

III-2 Pretreatment Effect Research - Reaction Studies with 100 Fe/0.3 Cu/0.8 K Catalyst

In this section we report our studies on pretreatment effect using a precipitated, unsupported iron catalyst with nominal composition 100 Fe/0.3 Cu/0.8 K in parts per weight. Pretreatment parameters investigated were: gas composition, temperature, duration and flowrate. Five pretreatment procedures were used to study their effect on subsequent catalyst performance in a fixed bed reactor. Two additional tests were carried out in a stirred tank slurry phase reactor. Test identifications and pretreatment conditions are listed in Table III-2.1.

Table III-2.1 Pretreatment Conditions and Test Designations

Test (ID)	Temp. (°C)	Reductant	Duration (h)	Pressure (MPa)	Flowrate (cm ³ /min)
FB-0403	250	H ₂	2	0.1	4,000
FB-3221	280	H ₂	8	0.1	175
FB-0352	280	H ₂ /CO=0.7	8	0.1	150
FB-0942	310	H ₂ /CO=2.0	6	0.1	1,200
FB-0021	280	CO	8	0.1	175
SA-0791	250	H ₂	2	0.8	7,500
SB-2262*	280	H ₂ /CO=0.7	12	0.8	343

FB = Fixed bed reactor test; SA, SB = Slurry phase reactor test;

* Different catalyst batch used in this test

III-2.1 Experimental Procedure

In fixed bed reactor tests, about 3.0 to 3.5 g of calcined catalyst was diluted 1:8 by volume with glass beads of the same size range (32/60 mesh) and loaded into the reactor. Helium was fed through the reactor at a gas space velocity of 3.0 NI/g-cat/h during heating-up. For the pretreatments using hydrogen, hydrogen was introduced to the reactor at a temperature about 10 °C below the desired pretreatment temperature, whereas for the pretreatments using CO or syngas, the activation gas was introduced usually at 20 - 30°C below the desired temperature. Such precaution is needed to prevent a temperature runaway. Following the catalyst pretreatment, flow was switched to helium and the reactor temperature was decreased to 190-200°C. The reactor system was then pressurized to 1.48 MPa (200 psig), the helium flow was stopped, and synthesis gas ($H_2/CO = 0.67$) was introduced at gas space velocity of 2.0 NI/g-cat/h (2.9 NI/g-Fe/h). The reactor temperature was then increased to 250°C according to a time-temperature schedule shown in Table III-2.2 (conditioning period). A gradual increase in reaction temperature was used to prevent development of hot spots within the reactor. After achieving desired process conditions of 250°C, 1.48 MPa, 2.0 NI/g-cat/h and $H_2/CO = 0.67$, the catalyst was tested over a period of 100 to 150 h, during which two or three mass balances were made at approximately 70, 90 and 140 h on stream (including 30 h conditioning period). Tail (exit) gas was analyzed frequently during the entire test. Detailed description of our fixed bed reactors, product analysis system and operating procedures is provided in Appendix A.

III-2.2 Results

Activity and Stability

Catalyst activity, measured by volumetric gas contraction, as a function of temperature and time during the conditioning period is shown in Figure III-2.1. Volumetric contraction, defined as $100 \times (\text{inlet flowrate} - \text{outlet flowrate}) / \text{inlet flowrate}$,

Table III-2.2 Start-up/Temperature Schedule Used during Conditioning Period following Catalyst Pretreatment

Time on stream, h	Temperature, °C	Duration, h
	reduction - 190	1
0	190 - 200	1
1	200	1
2	200 - 210	1
3	210	2
5	210 - 220	1
6	220	3
9	220-230	1
10	230	12
22	230-240	1
23	240	4
27	240-250	2

is a convenient measure of catalyst activity, since it changes nearly linearly with syngas (H_2+CO) conversion. It can be seen that the gas contraction increases with temperature and reaches different values at the end of the conditioning period. Results during the conditioning period are indicative of initial catalyst activity. During the first ten hours on stream the data are scarce and erratic due to non uniformity of reactor temperature and fluctuations in outlet gas flow rate. At temperatures of 230 °C and above (10 - 30 h on stream) the activity of hydrogen reduced catalysts was lower than that of the CO or syngas pretreated catalysts. Hydrogen reduction at 280 °C resulted in the lowest gas contraction (catalyst activity).

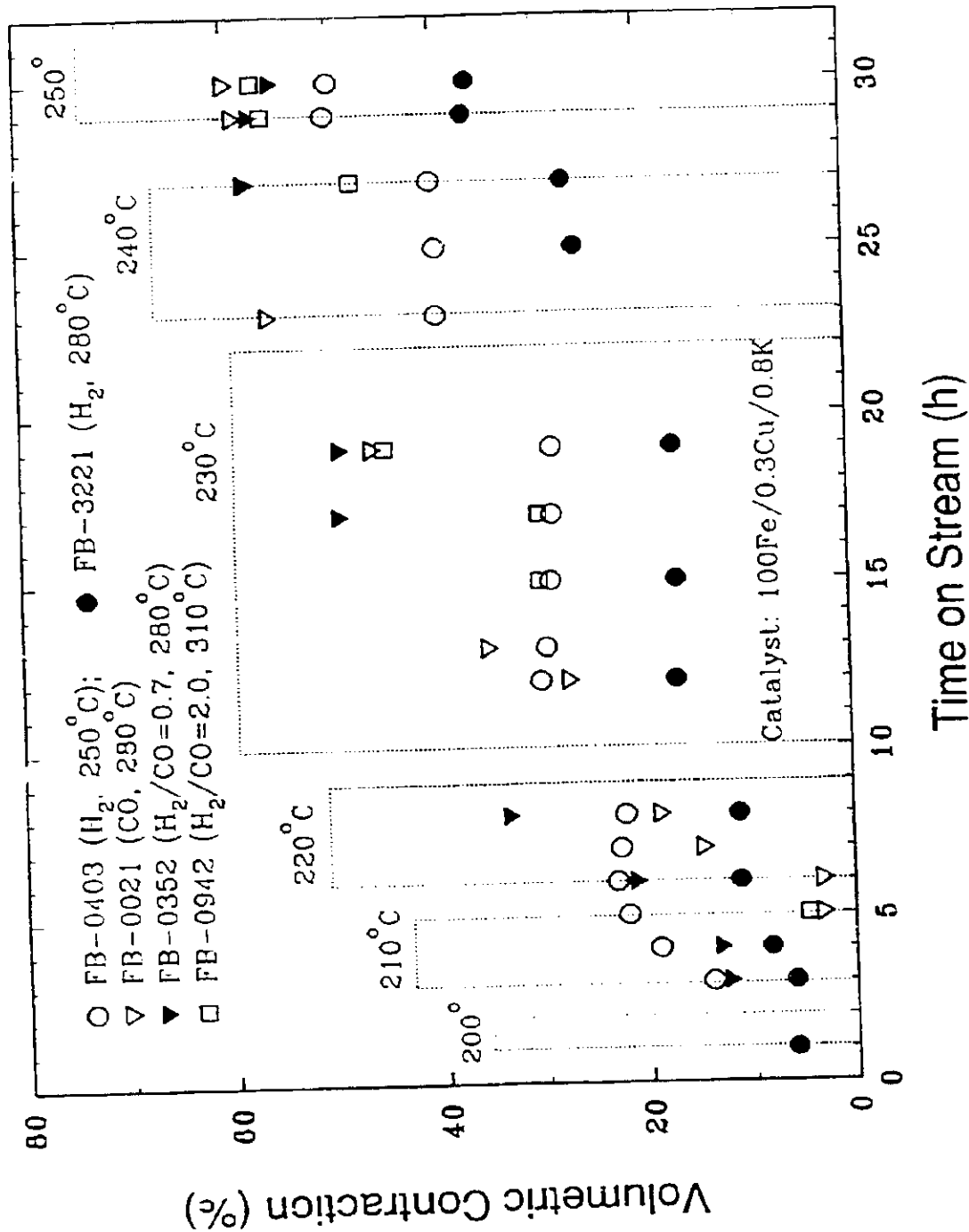


Figure III-2.1 Volumetric contraction during conditioning period.

Catalyst activity and stability, at the process conditions, as a function of time-on-stream (TOS) is shown in Figure III-2.2. The activity is represented by (H₂+CO) conversion (defined as mole of syngas consumed per mole of syngas fed). The catalyst exhibited similar activity behavior after pretreatments with carbon monoxide (280°C for 8 h) or syngas (both H₂/CO = 0.7 at 280°C for 8 h and H₂/CO = 2.0 at 310°C for 6 h). Initial (H₂+CO) conversion was between 85 and 93%. However, the catalyst deactivated with time-on-stream, following a similar time-dependent behavior in all three cases. The (H₂+CO) conversion decreased to about 55 % at 150 h on stream.

Catalyst activity after reduction with hydrogen was clearly dependent on the reduction conditions employed (temperature, duration and flowrate). After reduction at 250°C, flowrate 4000 cc/min (which corresponds to a linear gas velocity of 150 cm/s) for 2 h, the initial (H₂+CO) conversion was 77 %; whereas after reduction at higher temperature of 280°C, flowrate 175 cc/min (which corresponds to a gas space velocity of 3.0 NI/g-cat/h) for 8 h the (H₂+CO) conversion was only about 50 %. During the FT synthesis, the (H₂+CO) conversion increased steadily with time reaching 85 and 58 %, respectively. Such time-dependent behavior is in contrast to that observed following CO or syngas pretreatment.

