III-4 Pretreatment Effect Research - Reaction Studies with Ruhrchemie LP 33/81 Catalyst

Results from catalytic studies with the state-of-the-art Ruhrchemie catalyst LP 33/81 (100 Fe/5 Cu/4.2 K/25 SiO_2, in parts per weight) are reported in this section. Six different pretreatment procedures were employed in fixed bed reactor (FBR) tests, and two in stirred tank slurry reactor (STSR) tests. Test identifications and pretreatment conditions are listed in Table III-4.1. Tests FB-1588 and SA-0888 were completed earlier (Bukur et al. 1989b, 1990c), but the results are included here for the sake of completeness.

Table III-4.1 Pretreatment Conditions and Test Designations
Catalyst: Ruhrchemie LP 33/81

Test (ID)	Temp. (°C)	Reductant	Duration (h)	Pressure (MPa)	Flowrate (cm^3/min)
FA-0113	220	H_2	1	0.1	4,000
FB-0183	280	H_2	1	0.1	4,000
FB-1593	280	H_2	8	0.1	175
FB-1733	280	H_2	24	0.1	175
FB-2290	310	$H_2/CO=2.0$	6	0.1	1,200
FB-1588	280	CO	12	0.1	170
SA-0888	280	CO	16	0.8	1,730
SB-1370	220	H_2	1	0.8	7,500

FA, FB = Fixed bed reactor test.

SA, SB = Slurry phase reactor test.

Catalyst loading, dilution and other experimental procedures were the same as described in Section III-2. After the pretreatment, the catalyst was tested at baseline process conditions: 250°C, 1.48 MPa (200 psig), 2.0 Nl/g-cat/h (3.8 Nl/g-Fe/h) with syngas H_2:CO ratio of 2:3 in both fixed bed and slurry phase reactors. Results from the fixed bed reactor tests will be discussed first.

III-4.1 Fixed Bed Reactor Results

Table III-4.2 summarizes selected results from six tests in fixed bed reactors. Test FB-1588 lasted over 630 h under various reaction conditions (Bukur et al., 1990c). Only the results obtained from the first 160 h at the baseline conditions are discussed here. A power failure occurred at 100 h on stream during test FB-0183, and the test was terminated prematurely after completing only one mass balance.

Activity and Stability

Change in catalyst activity during the conditioning period is shown in Figure III-4.1. Activity of the H_2 reduced catalyst, measured by volumetric contraction, varied with reduction conditions and increased in the following order: 280°C, 8 h < 280°C, 24 h < 280°C, 1 h < 220°C, 1 h. Such differences in initial catalyst activity were observed at 220°C, and higher reaction temperatures. The CO pretreated catalyst had higher activity (since 220°C) than the H_2 reduced catalyst, regardless of reduction conditions, during the conditioning period. However, the CO pretreated catalyst started to deactivate upon reaching the steady state process conditions.

During the steady state FT synthesis, the catalyst was the most active after it was reduced according to the manufacturer's procedure, i.e. H_2 at 220°C, superficial gas velocity of 150 cm/s (corresponding to 4,000 cc/min) for 1 h. The syngas (H_2+CO) conversion was about 72-73% (Figure III-4.2). After reduction at higher temperature of 280°C for 1h, but maintaining the same H_2 flowrate, the syngas conversion was significantly lower, 63 % . When the catalyst was reduced at 280°C using a markedly

Table III-4.2 Summary of Results for Pretreatment Effect Study with Ruhrchemie LP 33/81 Catalyst -- Fixed Bed Reactor Tests

Test designation	FA-0113		FB-0183	FB-1593		FB-1733		FB-2290		FB-1588	
Time-on-stream, h	68	117	71	72	144	71	116	73	157	71	167
CO conversion, %	74.9	73.8	66.4	61.2	64.9	58.7	60.7	61.1	57.9	56.4	51.6
(H_2+CO) conversion, %	71.9	71.5	64.7	59.2	62.5	57.3	58.7	63.3	60.9	58.6	54.4
STY, mmol/g-cat/h	64.0	64.1	58.2	53.0	55.9	51.0	52.1	56.8	55.0	52.0	49.1
k, mmol/g-Fe/h/MPa[a]:	241	243	215	192	205	187	190	225	216	201	187
(H_2/CO) usage ratio	0.61	0.61	0.67	0.64	0.63	0.66	0.64	0.75	0.78	0.76	0.78
(H_2/CO) exit ratio	0.95	0.82	0.79	0.78	0.81	0.75	0.78	0.60	0.57	0.60	0.60
$K_p = P_{CO_2}P_{H_2}/P_{CO}P_{H_2O}$	12.7	9.9	12.5	13.0	16.0	11.1	11.0	2.28	1.71	2.20	2.00
mmol CH_4/g-Fe/h	1.99	2.01	2.98	2.43	2.69	2.33	2.36	2.04	1.94	1.41	1.33
Hydrocarbon selectivity, wt%											
CH4	6.1	6.4	10.4	9.4	10.0	9.0	8.6	7.0	6.9	5.6	5.6
C2-C4	16.8	18.0	24.2	22.5	23.2	25.3	23.0	22.7	23.3	22.7	22.8
C5-C11	19.8	21.7	32.8	29.6	31.7	32.9	31.6	22.4	31.7	18.6	20.2
C12+	57.3	53.9	32.6	38.5	35.1	32.8	36.8	47.9	38.1	53.1	51.4
Chain growth parameter, α_{1-10}[b]	0.59	0.61	0.68	0.69	0.70	0.69	0.69	0.65	0.64	0.65	0.67
Olefin content, wt%											
C2-C4	64.3	66.1	64.7	63.8	63.3	65.6	65.5	75.9	76.8	77.6	80.8
C5-C11	66.7	68.6	68.1	68.6	68.7	69.4	69.5	80.4	62.0	77.2	77.1

Process conditions: 250°C, 1.48 MPa (200 psig), 2.0 Nl/g-cat/h, H_2/CO=0.67

[a]: Apparent reaction rate constant for a first order reaction in hydrogen, based on measured usage ratio.

[b] : Parameter estimated from products with carbon number in the range C_1-C_{10}.

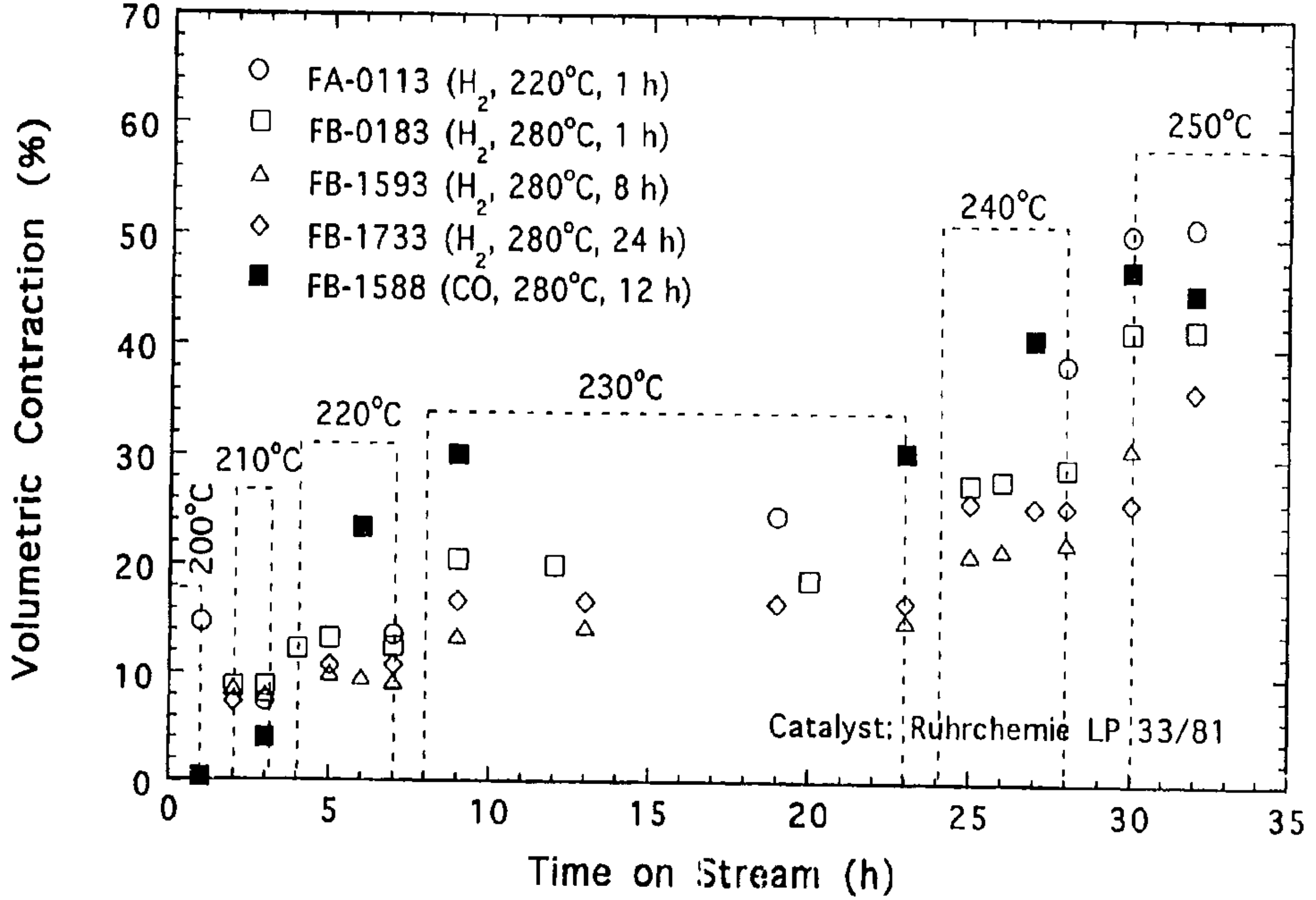

Figure III-4.1 Volumetric contraction during conditioning period.

