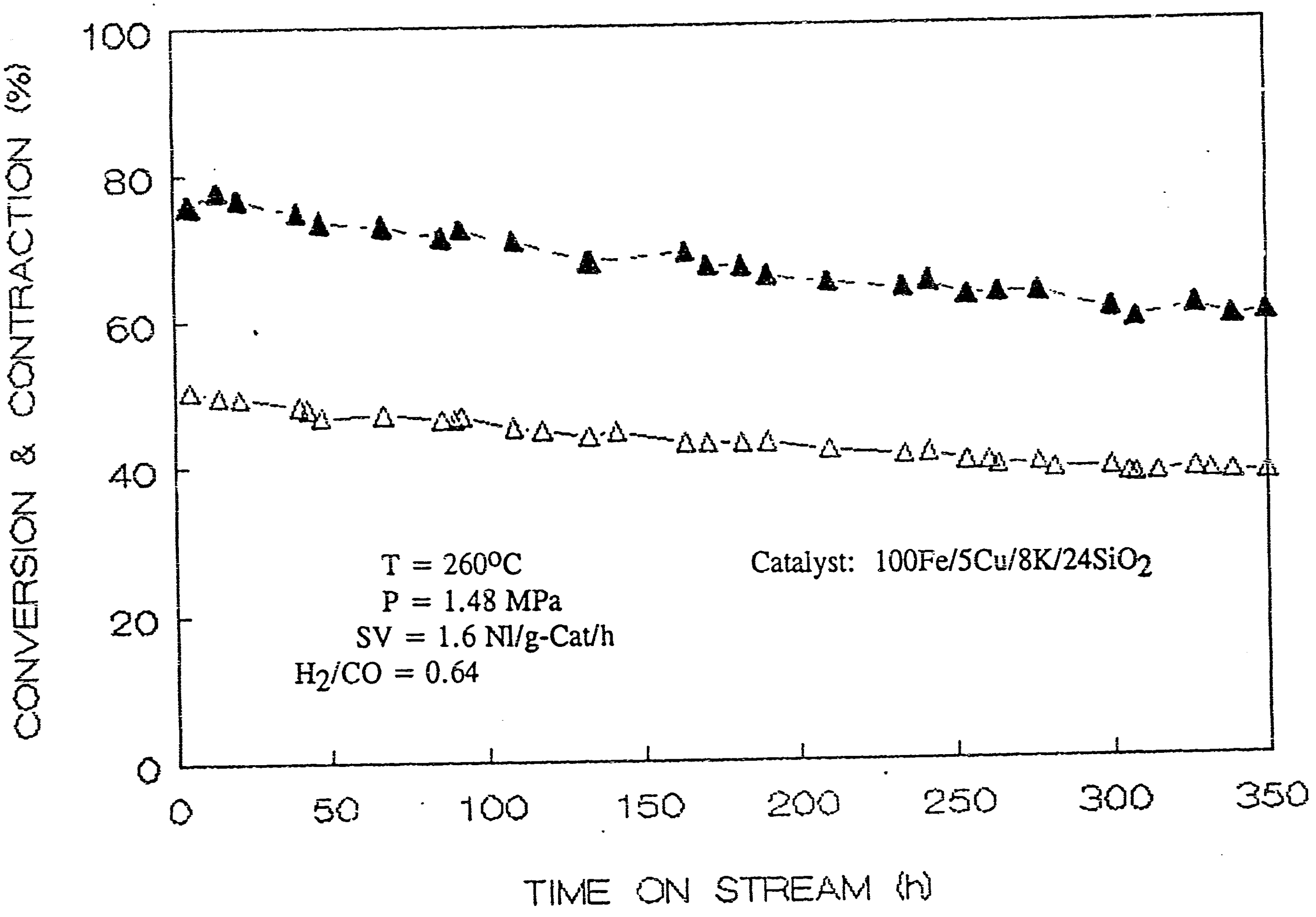


Figure 3. (H_2+CO) conversion (solid symbols) and volumetric contraction (open symbols) versus time on stream for run SB-3101.