Water gas shift (WGS) activity of the catalyst is related to H₂ to CO usage ratio (UR), and partial pressure quotient ($K_p = P_{CO_2} P_{H_2} / P_{CO} P_{H_2O}$). Lower values of the usage ratio, or higher values of the K_p imply higher WGS activity. In both tests, after hydrogen reduction, the usage ratios were similar, about 0.60-0.61, and stable with time on stream (Table III-2.3). For the catalyst pretreated with CO and H₂/CO = 2, the usage ratio was 0.61 - 0.64, whereas for the catalyst pretreated with syngas H₂/CO = 0.7 the usage ratio was 0.59. In the latter three cases, even though the overall catalyst activity decreased continuously, the usage ratio did not change with time. Hydrogen reduced catalyst had higher K_p values, than either CO or syngas pretreated catalyst. In

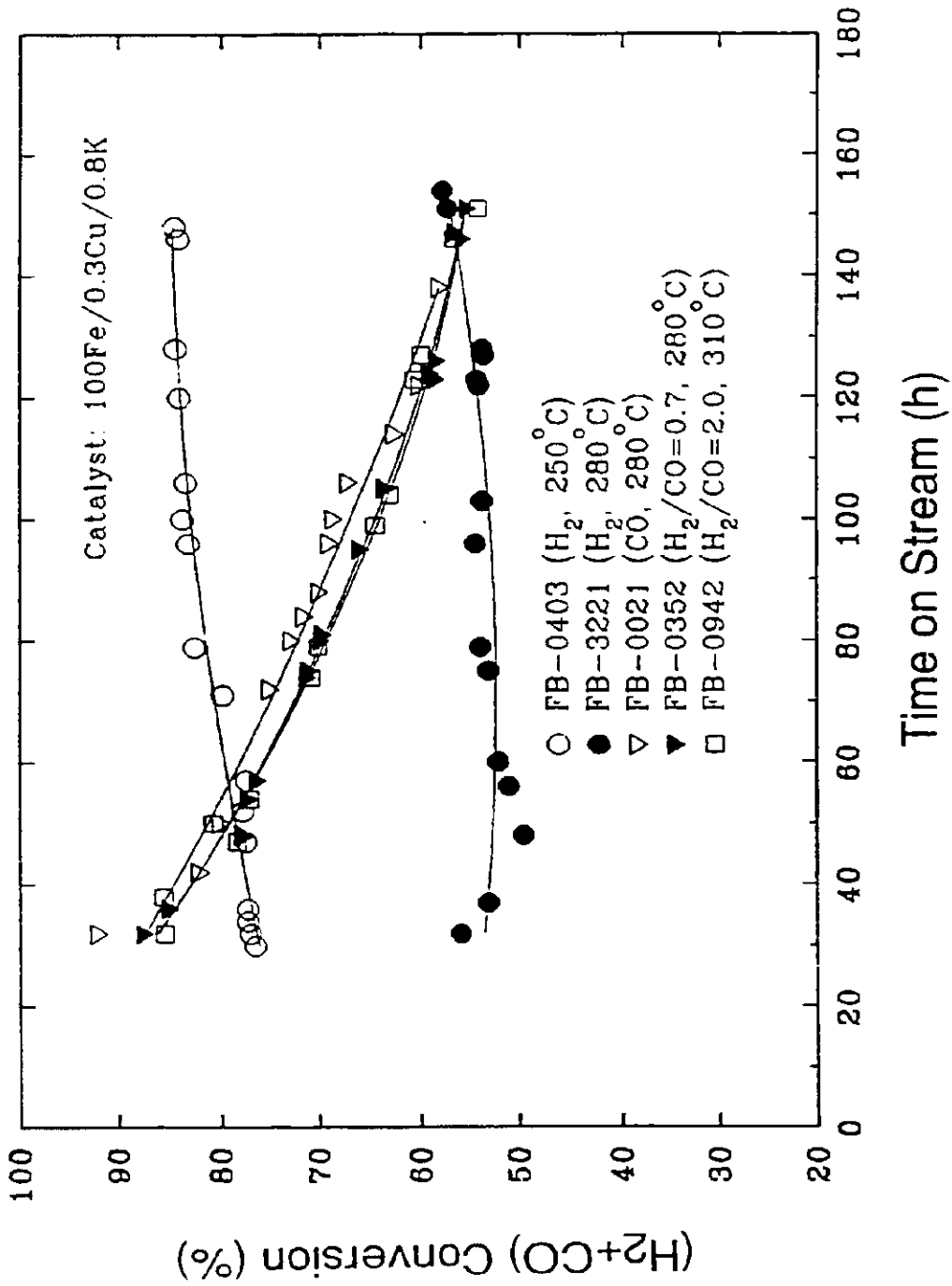


Figure II-2.2 Effect of pretreatment conditions on conversion and catalyst stability.

Table III-2.3. Summary of Results for Pretreatment Effect Study with 100 Fe/0.3 Cu/0.8 K Catalyst - Fixed Bed Reactor Tests

Test designation	FB-0403		FB-3221		FB-0352		FB-0942		FB-0021	
Time-on-stream, h	67	116	72	149	72	144	62	134	68	92
CO conversion, %	86.4	89.5	56.0	61.0	76.8	59.7	72.8	57.9	73.0	70.1
(H ₂ +CO) conversion, %	81.4	84.3	54.1	58.2	70.7	55.7	70.7	56.6	70.0	67.6
S _T ⁻¹ , mmol/g-cat/h	73	75	48	52	63	50	63	50	63	60
k, mmol/g-Fe/h/MPa ^a	218	229	134	142	177	134	190	142	180	171
(H ₂ /CO) usage ratio	0.61	0.61	0.60	0.60	0.59	0.59	0.64	0.64	0.61	0.61
(H ₂ /CO) exit ratio	1.30	1.54	0.74	0.80	1.18	0.86	0.79	0.74	0.82	0.81
$K_p = P_{CO_2} P_{H_2} / P_{CC} P_{H_2O}$	77.0	78.1	46.1	48.0	20.0	17.8	5.60	4.10	18.0	15.0
mmol CH ₄ /g-Fe/h	2.44	2.44	1.23	1.35	1.11	1.00	1.21	1.00	1.00	0.89
Hydrocarbon selectivity, wt%										
CH ₄	9.1	8.4	6.8	6.8	4.3	5.0	4.4	4.8	3.1	3.7
C ₂ -C ₄	26.5	24.4	23.0	22.4	18.6	20.6	18.8	19.5	18.1	18.2
C ₅ -C ₁₁	41.3	41.7	37.8	30.2	23.1	24.0	24.6	24.0	23.5	22.5
C ₁₂ ⁺	23.1	25.5	32.4	40.6	54.0	50.4	52.2	51.7	55.3	55.5
Chain growth parameter, α_{1-10} ^b	0.73	0.75	0.72	0.70	0.72	0.70	0.75	0.73	0.77	0.75
Olefin content, wt%										
C ₂ -C ₄	75.2	73.2	77.3	76.3	79.8	78.0	81.3	80.2	81.3	81.5
C ₅ -C ₁₁	73.0	72.7	79.9	71.8	85.2	84.6	86.1	85.6	80.6	82.1

Process conditions: 250°C, 1.48 MPa (200 psig), 2.0 NI/g-cat/h, H₂/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 in the carbon number range C₁ - C₁₀.

general, the pretreatment procedure had small effect on WGS activity under the conditions studied.

Selectivity

Hydrocarbon product distribution and the fraction of olefins in hydrocarbons obtained during two mass balances for each of the five pretreatment procedures are given in Table III-2.3. Hydrocarbon selectivity remained relatively stable in tests in which hydrogen reductions were employed. After CO or syngas pretreatment, hydrocarbon selectivity usually shifted towards lower molecular weight hydrocarbons, especially methane, as the catalyst deactivated with time. For example, methane selectivity gradually increased from 4.3 to 5.0 wt % between 70 to 150 h on stream in test FB-0352 (i.e. the increase of about 16 %). However, such changes with time on stream for a given pretreatment procedure were small in comparison to more profound differences in selectivity resulted from the use of different pretreatment procedures. Therefore, the average values from two and/or three balances (not shown in Table III-2.3) were used to compare the effect of pretreatment procedures on selectivity.

Figure III-2.3 compares hydrocarbon product selectivity, lumped into four groups of products C₁ (methane), C₂-C₄ (light gases), C₅-C₁₁ (gasoline fraction), and C₁₂+ (diesel fuel and hydrocarbon wax). Low methane and gaseous hydrocarbon selectivities, and high C₁₂+ selectivities were obtained when CO and/or syngas pretreatments were employed. CO pretreated catalyst had the lowest methane selectivity, less than 4 %. On the other hand, hydrogen reduced catalyst produced more methane and other low molecular weight products. The highest methane selectivity, about 9 %, was obtained following reduction with H₂ at 250°C.

Rate of methane formation as a function of time on stream for different pretreatment procedures is shown in Figure III-2.4. The catalyst pretreated with CO or syngas produces significantly less methane than the one reduced with hydrogen at