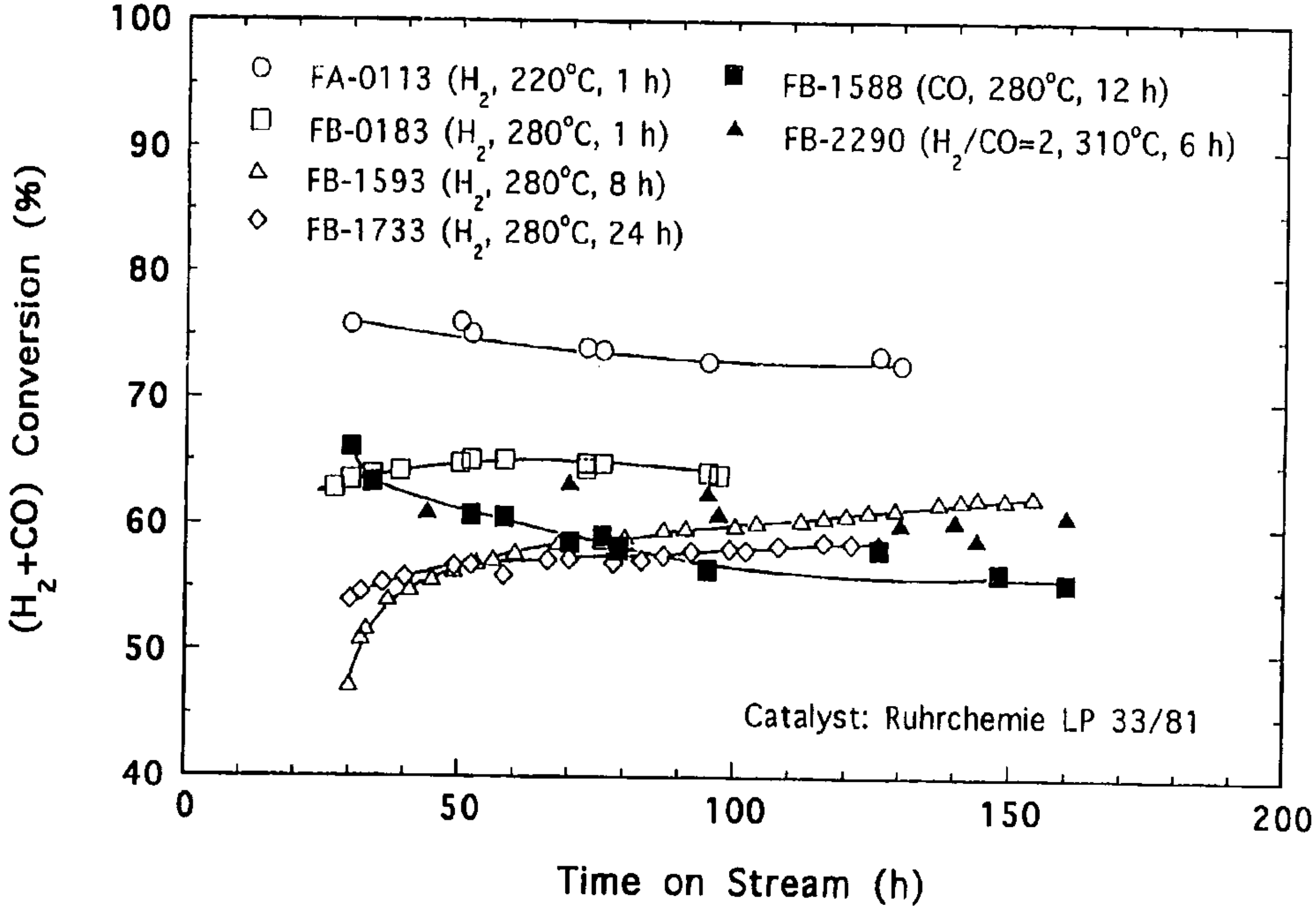

Figure III-4.2 Effect of pretreatment conditions on conversion and catalyst stability.

lower H_2 flowrate (corresponding to a gas space velocity of 3.0 Nl/g-cat/h) for 8 h and 24 h, respectively, the syngas conversion decreased further. After 8 h reduction the initial syngas conversion (1 h at the process conditions) was only 47 %; it then continued to increase with time, reaching 62 % at 154 h on stream. After 24 h reduction the initial syngas conversion was somewhat higher, 54 %, and it increased with time to stabilize at about 58 %. Thus, the steady state activities after 8 h and 24 h H_2 reductions at 280°C were similar. The corresponding values of the apparent reaction rate constant are listed in Table III-4.2, and they follow the same trend as syngas conversions. All four H_2 reduction procedures led to either a stable or gradually increasing activity during the synthesis.

After CO pretreatment (280°C, 12 h) the initial (H_2+CO) conversion was 66 %, it then gradually decreased with time to 55 % at 160 h on stream. Though not shown here, the conversion was 50 % after 460 h testing. The rate of deactivation was moderate with the conversion loss of 0.9 % per day. The activity of the syngas pretreated catalyst (H_2:CO = 2, at 310°C, flowrate 1,200 cc/min for 6 h) was fairly stable between 50 and 160 h on stream, and the (H_2+CO) conversion was about 62%. The apparent reaction rate constant (220 mmol/g-Fe/h/MPa) of the syngas pretreated catalyst was slightly greater than the corresponding rate constants of H_2 reduced catalyst at 280°C(187 - 215 mmol/g-Fe/h/MPa), but smaller than the apparent rate constant of H_2 reduced catalyst at 220°C (242 mmol/g-Fe/h/MPa).

The effects of pretreatment procedures on WGS activity, measured by H_2 to CO usage ratio and partial pressure quotient K_p, are illustrated in Table III-4.2. The K_p values during FT synthesis following H_2 reductions were about one order of magnitude greater than those obtained after CO and syngas pretreatments (Table III-4.2). The usage ratio was stable with time on stream in all tests (0.62 - 0.65 after H_2 reductions, and 0.76 - 0.78 following CO and/or syngas pretreatments). Thus, the

WGS activity of the Ruhrchemie catalyst was higher (smaller usage ratio, greater K_p) after H_2 reductions than after CO and/or syngas activation.

Selectivity

The effect of pretreatment conditions on hydrocarbon product distribution is illustrated in Table III-4.2 and Figure III-4.3. The catalyst selectivity remained relatively stable between 70 and 170 h on stream. Therefore, the average values from 2-3 mass balances were used in Figure III-4.3 for comparison of different pretreatment procedures. The CO activated catalyst had the lowest methane selectivity (~5.6 %). The catalyst reduced with H_2 at 220°C for 1 h also had relatively low methane selectivity (6.2 %), and had the lowest selectivity to C_2-C_4 hydrocarbons (17.4 %). These two pretreatment procedures resulted in high C_{12}+ selectivities, about 55.6% (H_2 at 220°C) and 52.2 % (CO activation). Hydrocarbon selectivities were similar following three procedures using hydrogen reduction at 280°C with different flowrates and/or durations. In all three cases, methane selectivity was high (8.8 to 10.4 %), whereas C_{12}+ selectivity was low, only 32 to 36 %. The syngas pretreatment gave an intermediate behavior: 7 % methane selectivity and 43 % C_{12}+ selectivity.

Methane formation rate (per gram of iron in the catalyst) as a function of time on stream for different pretreatment procedures is shown in Figure III-4.4. Methane formation rate follows the same trends as methane selectivity, with the exception of H_2 reduction at 220 °C and the syngas pretreatment. Methane formation rates for these two pretreatments are the same (Figure III-4.4), whereas methane selectivity after H2 reduction is about 10% less than that after the syngas pretreatment. This is caused by differences in conversions, i.e. differences in total hydrocarbon production rates. After H_2 reduction, both the syngas conversion and the total hydrocarbon production rate are higher than after the syngas pretreatment. Thus methane selectivity (mass fraction

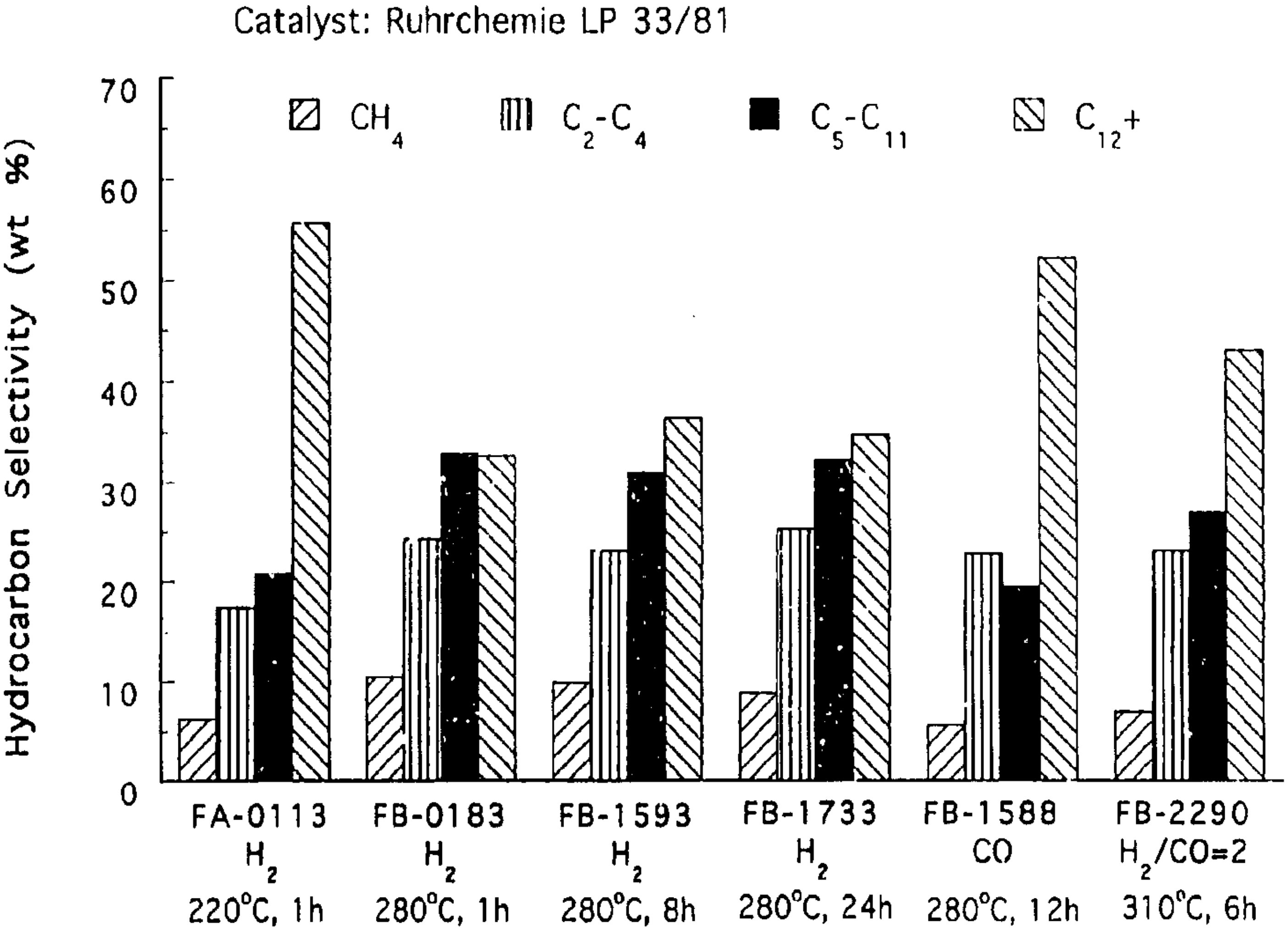

Figure III-4.3 Effect of pretreatment conditions on hydrocarbon product distribution.