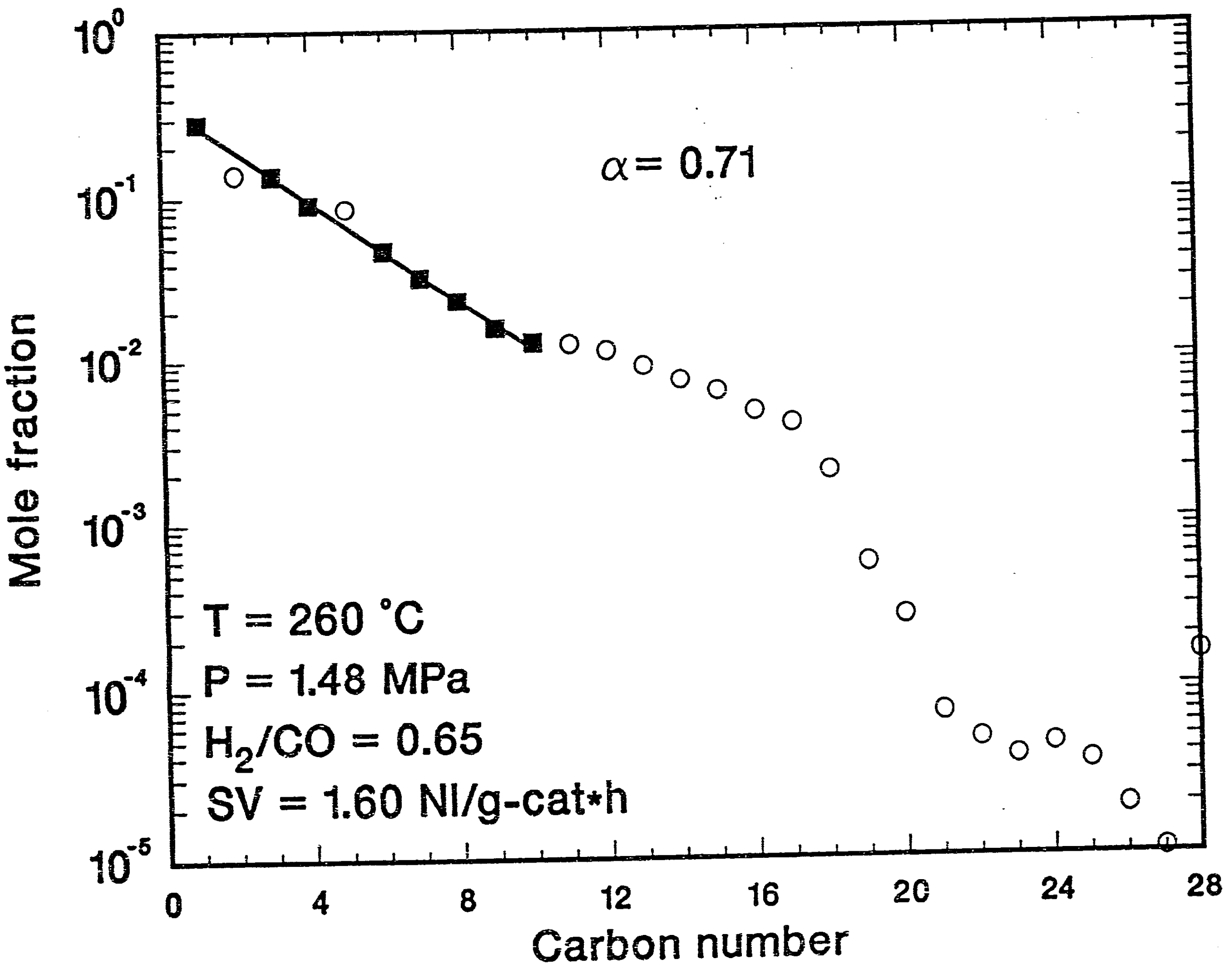


Figure 4. Anderson-Schulz-Flory plot for run SB-3101, balance 4, total products excluding wax.