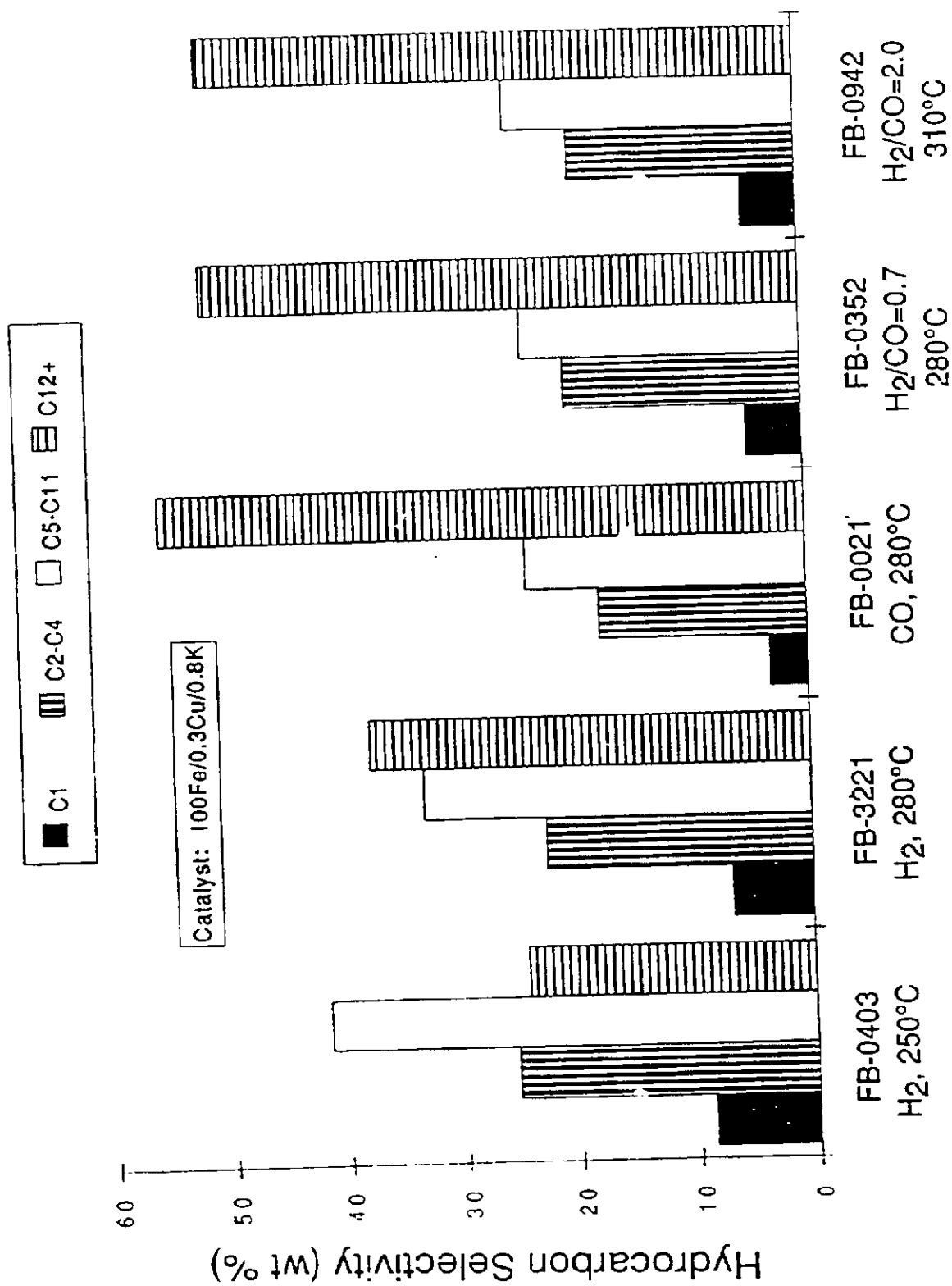


Figure III-2.3 Effect of pretreatment conditions on hydrocarbon product distribution.

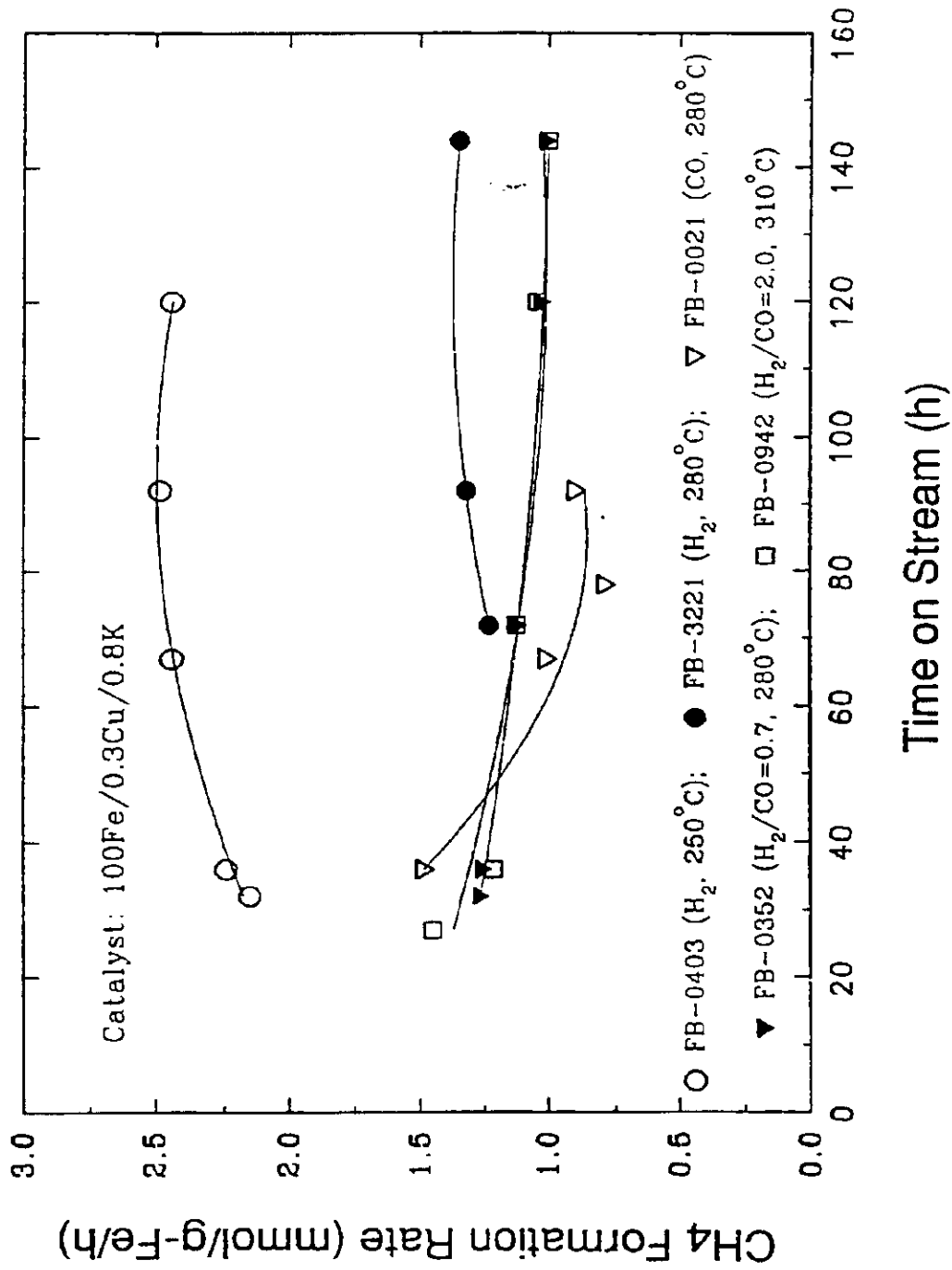


Figure III-2.4 Methane formation rate vs. time on stream following different pretreatment conditions.

250°C. The methane formation rate of the catalyst reduced by hydrogen at 280°C was much lower than that obtained following hydrogen reduction at 250 °C, and slightly higher than those obtained following CO or syngas pretreatment. It is interesting to note that methane formation rate per gram of iron in the catalyst decreases with time for CO and syngas pretreatments, but methane selectivity (expressed as weight percent of methane in hydrocarbons) increases with time (Table III-2.3). These opposite, and seemingly contradictory trends, are due to catalyst deactivation. In this case the rates of production of other hydrocarbons also decrease with time, but at a faster rate than the rate of methane formation, and as a result the methane selectivity increases with time. The opposite trend is observed with the catalyst after hydrogen reduction at 250°C, where methane production rate increases with TOS (Figure III-2.4), but the methane selectivity decreases with time (Table III-2.3). In this case the rate of FT synthesis, and rates of production of other hydrocarbons also increase with time but at the faster rate than the methane production. Similar trends were observed for the rate of formation of light gases, but are not shown here.

Primary products of Fischer-Tropsch synthesis are 1-olefins, which are converted to paraffins and 2-olefins via secondary reactions. The olefin content, defined as $100 \times \text{olefin}/(\text{olefin} + \text{paraffin})$, is a measure of hydrogenation activity. Weight percent olefin content in C₂-C₄, and C₅-C₁₁ hydrocarbons is given in Table III-2.3, whereas its variation with carbon number (up to C₁₅) is illustrated in Figure III-2.5. For each pretreatment the ethene content is always low, since it readsorbs and undergoes secondary hydrogenation more readily than other low molecular weight olefins. The olefin content has a maximum at C₃, and then decreases with carbon number. The olefin contents are generally lower after hydrogen reductions than after CO or syngas pretreatments (Figure III-2.5). These results are not due to differences in conversions. The two hydrogen reductions resulted in nearly the same olefin