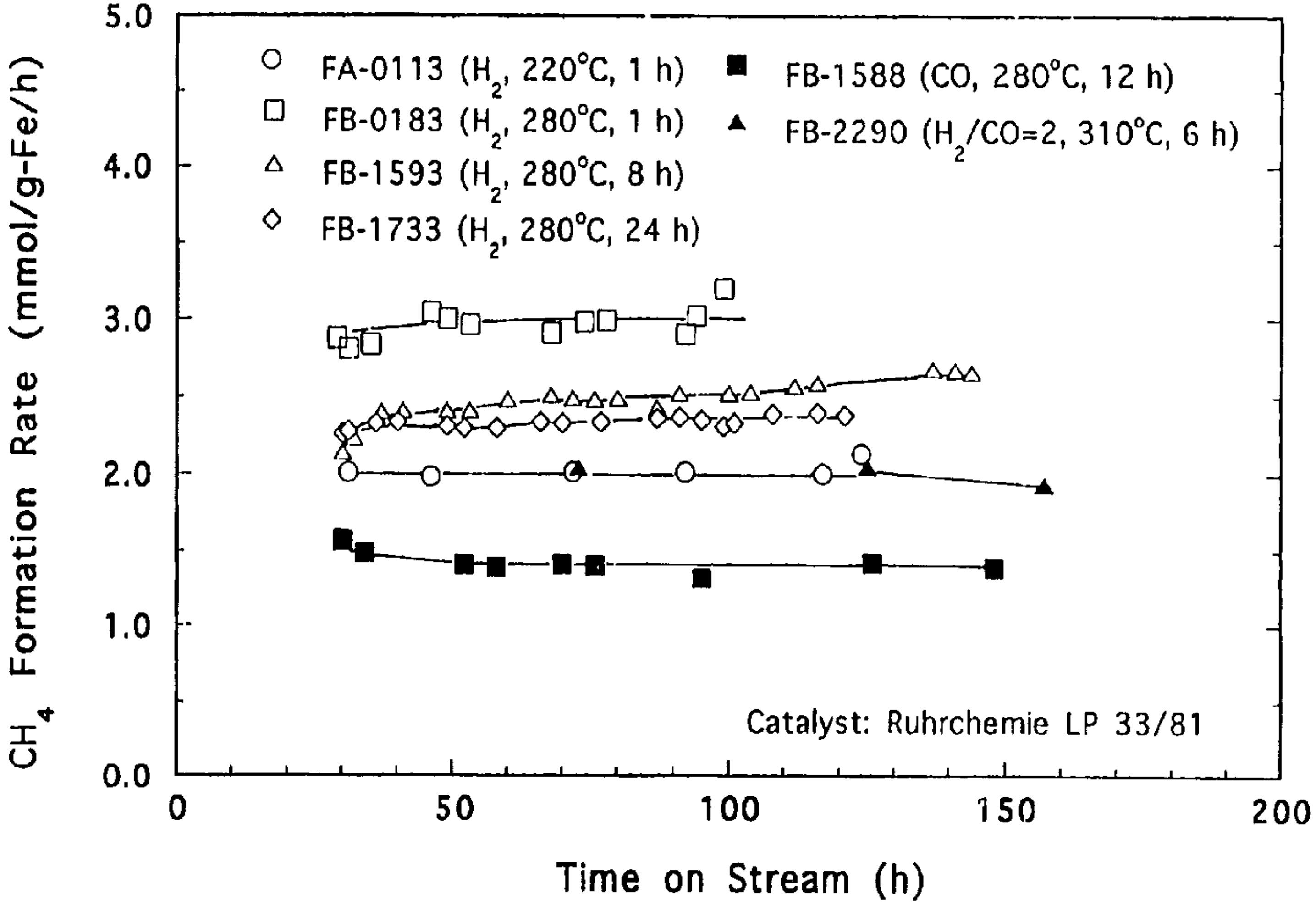

Figure III-4.4 Methane formation rate as a function of time on stream following different pretreatment conditions.

of methane in total hydrocarbons) is lower with the former pretreatment procedure, even though the methane formation rates are the same.

Representative carbon number product distributions are presented in Figure III-4.5 in the form of Anderson-Shulz-Flory plots. The two ASF plots were fitted well using the three parameter (double alpha) model of Huff and Satterfield (1984). The model parameters (chain growth parameters - α_1 and α_2, and the fraction of type 1 sites - β) were estimated by nonlinear regression.

Olefin selectivity following different pretreatment conditions is plotted in Figure III-4.6 for carbon numbers up to C_{15}. Catalyst pretreated with CO had higher olefin selectivity than the catalyst reduced with H_2. For example, the olefin content in C_2-C_4 and C_5-C_{11} ranges were about 10 - 15 wt % higher after the CO pretreatment (Table III-4.2). Different temperatures, flowrates and/or durations used during H_2 reductions did not have a marked effect on olefin selectivity. The olefin selectivity obtained after the syngas pretreatment, was, in general, between values obtained after CO and H_2 pretreatments.

Olefin isomerization activity, measured by 2 - olefin content, varied markedly with pretreatment conditions. As shown in Figure III-4.7 (the average values from multiple mass balances were used in this plot) the isomerization of C_8+ olefins was significantly higher after H_2 reductions than after CO or syngas pretreatments. The 2 - olefin content of C_{15} hydrocarbons reached 90 % after H_2 reduction at 220°C for 1h, whereas it was about 30 % after CO or syngas pretreatment. The 2-olefin selectivity was also influenced by different H_2 activation conditions and increased in the same order as the overall catalyst activity. Reduction at high flowrate of H_2 and low temperature, which resulted in the highest activity, also yielded the highest olefin isomerization activity.

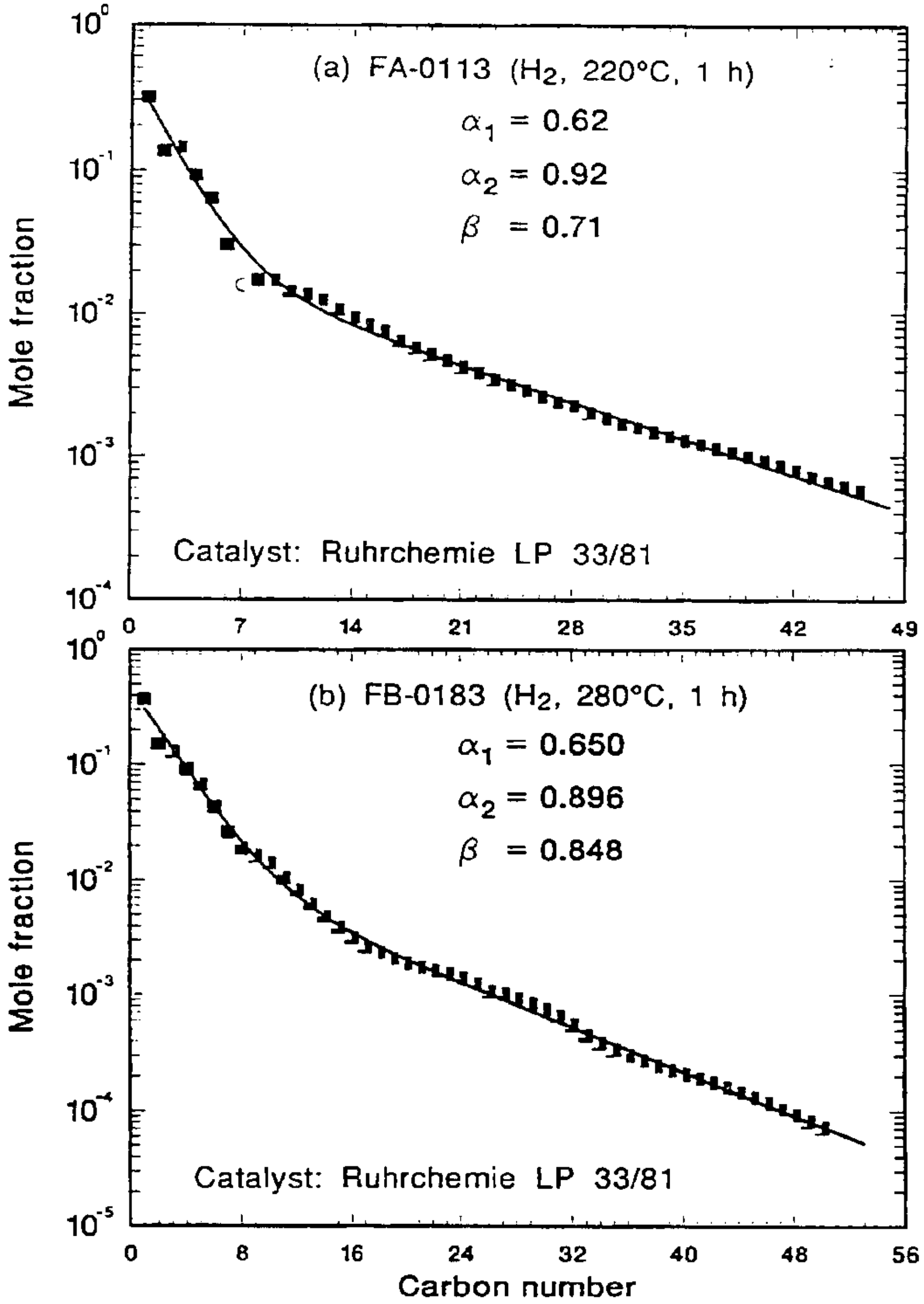

Figure III-4.5 Carbon number product distribution for selected pretreatment conditions: (a) FA-0113 (68 h on stream); (b) FB-0183 (71 h on stream).