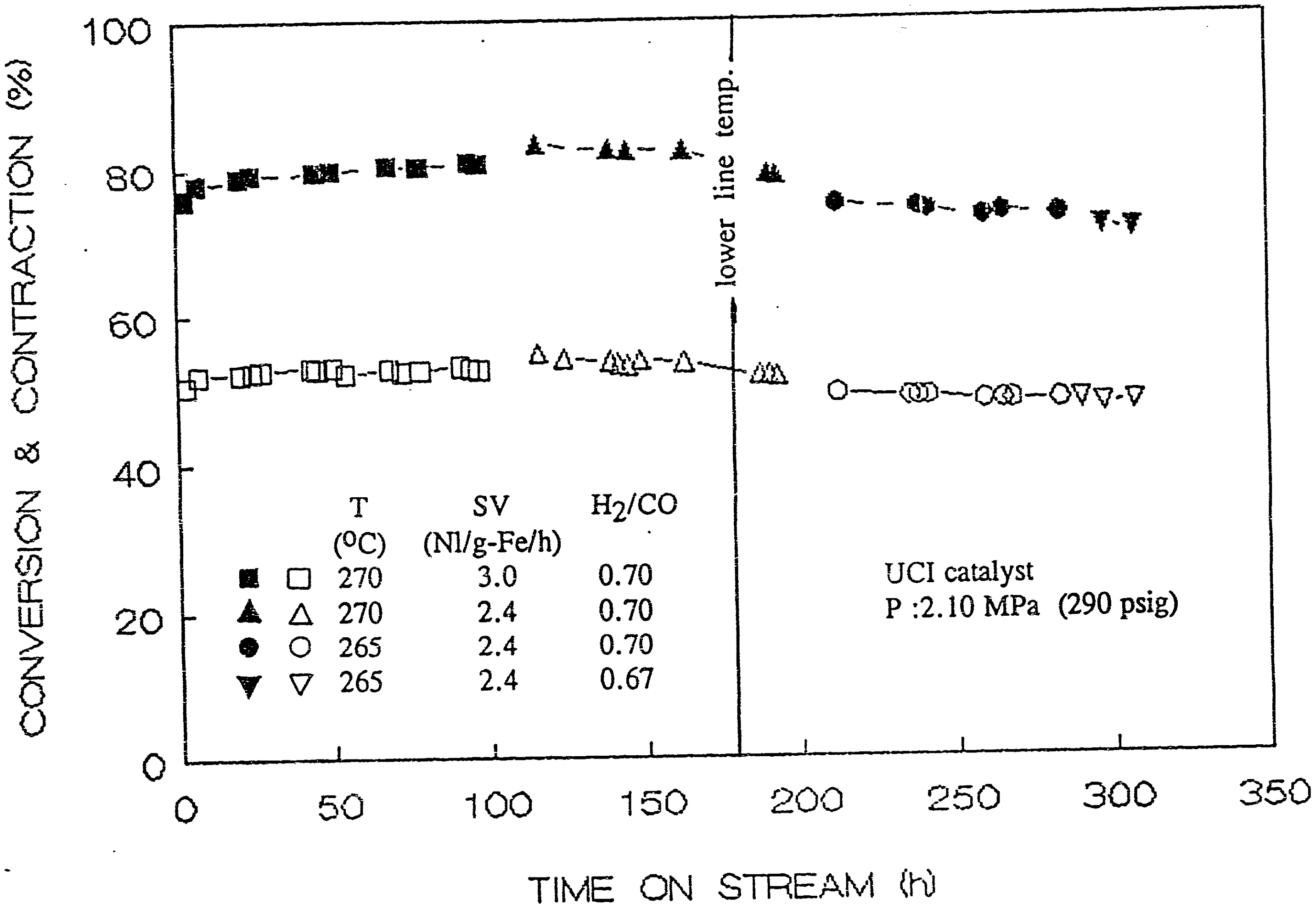


Figure 5. (H_2+CO) conversion (solid symbols) and volumetric contraction (open symbols) versus time on stream for run SA-3391.