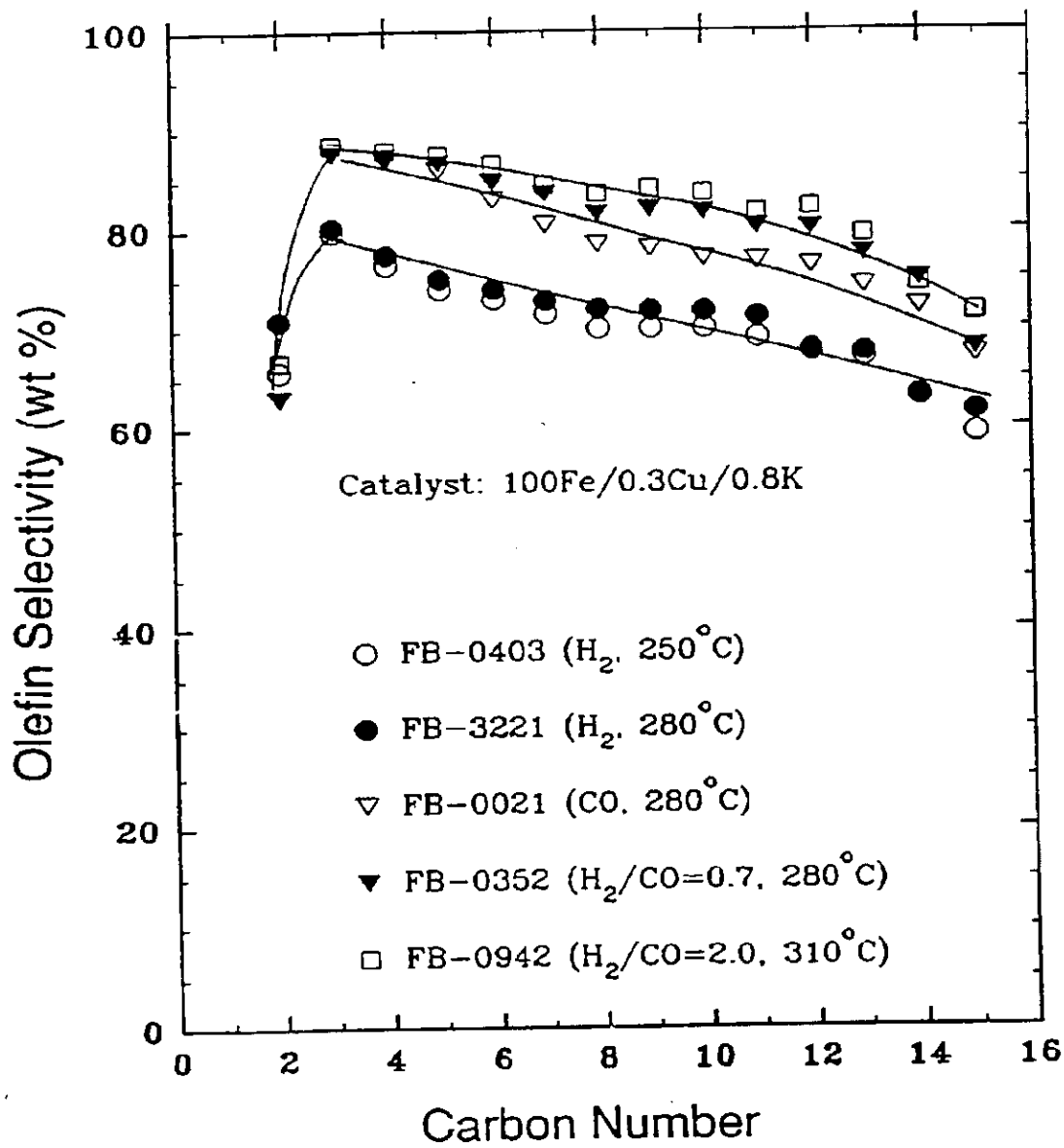


Figure III-2.5 Effect of pretreatment conditions on olefin selectivity.

selectivities, in spite of differences in conversions (Figure III-2.2). Also for CO and syngas reductions, the olefin selectivity did not vary with time on stream, in spite of catalyst deactivation.

Ratio of 2-olefin/(1+2) olefins is indicative of olefin isomerization activity. This ratio usually increases with carbon number, especially for hydrocarbons in the liquid phase (C₈+). The 2-olefin content is higher after H₂ reductions, and is the lowest after the CO pretreatment (Figure III-2.6). In general, the 2-olefin selectivity (i.e. 1-olefin isomerization activity) is low for this catalyst, which is due to its relatively high potassium content.

Carbon number product distributions, after two pretreatment procedures, are shown in Figure III-2.7 in the form of Anderson-Schulz-Flory (ASF) plots (mole fraction vs. carbon number). It can be seen that mole fractions of high molecular weight products are significantly smaller on the catalyst reduced with hydrogen. It was found that whenever all products collected were analyzed, including those in the high-pressure trap, two chain growth probabilities were needed to characterize the product distribution. A three parameter model of Huff and Satterfield (1984) was found to adequately represent these data:

$$x_n = (1 - \alpha_1) \alpha_1^{n-1} + (1 - \beta)(1 - \alpha_2) \alpha_2^{n-1}$$

where x_n is the mole fraction of products containing n carbon number atoms (hydrocarbons and oxygenates), β is the fraction of type 1 sites on the catalyst, and α_1 and α_2 are the chain growth probabilities associated with the type 1 and type 2 sites, respectively. The model parameters were estimated by a nonlinear regression, and their numerical values for all pretreatment procedures are summarized in Table III-2.4 together with 95% confidence interval limits for these parameters.

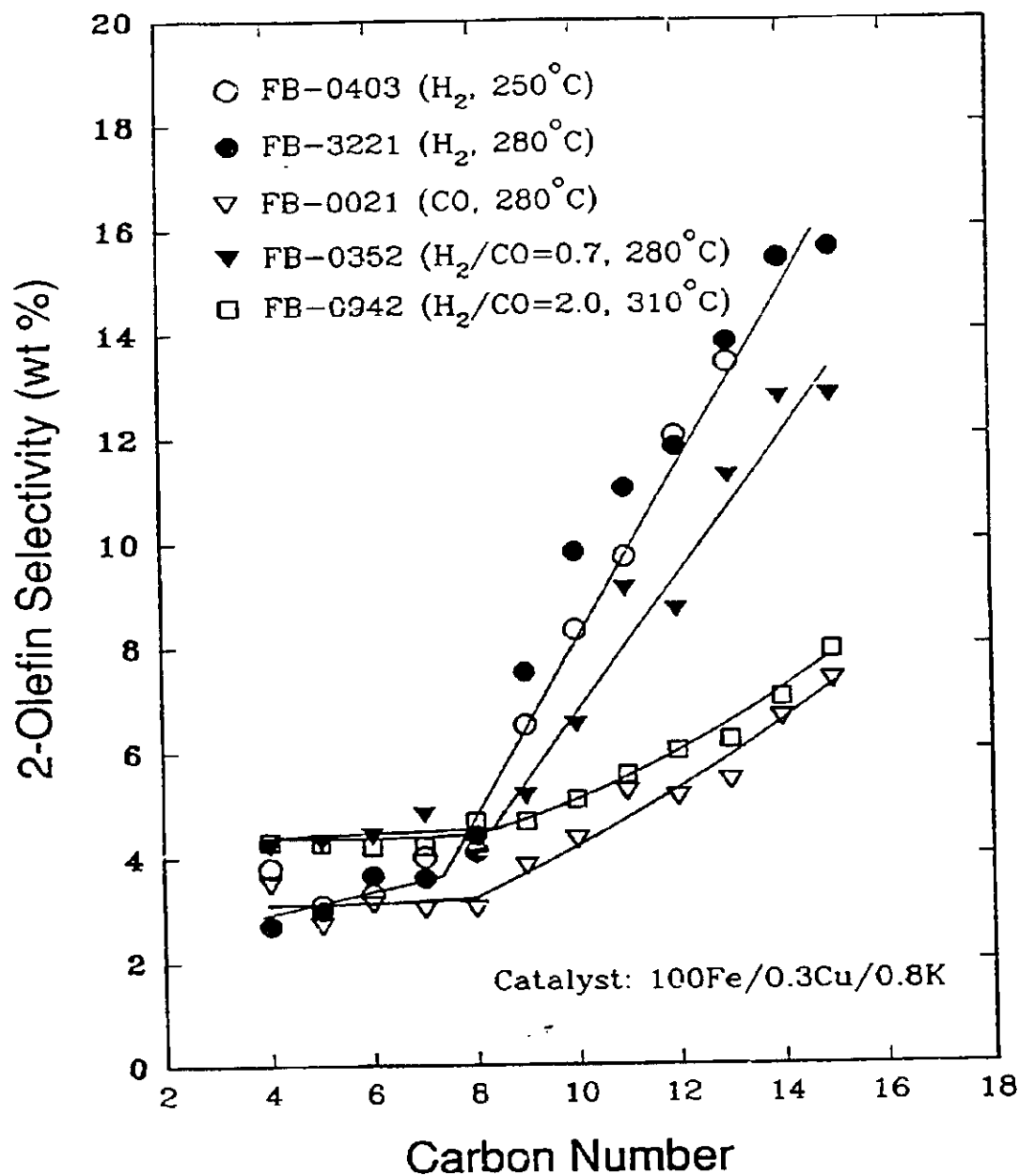


Figure III-2.6 Effect of pretreatment conditions on 2-olefin selectivity.

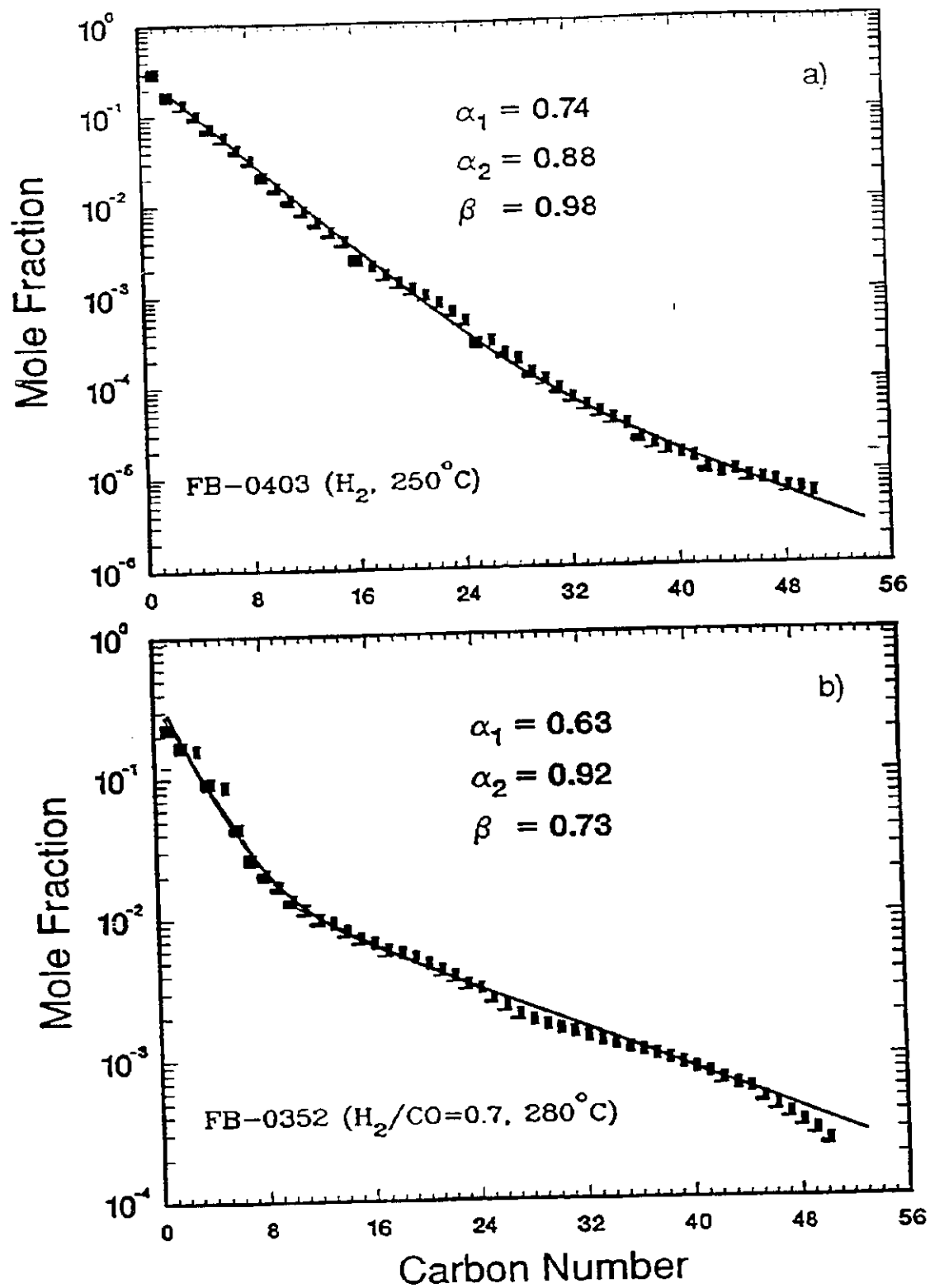


Figure III-2.7 Anderson-Schultz-Flory distribution for selected pretreatment conditions. a) Run FB-0403; b) Run FB-0352