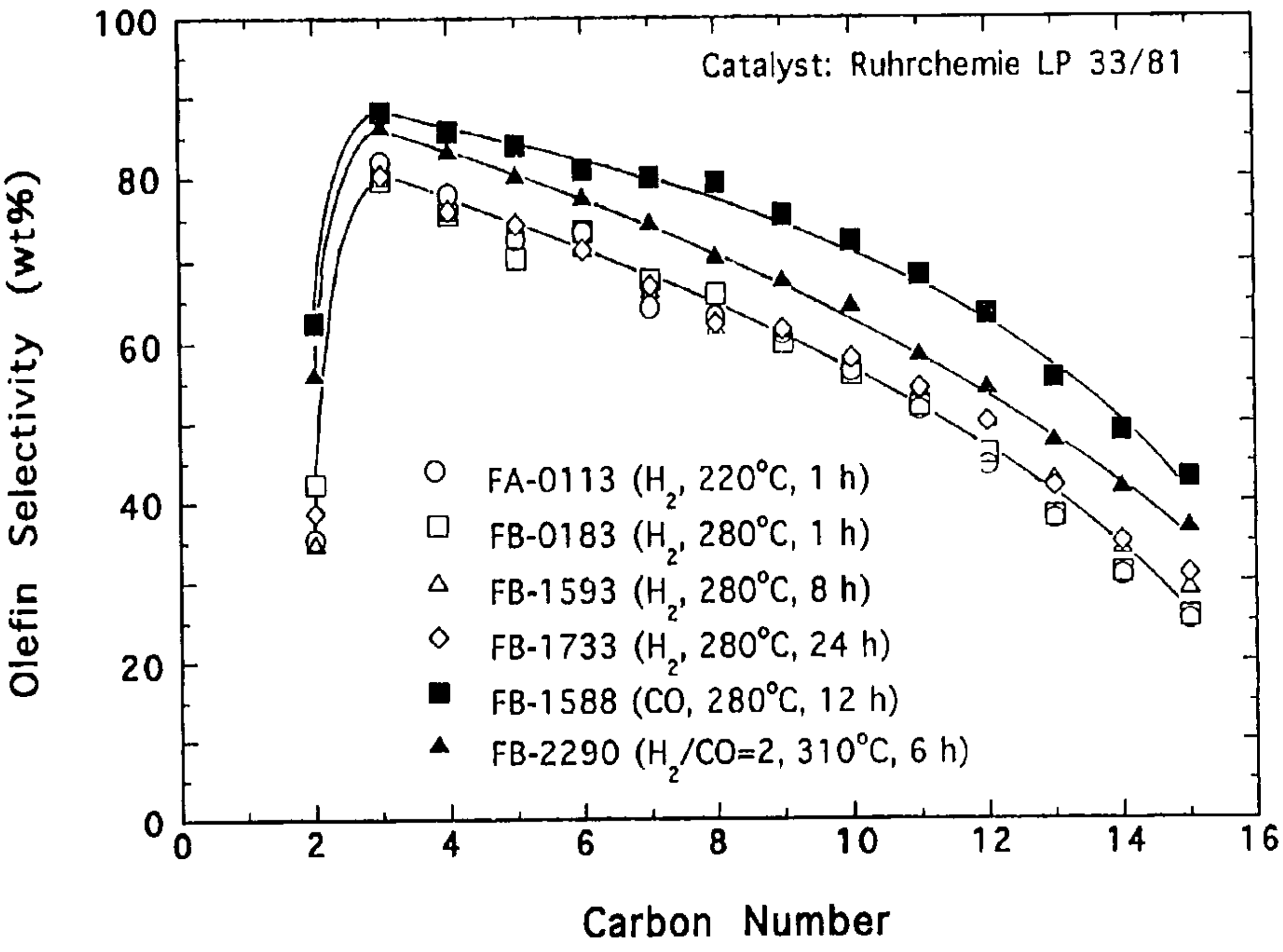

Figure III-4.6 Effect of pretreatment conditions on olefin selectivity.

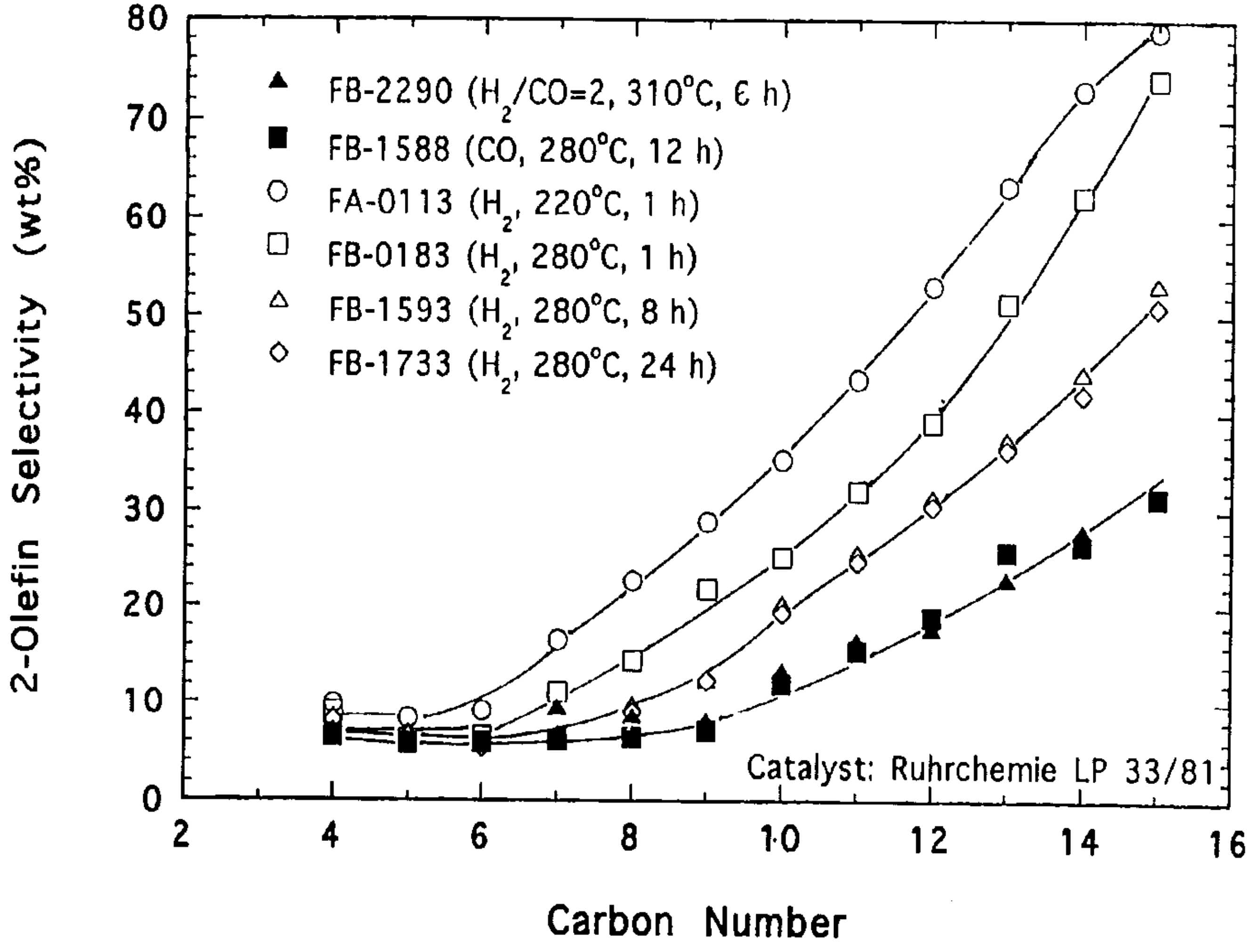

Figure III-4.7 Effect of pretreatment conditions on 2-olefin selectivity.

III-4.2 Discussion

The major findings from catalytic tests following six different pretreatment procedures are: (1) After CO pretreatment the catalyst activity was high initially, and then gradually decreased with time. Catalyst deactivation rate was moderate. (2) Reduction using high flowrate of H_2, low temperature (220°C) and short duration resulted in high activity and relatively low methane selectivity. (3) Reductions using low flowrate of H_2 at 280°C resulted in low catalyst activity, and relatively high methane selectivity. (4) Catalyst activity was either stable or gradually increasing with time on stream (up to 140 h) after all H_2 reductions. (5) Secondary reactions (olefin hydrogenation and isomerization) were higher after hydrogen reductions. (6) CO and syngas pretreatments favored production of higher molecular weight products, in comparison to H_2 reductions at 280°C. However, the catalyst reduced with H_2 at 220°C produced less gaseous hydrocarbons (C_1-C_4) and more C_{12+} hydrocarbons than either the CO or syngas pretreated catalyst.

These observations are in a qualitative agreement with those made in our previous studies with precipitated iron catalysts having nominal compositions 100 Fe/3 Cu/0.2 K (Bukur et al., 1989a) and 100 Fe/0.3 Cu/0.8 K (Section III-2 of this report). Most of these observations can be explained utilizing results from characterization studies, and previous FT reaction studies on the effects of promoters, binders and bulk iron phases on catalyst activity and selectivity.

After the pretreatments with CO and syngas, the Hägg carbide is formed in addition to fine oxide/hydroxide particles (probably magnetite) which exhibit superparamagnetic behavior (Table III-3.3). The catalyst surface areas and pore volumes were also similar. During the subsequent FT synthesis, the catalyst activity and selectivity were also similar. This represents a strong correlation between the catalytic behavior and the structural properties of the catalyst after the pretreatment. A moderate decrease of catalyst activity with time may be attributed to partial conversion of Hägg carbide to magnetite (Table III-3.4), and possible blocking of active sites by carbonaceous deposits on the surface of the catalyst (Dry, 1981; Krebs et al., 1979). In comparison with the precipitated iron catalysts without silica as a binder (100 Fe/3 Cu/0.2 K and 100 Fe/0.3 Cu/0.8 K) the activity of the Ruhrchemie catalyst was more stable during FT synthesis. The improvement in stability by incorporating silica into catalyst is in agreement with the results from our earlier studies on binder/support effect (Bukur et al; 1990b). On an unsupported catalyst the surface active sites are close to each other, which facilitates the crystallite size growth by sintering. Also, it is easier for carbonaceous deposits to grow and cover larger portion of the surface, both of which are resulting in faster catalyst deactivation. In contrast, the active sites are more isolated by silica binder on the Ruhrchemie catalyst. As a result the inactive carbon layer would cover a smaller number of active sites, and the growth of iron crystallites would be hindered during FT synthesis, and thus the catalyst deactivation would be slower. In addition, the incorporation of silica binder causes a decrease in surface basicity, which in turn lowers the carbon deposition rate and promotes the catalyst stability.

After H_2 reductions the initial catalyst activity during the conditioning period was lower than that of the CO pretreated catalyst (Figure III-4.1), which is consistent with the competition model of Niemantsverdriet and van der Kraan (1981). During FT synthesis with the H_2 reduced catalyst some of the active surface carbon is consumed to form bulk carbides, and thus the rate of FT synthesis is initially lower relative to a precarbided catalyst. In terms of bulk iron phases present after different pretreatments, these results could be interpreted as to imply that Hägg carbide is more active for FT synthesis than magnetite and/or metallic iron. During FT synthesis χ - carbide formed after CO and syngas pretreatments is gradually oxidized to magnetite, whereas magnetite and α - Fe phases formed after H_2 reductions are partially converted to iron carbides, and the working catalysts have similar bulk compositions regardless of the pretreatment procedure employed (Section III-3 of this report). Differences in the catalyst activity during the steady state FT synthesis are fairly small (Figure III-4.2 and Table III-2), and may be attributed to differences in the catalyst surface areas (crystallite size) and the catalyst bulk and surface compositions.