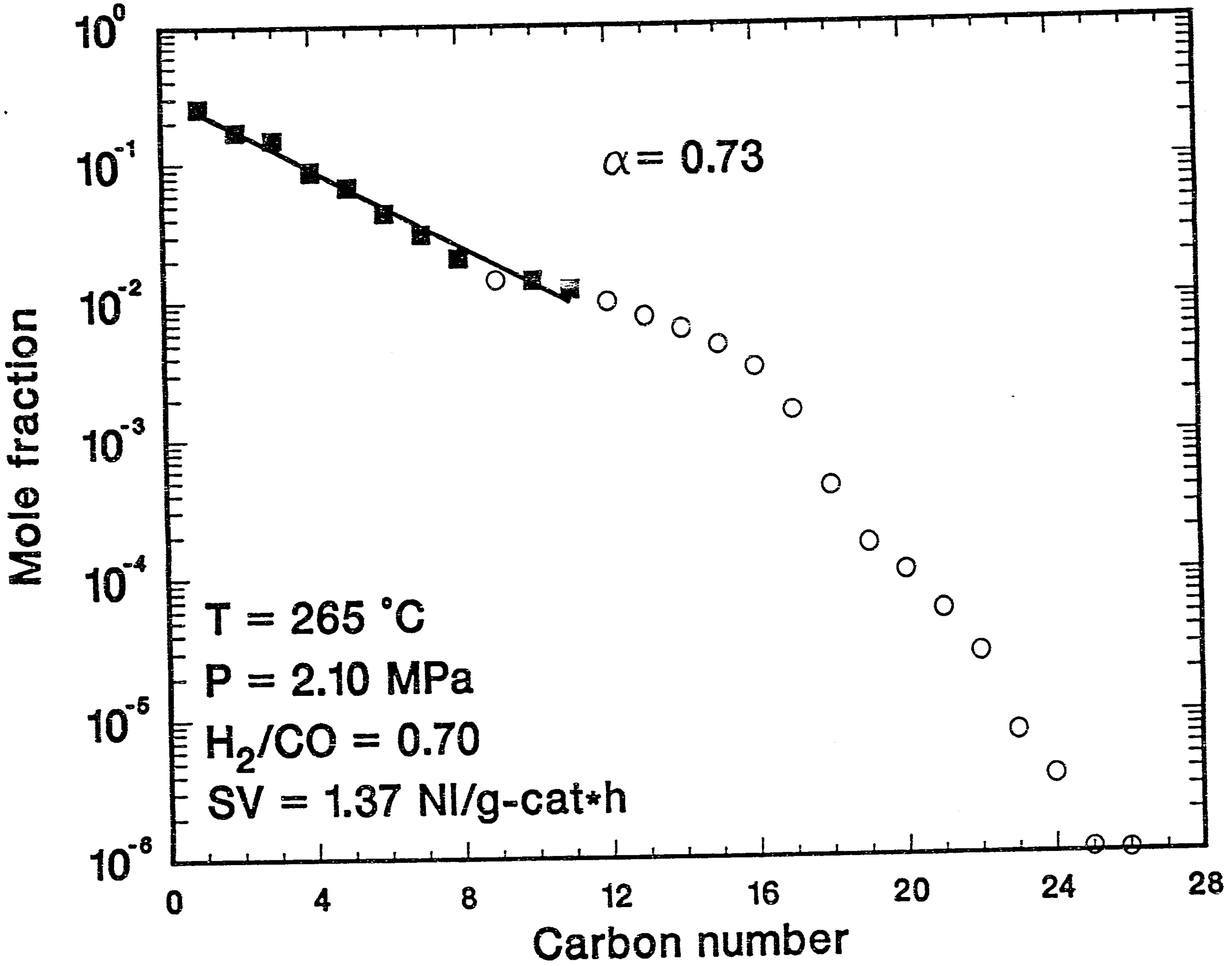


Figure 6. Anderson-Schulz-Flory plot for run SA-3391, balance 5, total products excluding wax.