Table III-2.4 Chain Growth Probability Factors for Different Pretreatment Procedures^a

Test	TOS, h	α_1 (95% CI) ^b	α_2 (95% CI) ^b	β (95% CI) ^b
FB-0403	67	0.74 (0.73-0.75)	0.88 (0.87-0.90)	0.98 (0.97-0.99)
FB-3221	120	0.61 (0.57-0.65)	0.86 (0.85-0.87)	0.75 (0.71-0.79)
FB-0352	72	0.63 (0.61-0.65)	0.92 (0.91-0.93)	0.73 (0.71-0.75)
FB-0942	62	0.68 (0.67-0.69)	0.92 (0.91-0.93)	0.77 (0.76-0.78)
FB-0021	88	0.68 (0.64-0.72)	0.90 (0.89-0.91)	0.74 (0.69-0.79)

^a Parameters estimated from products with carbon number in the range C₁-C₄₀.

^b 95% confidence interval.

III-2.3 Discussion

Five different pretreatment procedures were employed in the present study, and their effects on catalyst activity, stability and selectivity during the Fischer-Tropsch synthesis may be summarized as follows: (1) After CO or syngas pretreatments, the catalyst achieved high initial activity, which then decreased with time on stream. The catalyst behavior with time-on-stream, and product selectivities were similar after CO and syngas pretreatments. Initial activities of CO and syngas pretreated catalysts were higher than those of hydrogen reduced catalysts. (2) After H₂ reductions, catalyst activity was stable or gradually increased with time on stream. Activity of the catalyst reduced at 250°C for 2 h was significantly higher than that of the catalyst reduced at 280°C for 8 h. (3) CO and syngas activations favored production of higher molecular weight and more olefinic hydrocarbons, in comparison to H₂ reductions. (4) Olefin isomerization activity was low for all pretreatments, but relatively higher after hydrogen reductions. (5) Water gas shift activity was high, and did not vary markedly with pretreatment conditions.

The first three observations listed above are in agreement with our results from the study with a precipitated iron catalyst of nominal composition 100 Fe/3 Cu/0.2 K (Bukur et al., 1989a). A possible explanation for these observations is based on the fact that catalysts achieve different bulk structures after different pretreatment procedures, and in turn these structure differences affect CO and H₂ activation (chemisorption) during synthesis. Differences in bulk structures and surface concentrations of reactants result in different activity as well as selectivity trends.

After the pretreatment with CO or syngas, the dominant phase is the Hägg carbide. Surface areas and pore volumes of the catalyst were similar, too. During the subsequent FT synthesis reaction, 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. Decline in catalyst activity may be attributed to conversion of Hägg carbide (the most active phase) to inactive (or less active) phases such as magnetite and/or siderite. An alternative explanation for the catalyst deactivation with time, due to blocking of active sites by carbonaceous deposits, is provided below.

In FT synthesis, carbon monoxide undergoes dissociative adsorption (chemisorption) on the catalyst surface, forming a highly active species (Krebs and Bonzel, 1980; Ponc, 1982). The reactions of this surface carbon, C_S^{*}, proceed competitively with iron and hydrogen, or with itself, leading to: (1) formation of surface metal carbide, and then bulk carbide by carbon diffusion; or (2) hydrogenation to methyl species (synthesis of hydrocarbons); and (3) formation of inactive carbon. (Niemantsverdriet and van der Kraan, 1981). The competition depends on the concentration of hydrogen on the catalyst surface (Machocki, 1991).

The initial activity over carbided catalyst (CO or syngas pretreatment) is high, as shown in Figures III-2.1 and III-2.2. This indicates that the concentration of the surface carbon (formed from the synthesis gas) is high initially, and the dominant reaction is

hydrogenation to form hydrocarbons since the bulk of the catalyst has been already carbided. High synthesis rate implies that consumption of the surface hydrogen species is also high and on the surface of carbided catalyst, the abundant species is carbon rather than hydrogen. As a consequence of this, the rate of removal of surface carbon by hydrogenation is lower than the rate of CO dissociation. Then some of the C_S^* forms carbonaceous deposit, which eventually converts to inactive (graphitic) carbon. This inactive carbon can further block hydrogen chemisorption sites, lowering surface hydrogen concentration and leading to decrease in the rate of FT synthesis, i.e. catalyst deactivation. The formation of inactive carbon deposits on the surface of iron based FT catalysts is considered to be the major cause of catalyst deactivation (e.g., Krebs et al., 1979; Niemantsverdriet et al., 1980; Dwyer and Handenbergh, 1984).

The observation that the CO or syngas activated catalyst has higher initial activity than H_2 reduced catalyst is consistent with the competition model of Niemantsverdriet and van der Kraan (1981). During FT synthesis with 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 the 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 the metallic iron and/or magnetite.

Two different reduction procedures with H_2 were employed and they led to different degrees of catalyst reduction and different levels of stable catalyst activity. After reduction at $250^\circ C$, 4000 cc/min for 2h the catalyst was completely reduced to metallic iron and was very active in the subsequent synthesis. After reduction at higher temperature ($280^\circ C$, 175 cc/min for 8h) the reduction was incomplete (mostly magnetite) and the catalyst activity was much lower. It is known that water vapor inhibits the reduction of iron oxides in H_2 . High flowrate of H_2 during reduction

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decreases the water vapor pressure and facilitates the reduction. Surface area of the calcined catalyst was 130 m²/g, after H₂ reduction at 250°C and 280°C, it drops to only 21 m²/g in both cases, which indicates that sintering of Fe₂O₃ particles to Fe or Fe₃O₄, though very severe, is similar at two temperatures. Therefore, the difference in catalyst activity is mainly related to the initial degree of iron reduction. Completely reduced catalyst is more active for FT synthesis. Used catalyst samples contain two types of iron carbides (χ and ϵ'), and superparamagnetic oxides/hydroxides (probably magnetite, based on XRD results). The more active catalyst (H₂ reduction at 250°C) also has some α -Fe (Table III-1.5), whereas the less active catalyst does not contain metallic iron.

Another explanation for the observed differences in catalyst activity has been proposed by Sault (1991), on the basis of surface composition measurements by Auger Electron Spectroscopy. This study was conducted at Sandia National Laboratory using a catalyst synthesized in our Laboratory with nominal composition 100 Fe/3 Cu/0.2 K. In this study it was found that H₂ reductions are accompanied by sulfur migration to the surface of the catalyst. The sulfur arises from bulk sulfate impurities present in the metal nitrates used to prepare the catalyst. Sulfur coverage increases with both activation time and temperature, due to an increase in the rate of sulfur diffusion with temperature. Since sulfur is known to act as a poison for FT synthesis, the catalyst reduced at higher temperature and/or longer duration is expected to have lower FT activity, which is indeed observed in our studies with both 100 Fe/3 Cu/0.2 K and 100 Fe/0.3 Cu/0.8 K catalysts.

Catalyst stability with time-on-stream after hydrogen reductions, and the observed differences in product distributions resulting from the use of different reductants can be explained in terms of differences in surface concentrations of active carbon and hydrogen species.

When a catalyst reduced by hydrogen is exposed to a synthesis gas, the surface carbon species is formed which diffuses into the bulk to form bulk iron carbides. However, the catalyst can maintain a stable activity over a long period of time, in contrast to the precarbided catalyst (after CO or syngas pretreatment). A possible explanation for this observation is that concentration of surface hydrogen during the synthesis plays an important role in stabilizing the catalyst activity. We postulate that the hydrogen concentration on the surface is higher on an H₂ reduced catalyst than on a fully carbided catalyst following CO or syngas pretreatment. This could be due to a larger number of sites available for H₂ adsorption, or due to differences in strength of sites for hydrogen adsorption. Metallic iron (hydrogen reduced catalyst) is known to promote dissociative adsorption of hydrogen. When the concentration of surface hydrogen is sufficiently high the rate of removal of surface carbon through hydrogenation is higher than or equal to the rate of CO dissociation. In other words, the rates of surface carbon formation and removal are properly balanced, and the formation of carbonaceous, or inactive carbon, deposits is prevented or limited. Consequently, the catalyst does not deactivate, and its activity may increase as a result of continued creation of active sites.

Differences in selectivity obtained after H₂ and CO or syngas pretreatments may be due to differences in surface hydrogen concentrations during the FT synthesis. For example, the olefin contents in hydrocarbons were lower after H₂ reductions (Figure III-2.5). This is consistent with the assumption that the surface hydrogen concentration is higher on H₂ reduced than on CO or syngas reduced catalysts. Higher hydrogen concentration enhances hydrogenation of olefins. Similarly, higher methane selectivity and shorter chain length hydrocarbons (Figure III-2.3) obtained with H₂ reduced catalysts are the consequence of higher surface hydrogen concentration, since it favors methanation and chain termination reactions.