Four reduction procedures with H_2 were employed by changing the flowrate of H_2, temperature and/or duration of reduction. These procedures resulted in different degrees of reduction and different levels of stable catalyst activity. The Ruhrchemie catalyst is more difficult to reduce than a precipitated iron catalyst without silica. As XRD and MES results reveal after reduction with H_2 at 220°C, 150 cc/min for 1 h, the bulk phase of the Ruhrchemie catalyst was magnetite (Tables III-3.1 and III-3.3), and only after the reduction at 280°C the catalyst was partially reduced to metallic iron. With unsupported 100 Fe/0.3 Cu/0.8 K catalyst, the metallic iron was already formed after reduction with H_2 at 220°C, and the complete reduction occurred at 250°C. The Ruhrchemie catalyst which was reduced to a lesser degree after reduction with H_2 at 220°C (FA-0113) had higher activity during the subsequent FT synthesis than the one reduced to magnetite and metallic iron at 280°C (FB-0183). This trend of activity with iron reducibility is contrary to that obtained on the 100 Fe/0.3 Cu/0.8 K catalyst. There it was found that the catalyst activity increases with the degree of reduction (section III-2). A possible explanation for these opposite trends is related to differences in surface areas after the reduction. After the reduction at 220°C, the BET surface area of the Ruhrchemie catalyst is about 180 m^2/g, which is significantly higher than that obtained after one hour reduction at 280°C, 136 m^2/g. Apparently, the difference in surface area (i.e., crystallite size, 5 vs. 8 nm) played a more important role in determining the catalyst activity than the degree of reduction, and the catalyst with larger surface area had about 10% higher activity during the FT synthesis. In the case of the 100 Fe/0.3 Cu/0.8K catalyst the surface areas after reductions at 250°C and 280°C were the same, and the activity was higher on the catalyst which was completely reduced to α - Fe.

The Ruhrchemie catalyst was the least active after two H_2 reductions at 280°C (8 or 24 h in duration) using a low gas flow rate of 175 cc/min (STP), both during the conditioning period (Figure III-4.1) and the steady state FT synthesis (Figure III-4.2 and Table III-4.2). The apparent reaction rate constant in tests FB-1593 and FB-1733, was about 23% less than that obtained in the test FA-0113 (H_2 reduction at 220°C, 4000 cc/min for 1 h). Water vapor formed during reduction of metal oxides by hydrogen enhances sintering of metal particles (Coluccia et al., 1979). The use of higher reduction temperature favors faster reduction of the metal oxide and the water is released more rapidly. The use of low reductant flow rate increases the partial pressure of water, and both of these effects, the use of higher reduction temperature and low H_2 flowrate, would enhance sintering and thus decrease the catalyst activity. The average α - Fe particle size after H_2 reduction at 280°C was 10 nm (SA = 160 m^2/g), whereas the average particle size after H_2 reduction at 220°C for 1 h was only 5 nm (SA = 180 m^2/g). The use of high H_2 flowrate and low reduction temperature facilitates removal of water vapor and preserves the high surface area (Dry, 1981; Che and Bennett, 1989).

The above results show both similarities as well as differences with results obtained in studies with two precipitated iron having nominal compositions : 100 Fe/3 Cu/0.2 K (Bukur et al., 1989a) and 100 Fe/0.3 Cu/0.8 K (Section III-2 of this report). In the latter two studies the catalyst activity decreased markedly with increase in reduction temperature and/or duration of H_2 reduction, whereas in the present study decrease in activity with increase in reduction temperature was moderate, and the duration of reduction at 280°C (8 vs. 24 h) had no effect on the catalyst activity. The difference in sensitivity of the Ruhrchemie and the 100 Fe/3 Cu/0.2 K catalyst to reduction conditions may be explained in terms of sulfur migration and the extent of surface coverage by sulfur after the reduction (Sault, 1991). According to Sault (1991) the sulfur (the origin of which are bulk sulfate impurities present in the metal nitrates used to prepare the catalyst) migration to the surface increases with both reduction duration and temperature, due to increase in the rate of sulfur diffusion with temperature. Sulfur coverage is greater on a low surface area catalyst (SA = 10 m^2/g for reduced 100 Fe/3 Cu/0.2 K catalyst) than on the high surface area Ruhrchemie catalyst. FT activity of the catalyst decreases in proportion to the sulfur coverage, due to catalyst poisoning. Thus, the difference in sensitivity of the two catalysts to reduction conditions is due to differences in their surface areas, i.e. different levels of sulfur poisoning.

The WGS activity was higher over the catalyst reduced with H_2 than with CO or syngas. This observation is in agreement with the results obtained in our earlier study with the 100 Fe/3 Cu/0.2 K catalyst (Bukur et al., 1989a). Higher WGS activity results in a higher effective H_2/CO surface ratio, which in turn promotes secondary hydrogenation and isomerization of 1-olefins. Consequently, the olefin content in the hydrocarbon product decreased and 2-olefin isomerization increased on the catalyst following reductions with H_2, as shown in Figures III-4.6 and III-4.7. After all three H_2 reductions at 280°C (Runs FB-0183, FB-1593 and FB-1733) more gaseous hydrocarbons were produced than in tests following CO and syngas pretreatments (Figure III-4.3 and Table III-4.2). This is due to higher surface hydrogen concentration on H_2 reduced catalyst, which favors methanation and chain termination reactions. However, the catalyst reduced with H_2 at 220°C (FA-0113) produced less gaseous (C_1-C_4) and more C_{12+} hydrocarbons, than any other pretreatments employed. The reasons for this type of behavior are not clear at the present time.

III-4.3 Stirred Tank Slurry Reactor Tests

The results from slurry reactor test SA-0888 were described in detail elsewhere (Bukur et al 1989b, 1990c). Briefly, after pretreatment with CO at 280°C, 0.8 MPa, 1730 cc/min (3.0 Nl/g-cat/h) for 16 h, the catalyst activity was stable during the first 340 h of testing at the baseline process conditions of 250°C, 1.48 MPa, 2.0 Nl/g-cat/h and $H_2/CO = 0.67$, and the (H_2+CO) conversion was about 42.6 - 46.4 %. Following a period of process variable studies between 340 to 570 h on stream, the syngas conversion decreased to 36 %. Change in syngas conversion with time on stream at baseline conditions is shown in Figure III-4.8. The usage ratio was about 0.75 throughout the test. During 600 h of testing, the hydrocarbon selectivity shifted towards lower molecular weight products (Table III-4.3 and Figure III-4.9), the olefin content decreased, whereas 2-olefin selectivity increased with time on stream.

After reduction with H_2 at 220°C, 7,500 cc/min (15.0 Nl/g-cat/h) for 1 h the catalyst was tested over a long period of time in run SB-1370. Variation of the (H_2+CO) conversion with time on stream is also plotted in Figure III-4.8. The initial conversion was low. It reached the steady state after about 60 h on stream (36-38%), and remained stable during the next 300 h of testing at the baseline process conditions. Between 360 and 620 h on stream, the catalyst was tested under various process conditions but it had not deactivated. The (H_2+CO) conversion at 620 and 670 h, after returning to the baseline conditions, was essentially the same, about 38-40 %, as that observed between 60 and 360 h on stream. The usage ratio at baseline conditions varied between 0.68 to 0.72 during the test. Hydrocarbon selectivity shifted towards lower molecular weight products with time-on-stream (Table III-4.3 and Figure III-4.9). For example, at 65 h on stream, methane and $C_{12}+$ selectivities were 3.9 and 55.3 wt%, respectively. The fraction of high molecular weight hydrocarbons decreased with time, at 350 h $C_{12}+$ selectivity decreased to 46 %, and further to 35 % at 662 h on

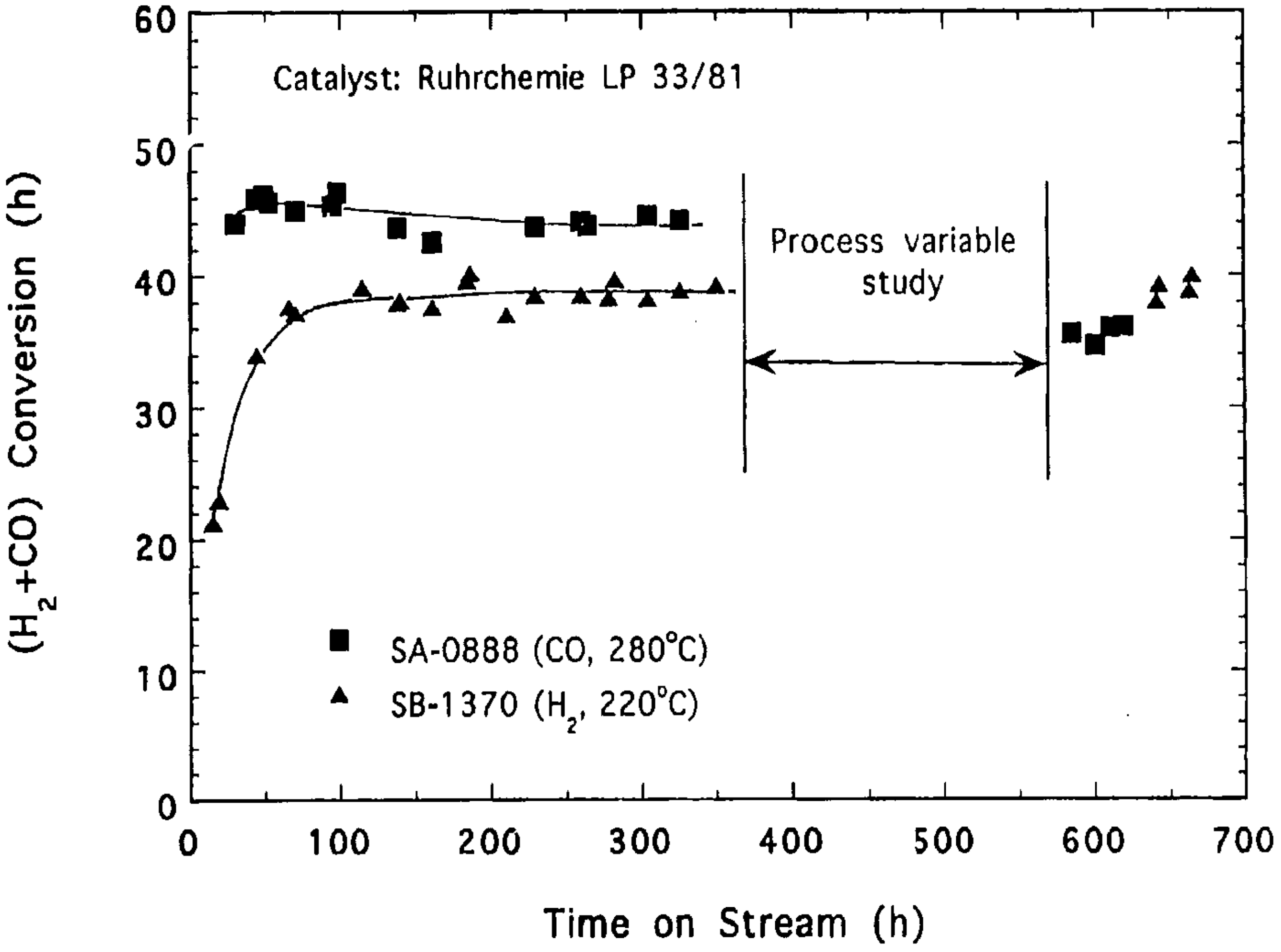

Figure III-4.8 Effect of pretreatment procedures on conversion and catalyst stability in slurry reactor tests.