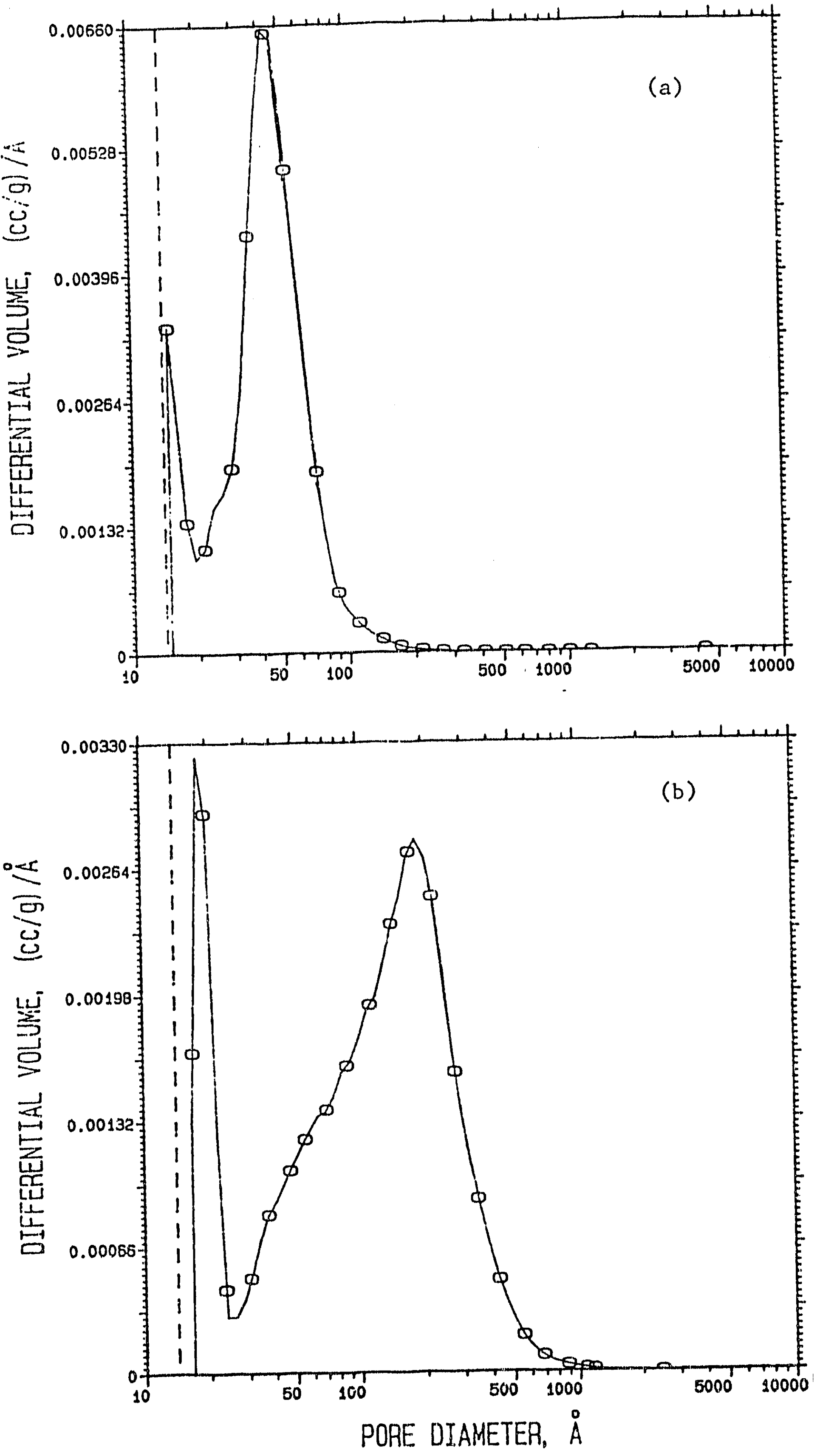
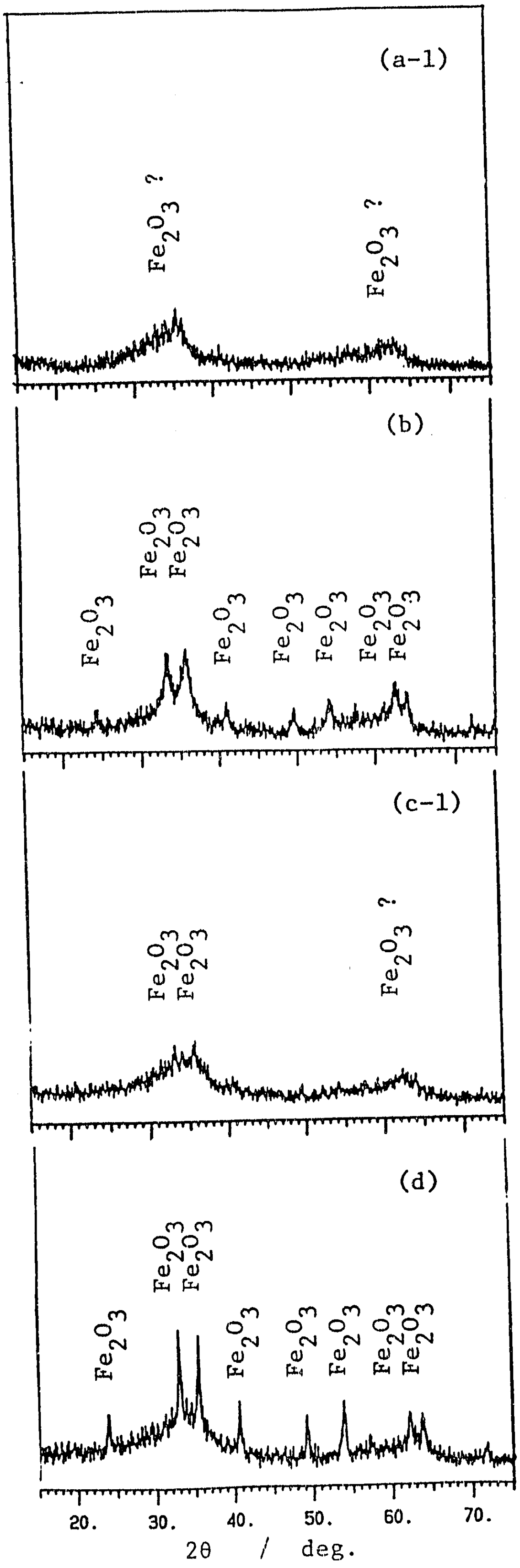


Fig. 7 Differential Pore Volume Distribution of Calcined Catalysts.

(a) 100Fe/0.3Cu/0.8K,

(b) 100Fe/5Cu/4.2K/100SiO_2.