It was found that the use of different pretreatment procedures did not have marked effect on secondary olefin isomerization and water-gas-shift reactions. This may be attributed to relatively high potassium content of the catalyst used in the present study. Potassium is known to promote the rate of WGS reaction (Anderson et al., 1952; Arakawa and Bell, 1983; Bukur et al., 1990a), and to suppress the olefin isomerization (Dictor and Bell, 1986; Herzog and Gaube, 1989; Bukur et al., 1990a). Thus the catalyst behavior was largely determined by its potassium content rather than by differences arising from the use of different pretreatment procedures.

III-2.4 Stirred Tank Slurry Reactor Tests

The study in slurry phase was conducted in an one liter stirred tank reactor (Autoclave Engineers). Catalyst was sieved through 270 mesh (53 μm) and was placed in the reactor containing n-octacosane as the initial medium. There was no conditioning period, and process conditions were achieved in 1 h after a pretreatment. A detailed description of the slurry phase reactor system used in this study is given in Appendix A.

Two tests were conducted in the slurry reactor in order to determine whether the trends found in fixed bed reactor tests remain the same during FT synthesis in slurry phase. After reduction with H_2 at 250°C, 0.8 MPa and a flowrate of 7,500 cc/min for 2 h (SA-0791), the catalyst activity was stable during 250 h of testing at 260°C, 1.48 MPa, 2 NI/g-cat/h and $\text{H}_2/\text{CO} = 0.67$, and the syngas (H_2+CO) conversion was about 80 % (Figure III-2.8). The usage ratio was about 0.60, and the partial pressure quotient for WGS reaction was greater than 30 (The equilibrium value of the reaction quotient at 250°C is 83.6). Both of these measures are indicative of high WGS activity. Hydrocarbon product distribution shifted gradually towards lower molecular weight products with time on stream, as indicated in Table III-2.5. Selectivities of methane and

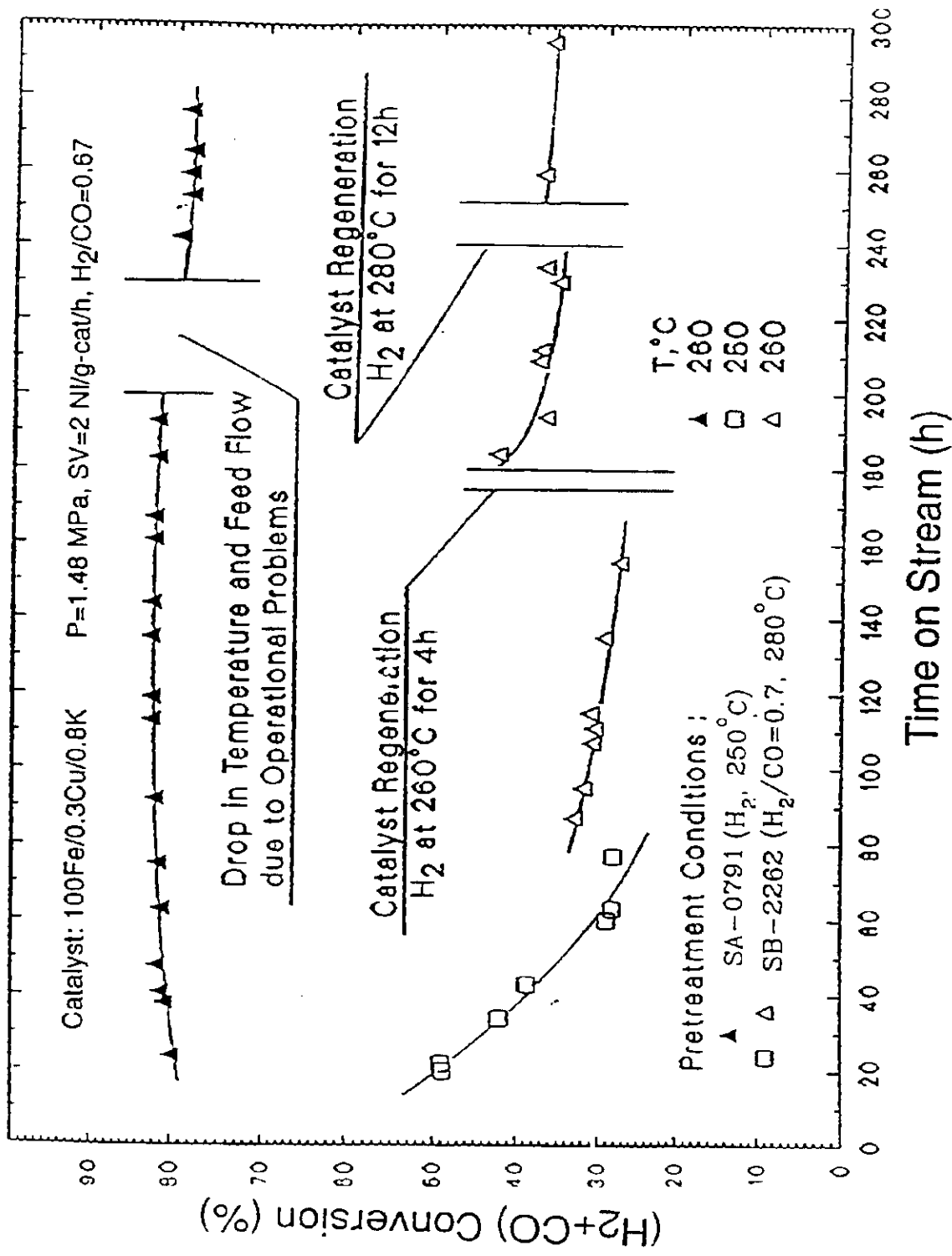


Figure III-2.8 Effect of pretreatment procedures on conversion and catalyst stability in slurry reactor tests.

Table III.2-5 Summary of Slurry Reactor Test Results for Pretreatment Effect Study with 100 Fe/0.3 Cu/0.8 K Catalyst

Test designation	SA-0791						SB-2262					
	260	260	260	260	260	260 ^a	250	260	260	260	260	260 ^a
Temperature, °C	1.48	1.48	1.48	1.48	1.48	1.48	1.48	1.48	1.48	1.48	1.48	1.48
Pressure, MPa	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
SV, Nl/g-cat/h	39	111	159	266	278	278	44	92	140	212	268	268
CO conversion, %	86.1	86.8	86.6	82.4	79.0	79.0	30.0	32.8	29.8	38.8	39.4	39.4
(H ₂ +CO) conversion, %	81.8	82.6	82.4	78.7	75.3	75.3	28.7	31.3	28.2	36.7	37.3	37.3
STY, mmol/g-cat/h	72.7	73.5	73.0	69.5	60.3	60.3	26.1	28.0	25.0	33.2	33.1	33.1
k, mmol/g-Fe/h/MPa	347	365	362	326	286	286	68.6	77.0	67.6	93.0	94.5	94.5
(H ₂ /CO) usage ratio	0.60	0.60	0.60	0.61	0.61	0.61	0.61	0.60	0.58	0.57	0.58	0.58
(H ₂ /CO) exit ratio	1.20	1.22	1.22	1.04	0.98	0.98	0.71	0.72	0.72	0.73	0.72	0.72
K _p =P _{CO₂} P _{H₂} /P _{CO} P _{H₂O}	33.2	42.2	38.5	39.6	80.6	80.6	26.0	10.4	9.48	12.7	12.8	12.8
mmol CH ₄ /g-Fe/h	1.66	1.86	1.88	1.88	1.86	1.86	0.64	0.85	0.84	0.90	1.02	1.02
Hydrocarbon selectivity, wt%												
CH ₄	5.5	6.0	6.5	6.8	7.2	7.2	6.2	7.4	8.2	7.0	7.4	7.4
C ₂ -C ₄	19.0	21.3	23.1	24.0	25.9	25.9	15.6	19.9	23.3	20.5	18.2	18.2
C ₅ -C ₁₁	30.0	38.5	38.4	41.0	40.6	40.6	14.5	14.8	17.3	15.3	14.0	14.0
C ₁₂ +	45.5	34.2	32.0	28.2	26.3	26.3	63.7	57.9	51.2	57.2	60.4	60.4
Chain growth parameter, α ₁₋₁₀ ^b	0.76	0.76	0.76	0.75	0.75	0.75	0.70	0.69	0.63	0.61	0.61	0.61
Olefin content, wt%												
C ₂ -C ₄	75.2	74.1	73.2	70.5	69.7	69.7	80.1	79.3	79.7	81.4	79.5	79.5
C ₅ -C ₁₁	73.5	73.2	73.5	72.8	73.1	73.1	74.7	76.4	76.6	78.5	79.2	79.2

H₂/CO=0.67 for all tests. ^a: Following H₂ regeneration. ^b: Parameter estimated from products with carbon number in the range C₁-C₁₀.

gaseous hydrocarbons ($C_2 - C_4$) varied between 5.5 - 6.5 and 19 - 23 wt%, respectively. The olefin selectivity was stable with time (Figure III-2.9a), whereas the 2-olefin selectivity increased steadily with time (Figure III-2.10).

Catalyst from a different batch of preparation was used in the second slurry phase test designated SB-2262. After pretreatment with syngas ($H_2/CO = 0.67$) at $280^\circ C$, 1.16 MPa (155 psig), 2.0 NI/g-Fe/h for 12 h, during the first 80 h on stream the catalyst was tested at $250^\circ C$, 1.48 MPa, and 2 NI/g-cat/h with $H_2/CO = 0.67$. (The same baseline process conditions as used in fixed bed reactor tests). The catalyst deactivated rapidly with time on stream (Figure III-2.8). (H_2+CO) conversion decreased from initial value of 49 % to 28 %, during the first 60 h of testing. Reaction temperature was then increased to $260^\circ C$, which was accompanied by increase in conversion followed by continued, but slower, deactivation. The catalyst was regenerated with H_2 at $260^\circ C$, 1.48 MPa, 5,000 cc/min for 4 h at about 162 h on stream, and again using more severe reduction conditions of $280^\circ C$ for 12 h at 224 h. Temporary improvements in catalyst activity were observed after each of these two regenerations, followed by deactivation. The syngas conversion after the second regeneration was about 37 % shortly before the test was terminated at 300 h on stream. WGS activity of the catalyst was high throughout the test. The usage ratio varied between 0.58 and 0.60, and the reaction quotient between 9.5 and 26. Methane selectivity was 6.2 wt % at $250^\circ C$, and it increased to 7.3 - 8.2 % during testing at $260^\circ C$ before the regeneration (80 - 140 h on stream). Hydrocarbon product distributions at $260^\circ C$ were similar before (92 h on stream) and after hydrogen regenerations (268 h), as can be seen from Table III-2.5. The olefin selectivity was also stable as shown in Figure III-2.9, despite catalyst deactivation with time. The 2-olefin selectivity was low (4-12%) and did not vary much with time on stream.