Table III-4.3 Summary of Results for Pretreatment Effect Study with Ruhrchemie LP 33/81 Catalyst -- Slurry Reactor Tests

Test designation	SA-0888					SB-1370				
Time-on-stream, h	45	166	264	336	619	65	134	253	349	662
CO conversion, %	42.1	41.5	41.2	40.4	32.8	35.3	36.3	39.8	38.3	38.1
(H_2+CO) conversion, %	45.9	43.1	43.9	44.4	35.9	36.6	37.6	40.2	39.3	38.7
STY, mmol/g-cat/h	41.0	38.1	39.1	40.0	32.0	33.2	34.1	36.1	36.0	35.3
k, mmol/g-Fe/h/MPa[a]	187	167	173	181	135	133	138	149	152	142
(H_2/CO) usage ratio	0.79	0.74	0.77	0.83	0.83	0.72	0.72	0.68	0.72	0.69
(H_2/CO) exit ratio	0.58	0.62	0.59	0.55	0.59	0.63	0.62	0.65	0.68	0.64
$K_p = P_{CO_2} P_{H_2} / P_{CO} P_{H_2O}$	1.21	1.19	1.34	1.20	1.13	3.00	2.94	3.11	2.40	3.40
mmol CH_4/g-Fe/h	0.86	1.00	1.02	1.02	1.09	0.71	0.97	0.99	0.93	0.80
Hydrocarbon selectivity, wt%										
CH4	4.3	5.1	5.1	4.6	6.6	3.9	5.2	5.2	4.8	4.3
C2-C4	17.8	20.8	22.3	21.3	27.3	15.3	16.0	15.9	16.2	21.6
C5-C11	22.1	21.9	22.8	29.5	32.6	25.5	27.1	28.8	31.2	39.4
C12+	55.8	52.2	49.8	44.6	33.5	55.3	51.7	50.1	45.8	34.7
Chain growth parameter, α_{1-10}[b]	0.76	0.73	0.73	0.75	0.71	0.78	0.76	0.73	0.74	0.75
Olefin content, wt%										
C2-C4	79.7	78.4	77.9	74.9	74.2	76.7	76.6	74.5	74.8	72.5
C5-C11	69.7	65.4	68.1	75.2	75.0	76.8	80.1	77.4	77.0	79.7

Process conditions: 250°C, 1.48 MPa (200 psig), 2.0 Nl/g-cat/h, H_2/CO=0.67

[a]: Apparent reaction rate constant for a first order reaction in hydrogen, based on measured usage ratio.

[b]: Parameter estimated from products with carbon number in the range C_1-C_{10}.

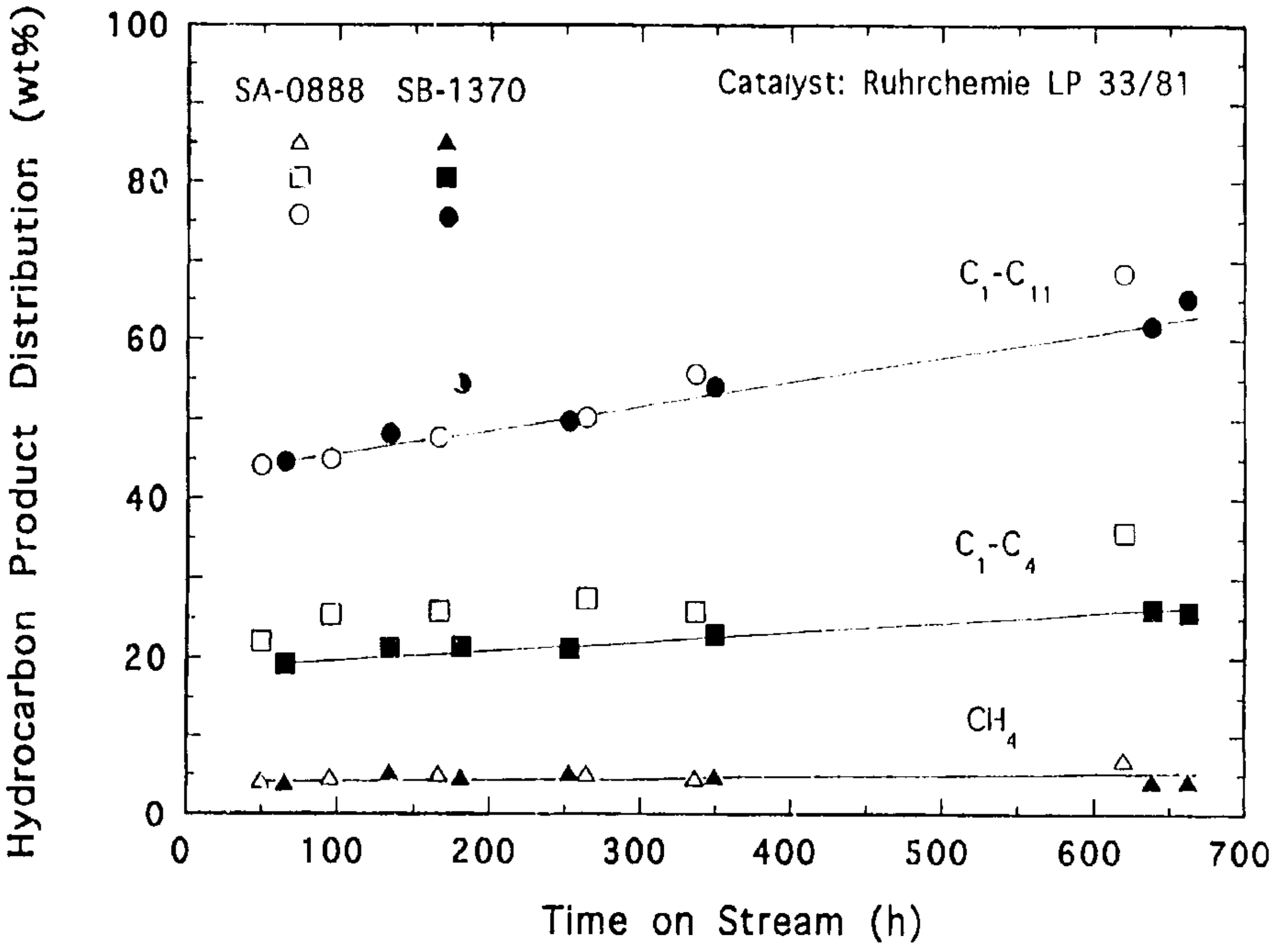

Figure III-4.9 Effect of time on stream on hydrocarbon product distribution in slurry reactor tests.

stream. Methane selectivity increased with time and at 662 h, it was 4.3 %. Figures III-4.10 and III-4.11 illustrate the effect of time on stream on the olefin content and the 2-olefin selectivity, respectively. The olefin content decreased whereas the 2-olefin selectivity increased with time, which is consistent with trends observed in Run SA-0888 (CO activated catalyst).

III-4.4 Comparison between FBR and STSR Results

The catalyst was reduced under similar conditions with H_2 at 220°C in the fixed bed test FA-0113 and in the slurry phase test SB-1370. Also, similar pretreatment procedures were employed in the fixed bed test FB-1588 and slurry phase test SA-0888 using CO as reductant. During the subsequent FT synthesis, the catalyst exhibited stable activity in both fixed bed and slurry phase reactors, as demonstrated in Figures III-4.2 (FBR) and III-4.8 (STSR). However, the catalyst activity was significantly lower in the slurry reactor than in the fixed bed reactor following the H_2 reduction. In the fixed bed test FA-0113 the syngas conversion was about 72%. In the slurry phase test SB-1370 the catalyst activity gradually increased during the first 60 h on stream and steady state syngas conversion was about 40 %. The apparent first order rate constant was about 240 mmol/g-Fe/h/MPa in the fixed bed test FA-0113, whereas only 133-152 mmol/g-Fe/h/MPa (see Tables III-4.2 and III-4.3). It appears that the H_2 reduction was less effective in the slurry reactor than in the fixed bed, and the catalyst in the slurry had undergone further activation during the initial period of synthesis. Nonetheless its steady state activity was still much lower than in the fixed bed reactor. On the other hand, following the pretreatment with CO, the apparent first order rate constant obtained after 40 h under the process conditions was about 200 and 187 mmol/g-Fe/h/MPa in the FBR and STSR, respectively. Thus, the intrinsic catalyst activity was the same in both reactors.

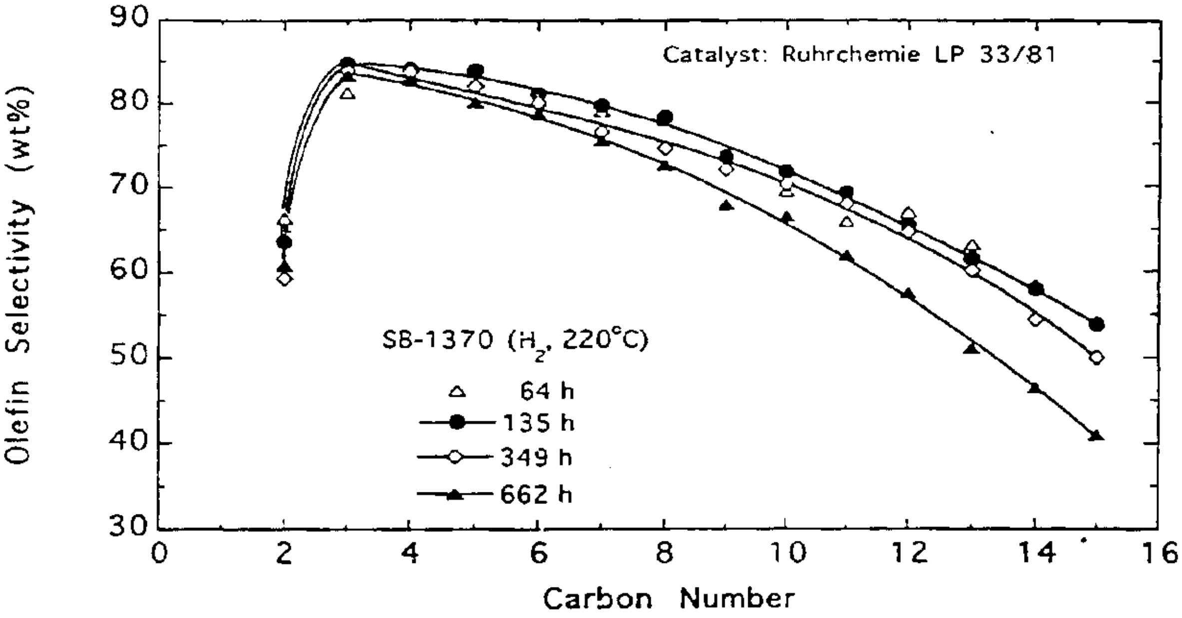

Figure III-4.10 Effect of time on stream on olefin selectivity in test SB-1370.