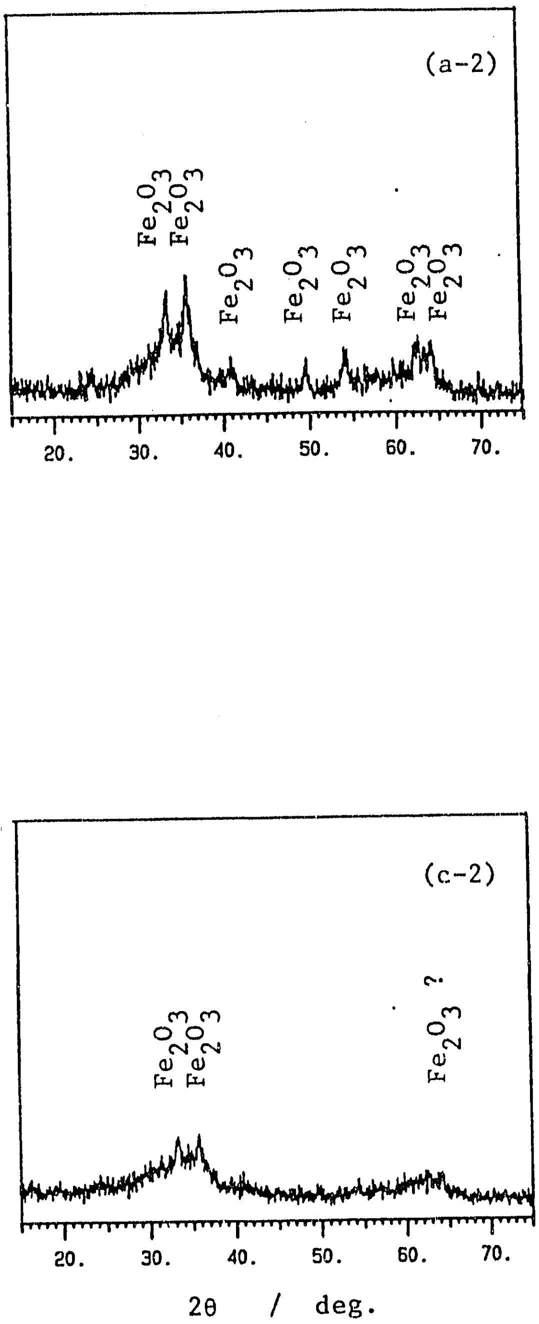


Fig. 8 XRD Patterns of Fresh Catalysts

(a-1) As-prepared 100Fe/0.3Cu/0.8K (C0308-1),
(a-2) Calcined 100Fe/0.3Cu/0.8K (C0308-1),
(b) As-prepared 100Fe/0.3Cu/0.8K (C0308-3),
(c-1) As-prepared Ruhrchemie catalyst,
(c-2) Calcined Ruhrchemie catalyst, and
(d) As-prepared UCI catalyst.