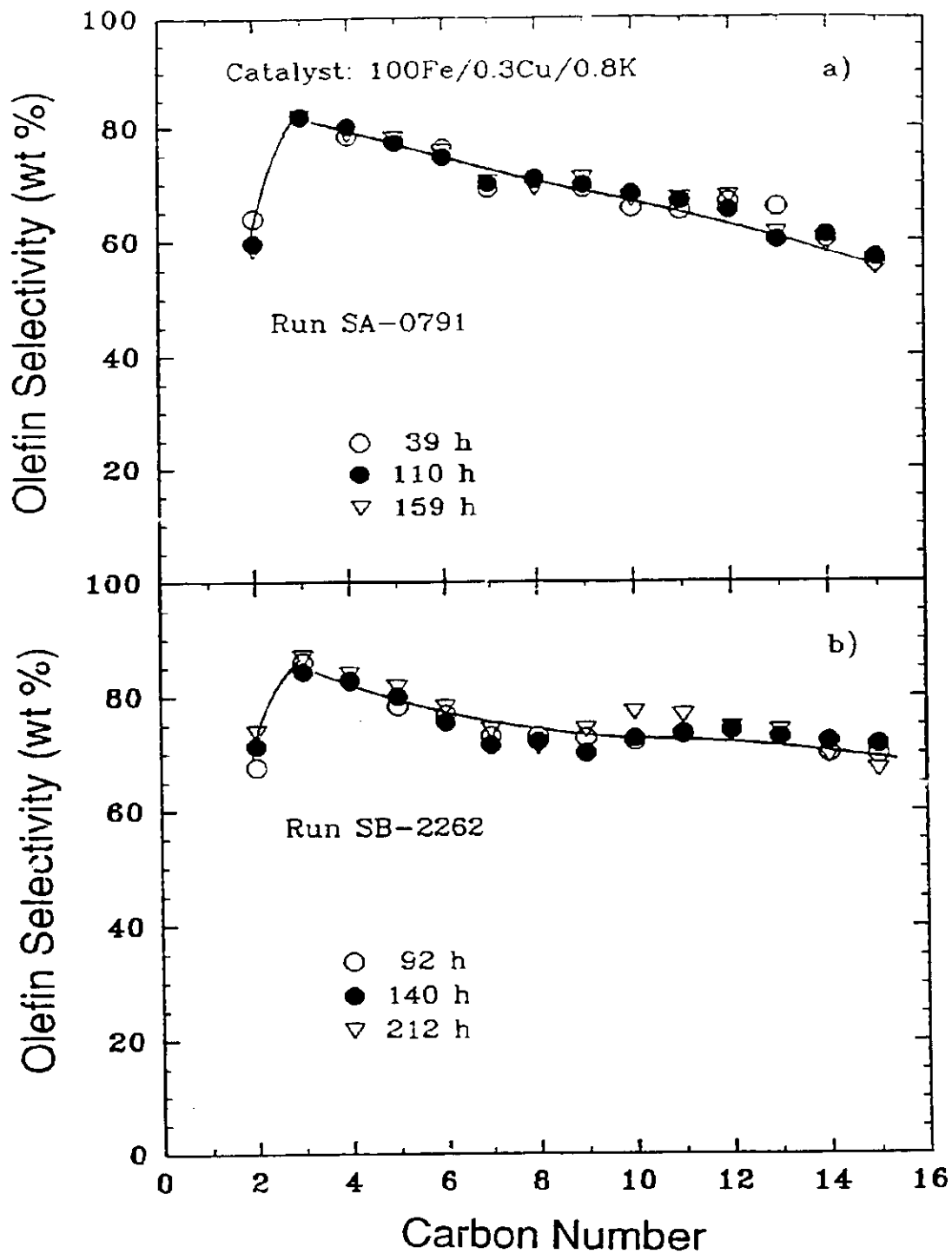


Figure III-2.9 Effect of time on stream on olefin selectivity in slurry reactor tests.

a) Run SA-0791; b) Run SB-2262

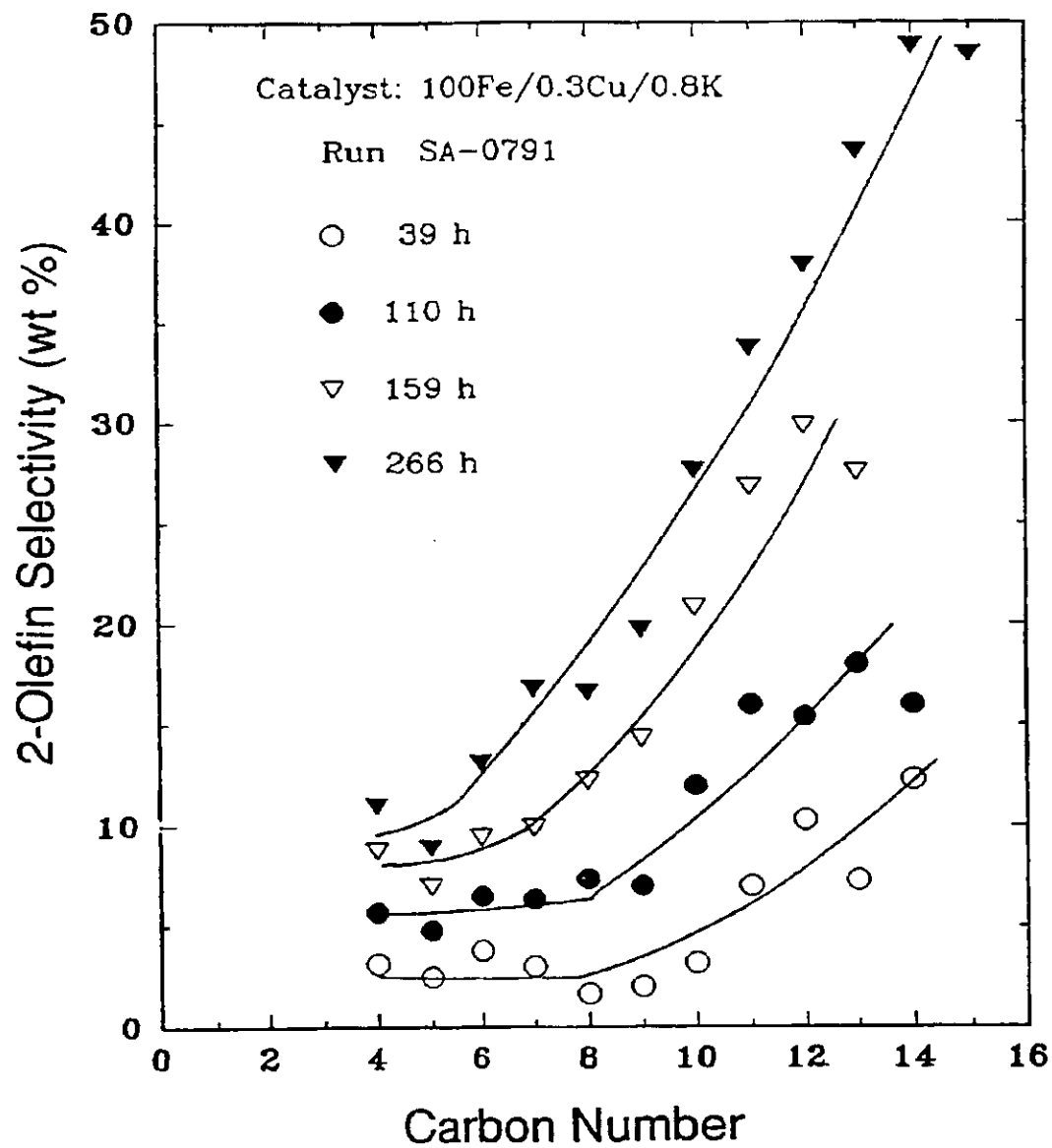


Figure III-2.10 Variation of 2-olefin selectivity with time on stream after H₂ reduction (Run SA-0791).

III-2.5 Comparison between FBR and STSR Tests

The effect of the nature of the pretreatment gas on the catalyst stability was qualitatively the same in both the fixed bed and slurry bed reactors. After hydrogen reduction at 250°C for 2 h in tests FB-0403 and SA-0791, the catalyst activity remained stable with time on stream, whereas following pretreatment with H₂/CO = 0.67 at 280°C in tests FB-0352 and SB-2262, the catalyst deactivated in both type of reactors (Figures III-2.2 and III-2.8). However, the rate of deactivation was faster and the catalyst activity lower in the STSR (Run SB-2262) than in the FBR (Run FB-0352).

Comparisons of catalyst activities in terms of (H₂ + CO) conversion or reactor space-time-yields (STY) are not meaningful when the reaction conditions are not the same and/or when the experiments are done in different types of reactors. In such cases an apparent reaction rate constant provides a better basis for comparison of catalyst activity. In this study the apparent reaction rate constant was calculated assuming that the reaction rate has a first-order dependence on hydrogen partial pressure and its units are : mmol (H₂ + CO) converted/h/g-Fe/MPa of H₂. In the STSR the STY is proportional to the rate of FTS reaction, and the apparent rate constant is obtained by dividing STY with the partial pressure of hydrogen at the reactor exit. On the other hand, in the FBR the reaction rate varies with position along the reactor and estimation of the apparent rate constant is not so straightforward. In this case, the rate constants were estimated using a procedure described by Zimmerman et al. (1989). Calculated values are listed in Table III-2.3 (FBR tests) and Table III-2.5 (STSR tests). Data obtained at 260°C (STSR) were converted to 250°C by using the activation energy of 90 kJ/mol, which is typical for FTS over iron catalysts (Zimmerman and Bukur, 1990). The average values of the apparent rate constants for H₂ reductions in FBR and STSR reactors are: 233 and 247 (mmol/h/g-Fe/MPa), respectively. This indicates that the intrinsic catalyst activity is nearly the same in both types of reactors.