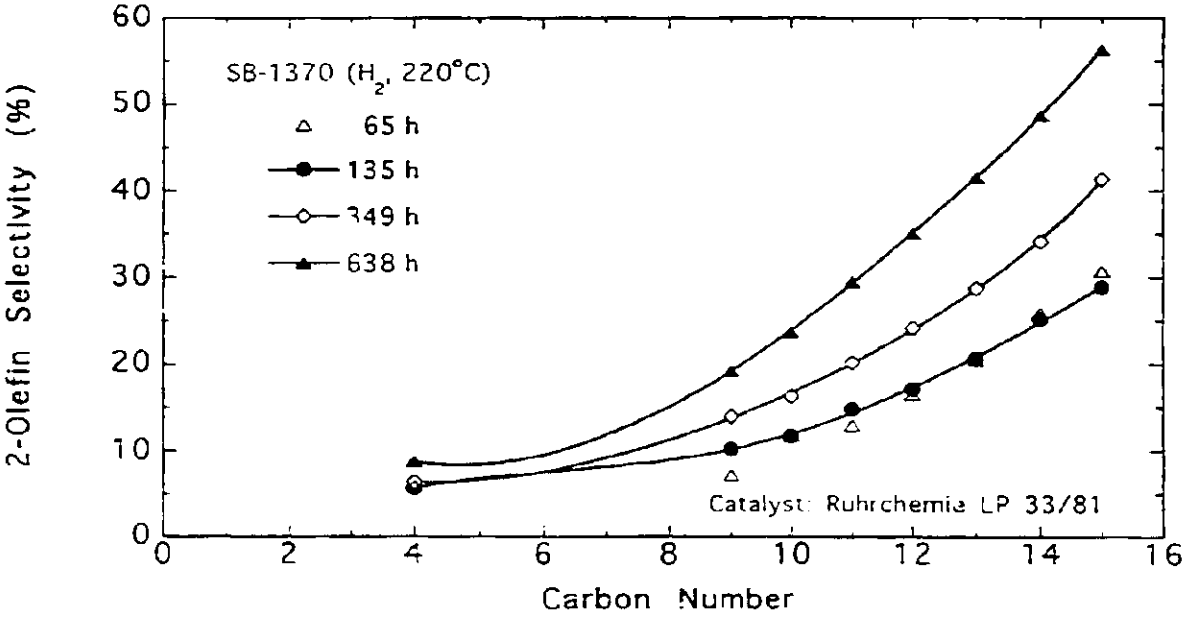

Figure III-4.11 Variation of 2-olefin selectivity with time on stream in test SB-1370.

The effect of reactor type on hydrocarbon selectivity is shown in Figure III-4.12. Following CO activations, the hydrocarbon distributions were similar: 5.6 wt% (CH_4), 22.7% (C_2-C_4), 19.1% (C_5-C_{11}) and 52.2% (C_{12}+) in the fixed bed reactor, and 4.7 % (CH_4), 19.8% (C_2-C_4). 21.1% (C_5-C_{11}) and 54.2% (C_{12}+) in the slurry phase reactor. After H_2 reduction, selectivities to methane and C_2-C_4 hydrocarbons were similar in fixed bed and slurry reactors. However, C_5-C_{11} selectivity was higher (29 vs. 21%), and C_{12}+ selectivity was lower (50 vs. 55%) in the STSR than in the FBR.

The olefin content and 2-olefin selectivity changed with time on stream in the STSR test. In Figures III-4.13 and III-4.14, the initial selectivities, obtained in the first mass balance, were chosen to assess the effects of pretreatment and reactor type on olefin selectivities. Both the olefin content and the 2-olefin selectivity were similar in the fixed bed and slurry reactors after about 40 h at the process conditions following the CO pretreatment. In the case of H_2 reduction, the olefin content was lower and the olefin isomerization activity was markedly higher in the fixed bed (FA-0113) than in the slurry reactor (SB-1370). These differences in olefin selectivities are at least partly caused by differences in conversion levels, higher conversions favor secondary reactions. It is interesting to note that the initial olefin and 2 - olefin selectivities in the slurry reactor test SB - 1370 were similar to those obtained after the CO pretreatment. A possible explanation for this type of behavior is discussed below.

After the CO pretreatments, the catalyst intrinsic activity and selectivity was similar in fixed bed and slurry reactors, i.e. the catalyst performance was independent of the reactor type used, particularly during the initial period of synthesis following the pretreatment. An iron catalyst changes its structure during the FT synthesis (e.g., transformation of iron carbides to iron oxides), and these changes over long time periods could be different in a fixed bed reactor than in a slurry reactor environment.

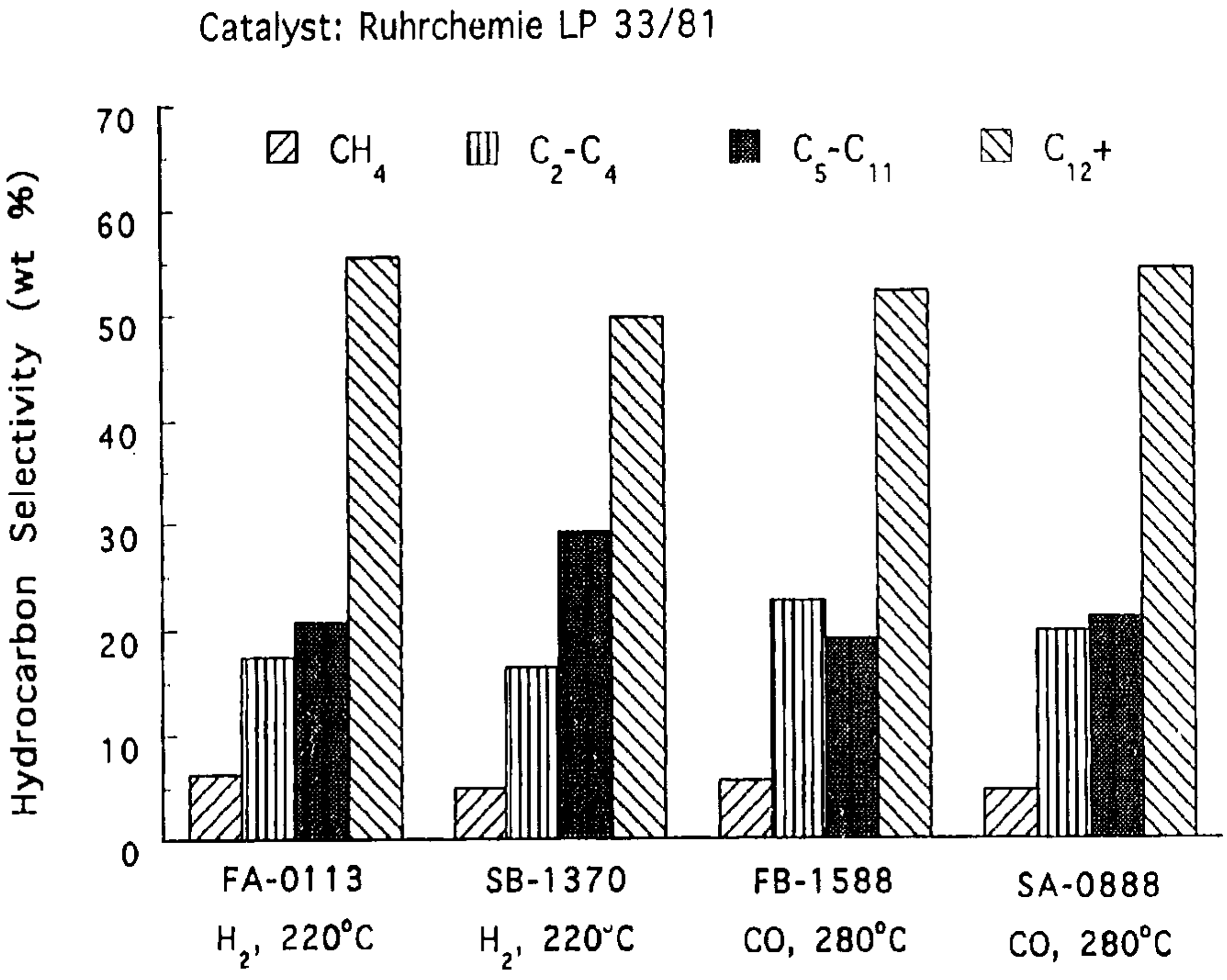

Figure III-4.12 Comparison of hydrocarbon selectivities in fixed bed and slurry reactor tests.