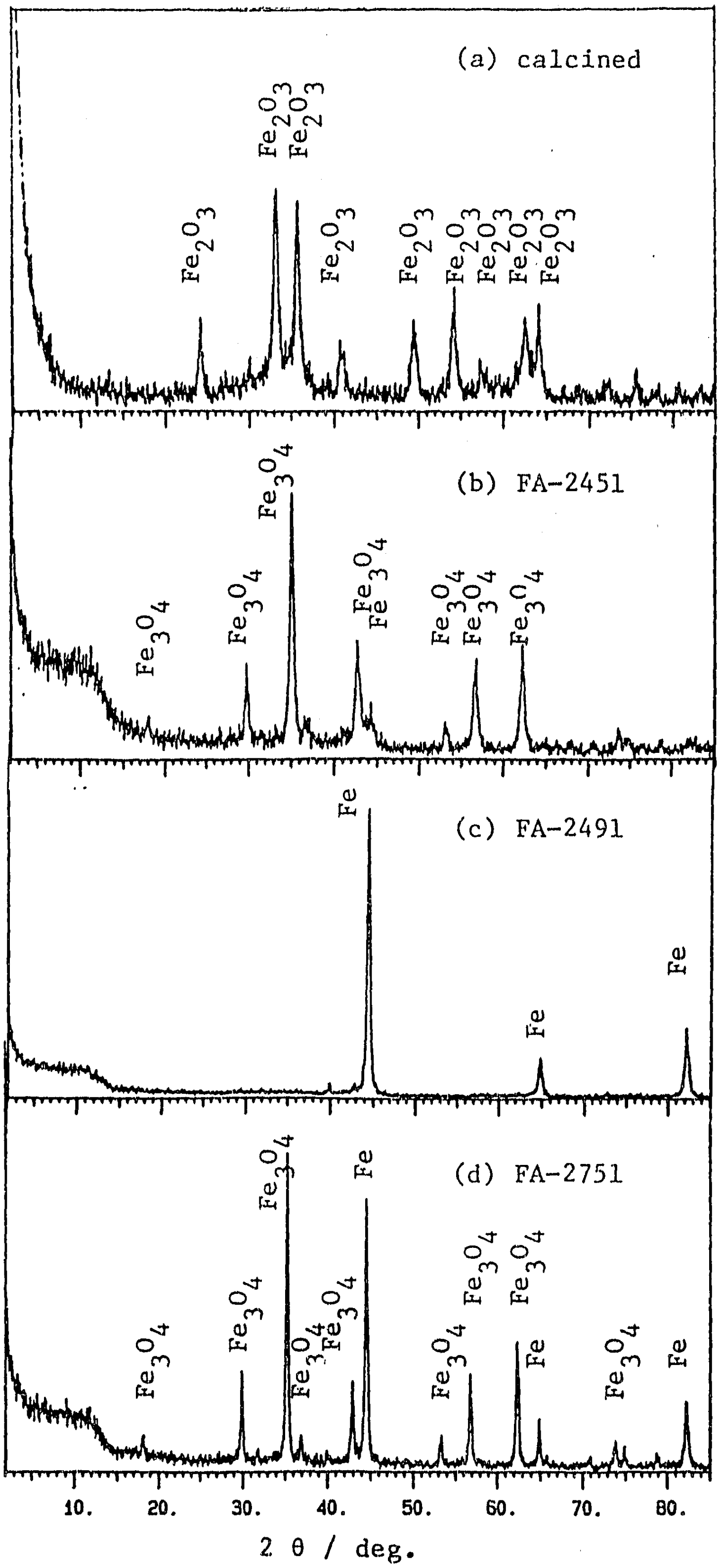


Fig. 9 XRD Pattern of 100Fe/0.3Cu/0.8K Catalyst

(a) calcined, (b) reduced with H_2(3550 ml/min) at 220°C for 1 h,
(c) reduced with H_2 (3350 ml/min) at 250°C for 2 h,
(d) reduced with H_2 (85 ml/min) at 280°C for 8 h.

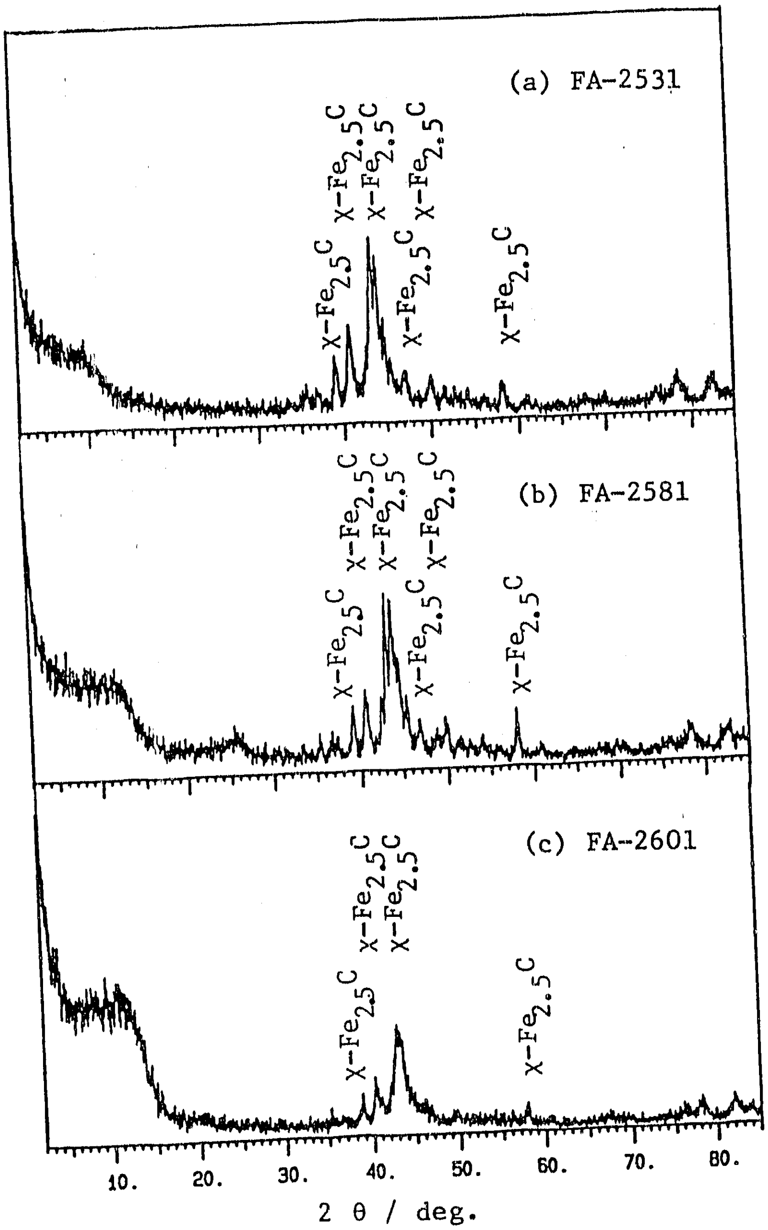


Fig. 10 XRD Pattern of 100Fe/0.3Cu/0.8K Catalyst Reduced with
(a) CO (85 ml/min) at 280°C for 8 h,
(b) $H_2/CO = 2$ (1200 ml/min) at 310°C for 6 h, and
(c) $H_2/CO = 0.67$ (85 ml/min) at 280°C for 8 h.