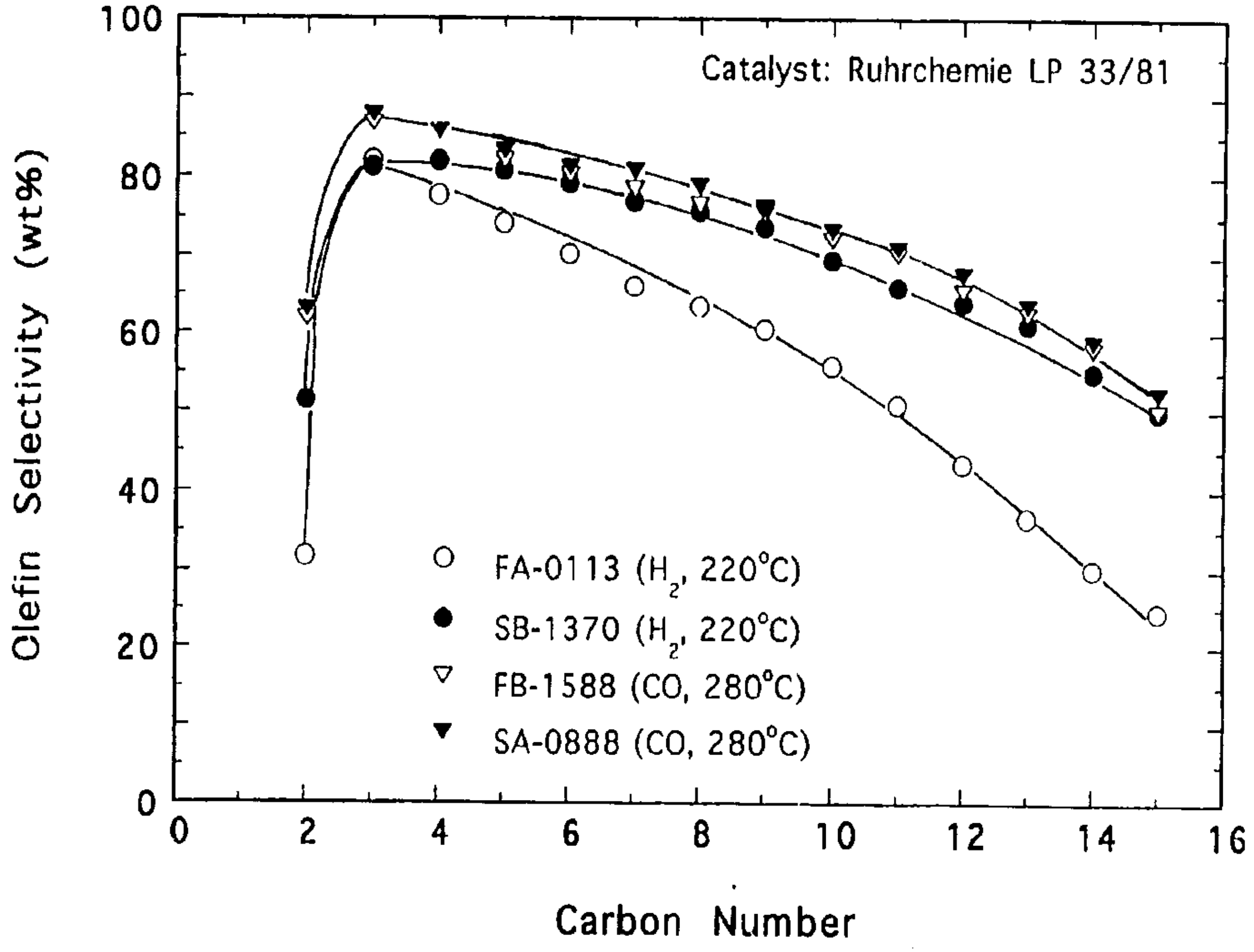

Figure III-4.13 Comparison of olefin selectivities in fixed bed and slurry reactor tests.

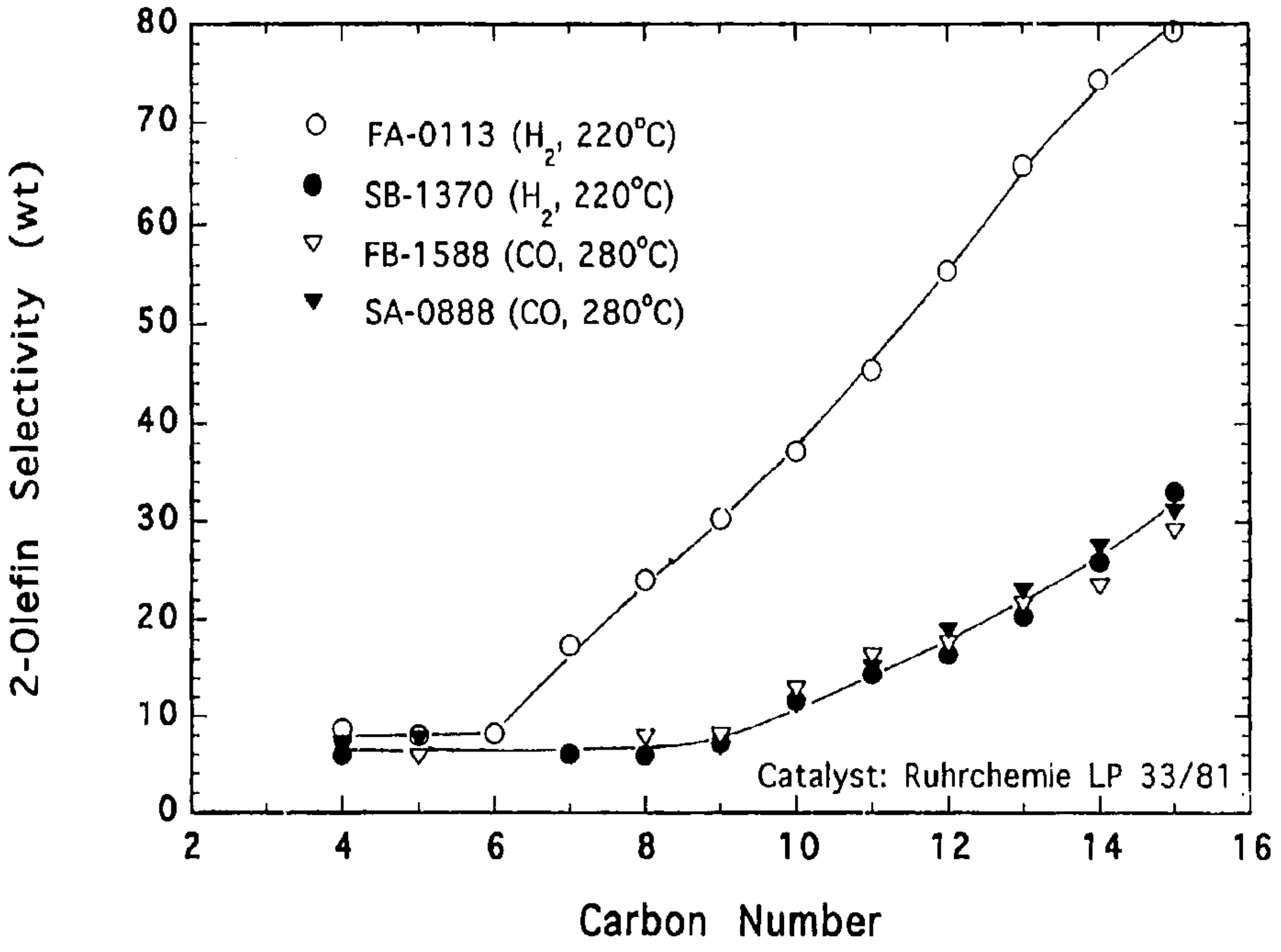

Figure III-4.14 Comparison of 2-olefin selectivities in fixed bed and slurry reactor tests.

Thus, the long term catalyst activity and selectivity could become different in these two types of reactors, which was observed to some extent in our study (Bukur et al., 1990c).

Results after H_2 reductions show different type of behavior. Significant differences in catalyst activity and selectivity were observed between the fixed bed and slurry reactor tests, even during early periods of FT synthesis. Due to lack of catalyst characterization data of the reduced slurry catalyst, we could only speculate about possible reasons for the observed differences in the catalytic behavior. As already mentioned earlier, by employing low reduction temperature (220°C) and short duration (1 h), the Ruhrchemie catalyst was only reduced to Fe_3O_4 in the fixed bed reactor (Table III-3.1). It is likely that the extent of reduction was even lower in the slurry reactor. The existence of induction period following the reduction in the test SB - 1370 suggests that the catalyst was not properly activated. Instead, the catalyst activation took place under the synthesis conditions (i.e. activation with a syngas). These differences in pretreatment procedures, giving rise to different initial phases, may be the reason for the observed differences in catalyst activity and selectivity in the fixed bed and stirred tank reactor tests. In particular, the above hypothesis also provides an explanation for the observation that the olefin selectivities in the slurry test SB - 1370 were similar to those obtained after the CO pretreatments (Tests SA - 0880, and FB - 1588). It is known, from our studies with this and other precipitated iron catalysts, that olefin selectivities following CO and syngas pretreatments are similar.

III-4.5 Summary

The effects of pretreatment conditions on the Ruhrchemie catalyst performance (activity, selectivity and stability with time) during Fischer-Tropsch synthesis were studied in fixed bed (six pretreatment procedures) and stirred tank slurry (two pretreatment procedures) reactors. The major findings from these tests are summarized below.

It was found that hydrogen reductions (four different pretreatments) result in stable or increasing catalyst activity with time on stream. Pretreatment conditions (temperature, duration and/or gas flow rate) have some effect on subsequent catalyst activity. Activity of the catalyst reduced at 220°C was about 20% higher than that of the catalyst reduced at 280°C for 24 hours. This is believed to be due to higher surface area (smaller crystallite size) of the catalyst reduced at low temperature, and differences in oxidation states of iron in the bulk and on the surface of the catalyst during the FT synthesis. In tests following hydrogen reductions at 280°C (three different procedures) the catalyst produced more methane and gaseous hydrocarbons than the catalyst reduced at 220°C, and CO or syngas pretreated catalyst. Secondary reactions (olefin hydrogenation and isomerization) were more pronounced in tests in which hydrogen reductions were employed.

Pretreatments with carbon monoxide and syngas result in formation of Hägg χ - carbide, which is very active for FT synthesis. The CO pretreated catalyst deactivated with time on stream due to conversion of χ - carbide to less active iron oxide phases, and buildup of inactive carbonaceous species which block the active sites on the surface. Activity of the syngas pretreated catalyst was stable during 130 h of testing at the baseline conditions. The apparent rate constant of the syngas pretreated catalyst was about 10% less than that of the catalyst reduced with H_2 at 220°C, even though its surface area after the pretreatment was significantly smaller than that of the H_2 reduced catalyst (99 vs. 179 m^2/g). Hydrogenation activity of the syngas pretreated catalyst is slightly greater than that of the CO pretreated catalyst.

Two pretreatment procedures (H_2 reduction at 220°C, and CO pretreatment at 280°C) were employed in stirred tank slurry reactor tests. These tests were of much longer duration than the corresponding fixed bed reactor tests, and they lasted over

700 hours. The activity of the H_2 reduced catalyst increased by about 10% during the first 360 h on stream and than remained stable for the remainder of the test, whereas the apparent rate constant of the CO pretreated catalyst was fairly stable during the first 390 h but declined sharply by 36% at 420 h on stream. After this unexpected step change in activity, it remained stable during the next 300 h of testing. The activity of the CO pretreated catalyst during the first 360 h on stream (before the abrupt drop in activity) was about 25% higher than that of H_2 reduced catalyst. This is attributed to incomplete reduction in the case of the latter, and higher FT activity of χ - carbide relative to magnetite. In both tests the catalyst selectivity changed with time on stream. Hydrocarbon product distribution shifted toward lower molecular weight products, and the secondary reactions (olefin hydrogenation and isomerization) increased with time.

III-4.6 References

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