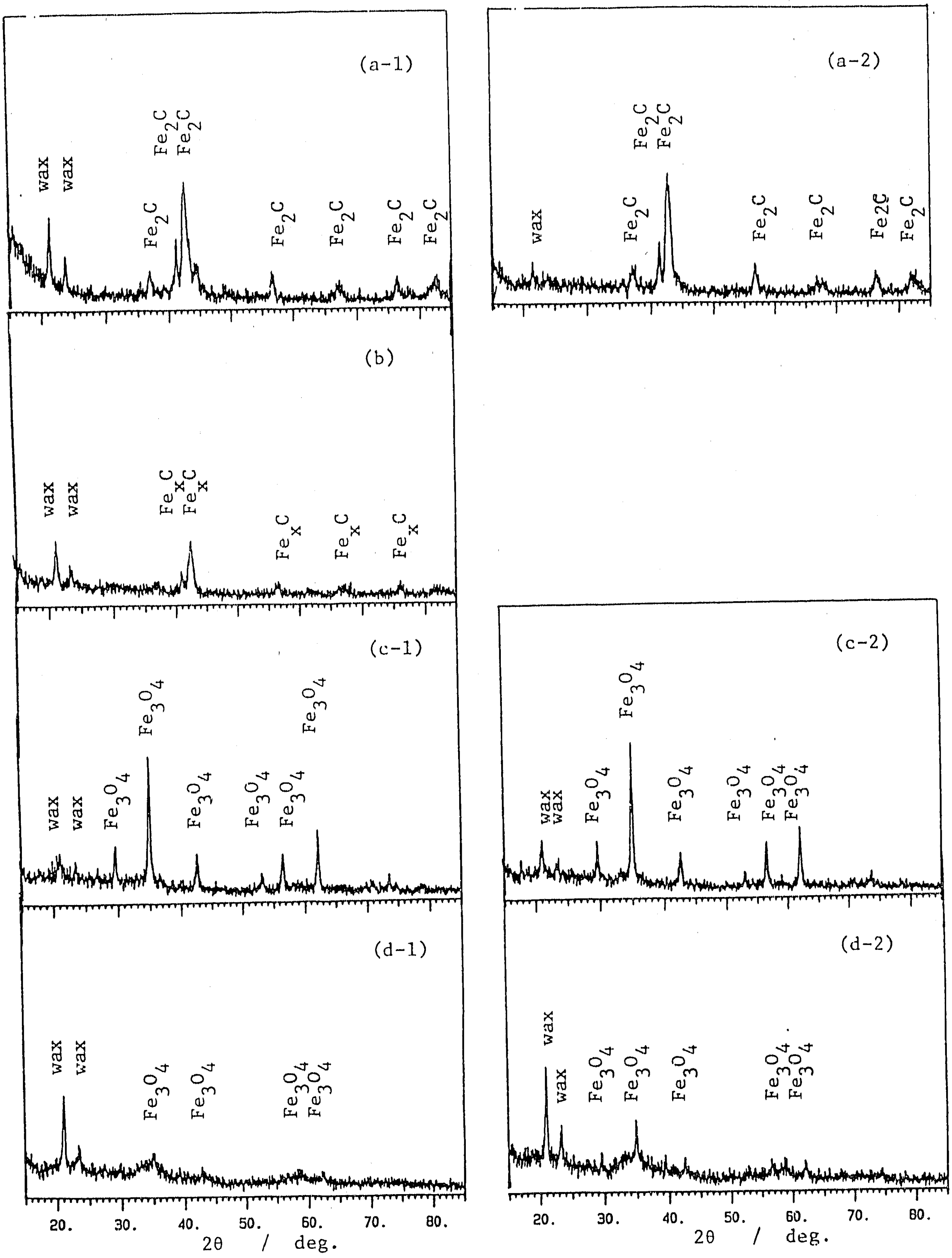


Fig. 11 XRD Patterns of Used Catalysts from Fixed Bed Reactor (see text and Table 12)

(a-1) FB-3221 (top); (a-2) FB-3221 (bottom); (b) FA-0959; (c-1) FB-2671 (top); (c-2) FB-2671 (bottom); (d-1) FB-2391 (top); and (d-2) FB-2391 (bottom).

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