With syngas pretreated catalysts the corresponding values were: 134 - 177 (FBR), and 46 - 68 mmol/h/g-Fe/MPa (STSR). The intrinsic catalyst activity was lower in the STSR than in the FBR, which is probably due to the use of catalysts from two different batches and differences in the pretreatment procedures (duration and reductant flow rate per gram of Fe in the catalyst).

Hydrocarbon selectivities (average values from several mass balances) are compared in Figure III-2.11. Reaction temperature in the fixed bed tests was 250°C, but mostly 260°C in the slurry reactor tests. Higher temperature is known to favor the formation of methane and lower molecular weight hydrocarbons. The reactor type did not have a strong effect on hydrocarbon product distribution with syngas pretreated catalyst (tests FB-0352 and SB-2262), if the difference in reaction temperature is taken into account. However, when H₂ reduction was employed, methane selectivity in the slurry reactor (SA-0791) varied from 5.5 to 6.5 % (before operational incident), and was markedly lower than that in the fixed bed reactor (about 9%), even though the reaction temperature was 10°C higher in the STSR. This is probably due to a better temperature control in the STSR, and/or due to differences in the catalyst composition (iron phases) after the reduction.

The effects of pretreatment conditions and the reactor type on olefin selectivity are shown in Figure III-2.12. The average values from multiple mass balances are used in this comparison, since olefin selectivity generally does not change with time on stream. In both FBR and STSR, the olefin content was higher with syngas pretreated catalyst than with H₂ reduced catalyst. This indicates that higher hydrogenation activity of H₂ reduced catalyst is related to the catalyst structure determined by the pretreatment, but not to the reaction environment (conversion, reactor type, etc.). Hydrogenation activity was slightly higher in the slurry reactor than in the fixed bed reactor after the syngas pretreatments.

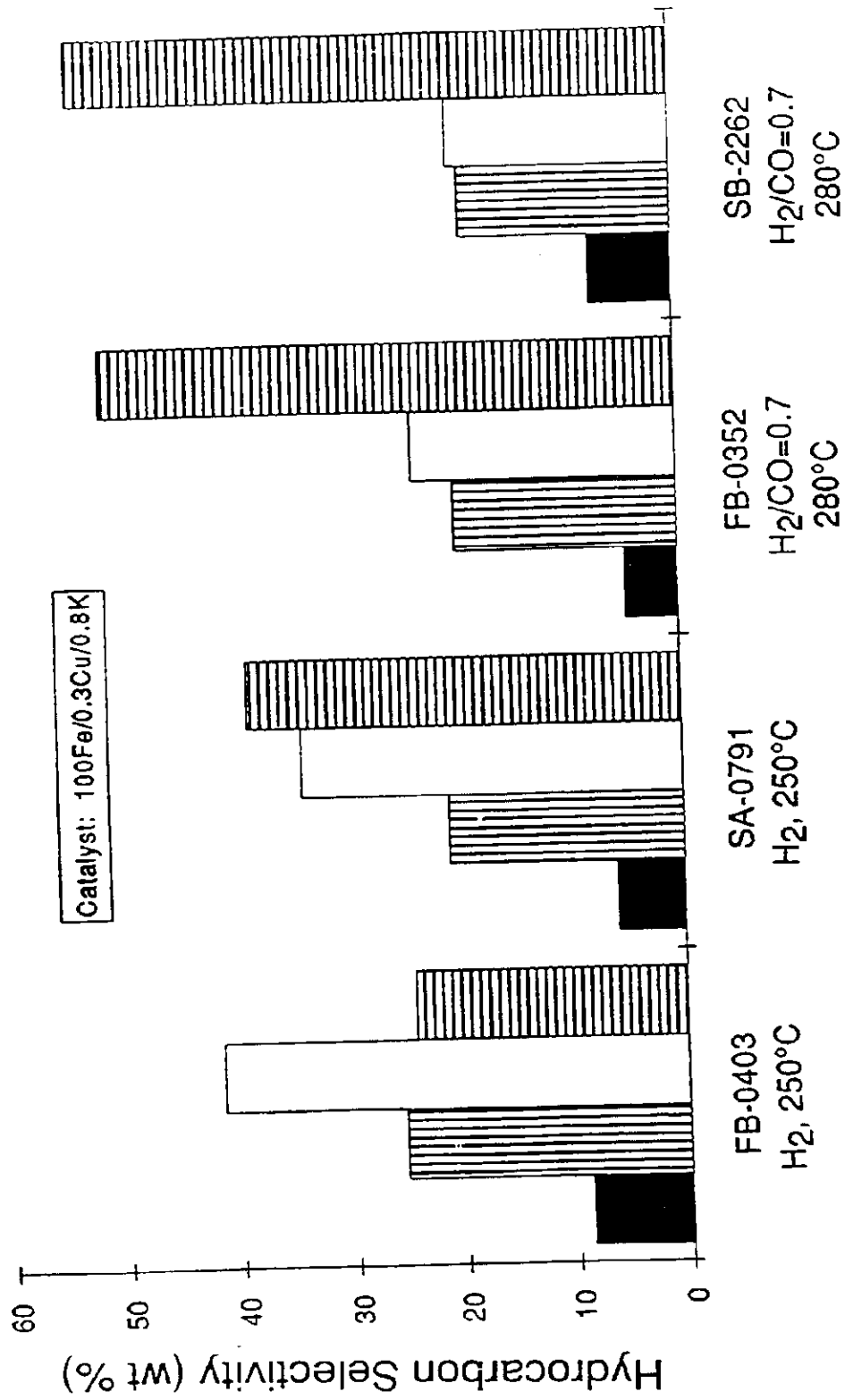


Figure III-2.1.1 Comparison of hydrocarbon selectivities in fixed bed and slurry reactor tests.

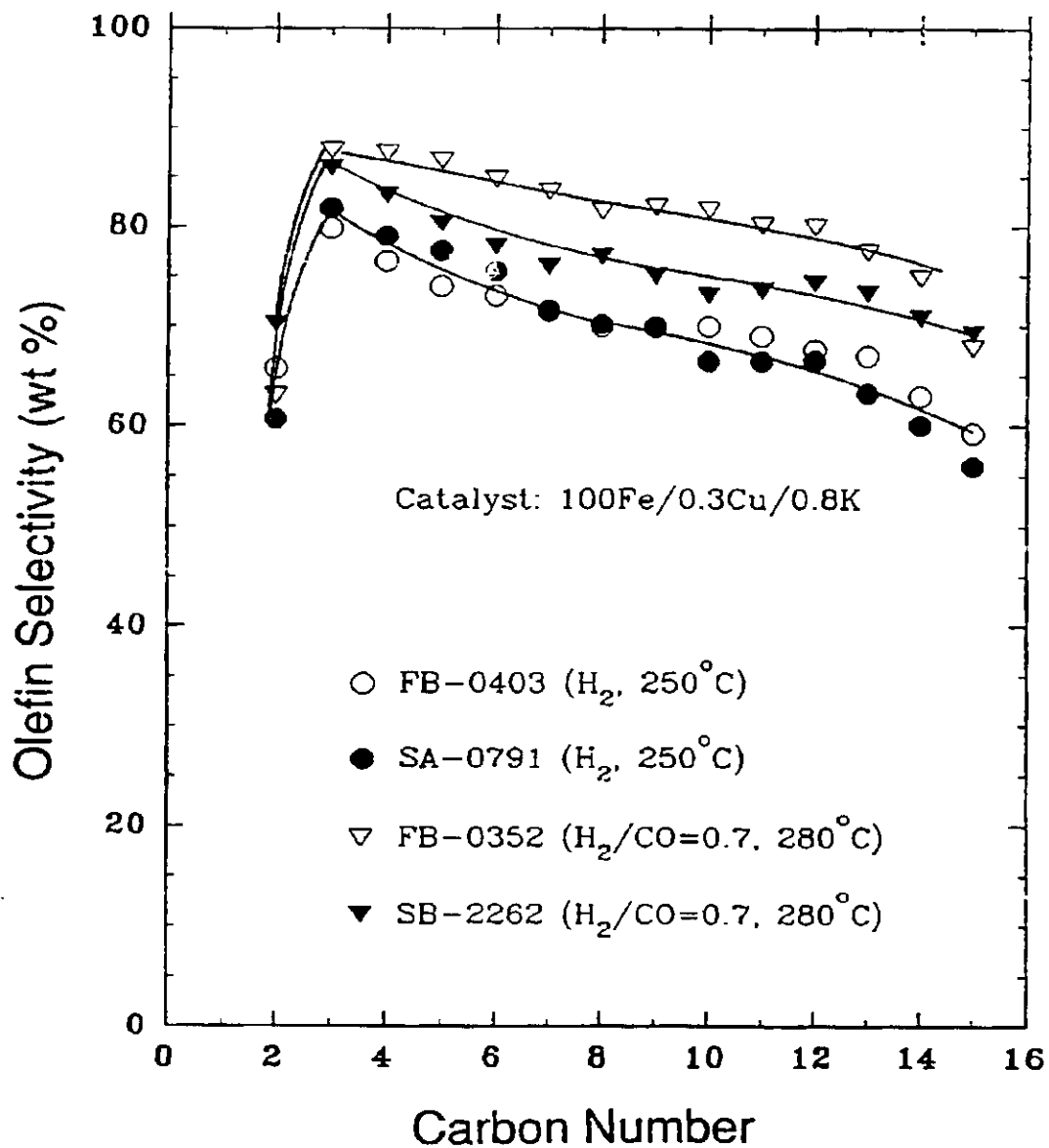


Figure III-2.12 Comparison of olefin selectivities in fixed bed and slurry reactor tests.

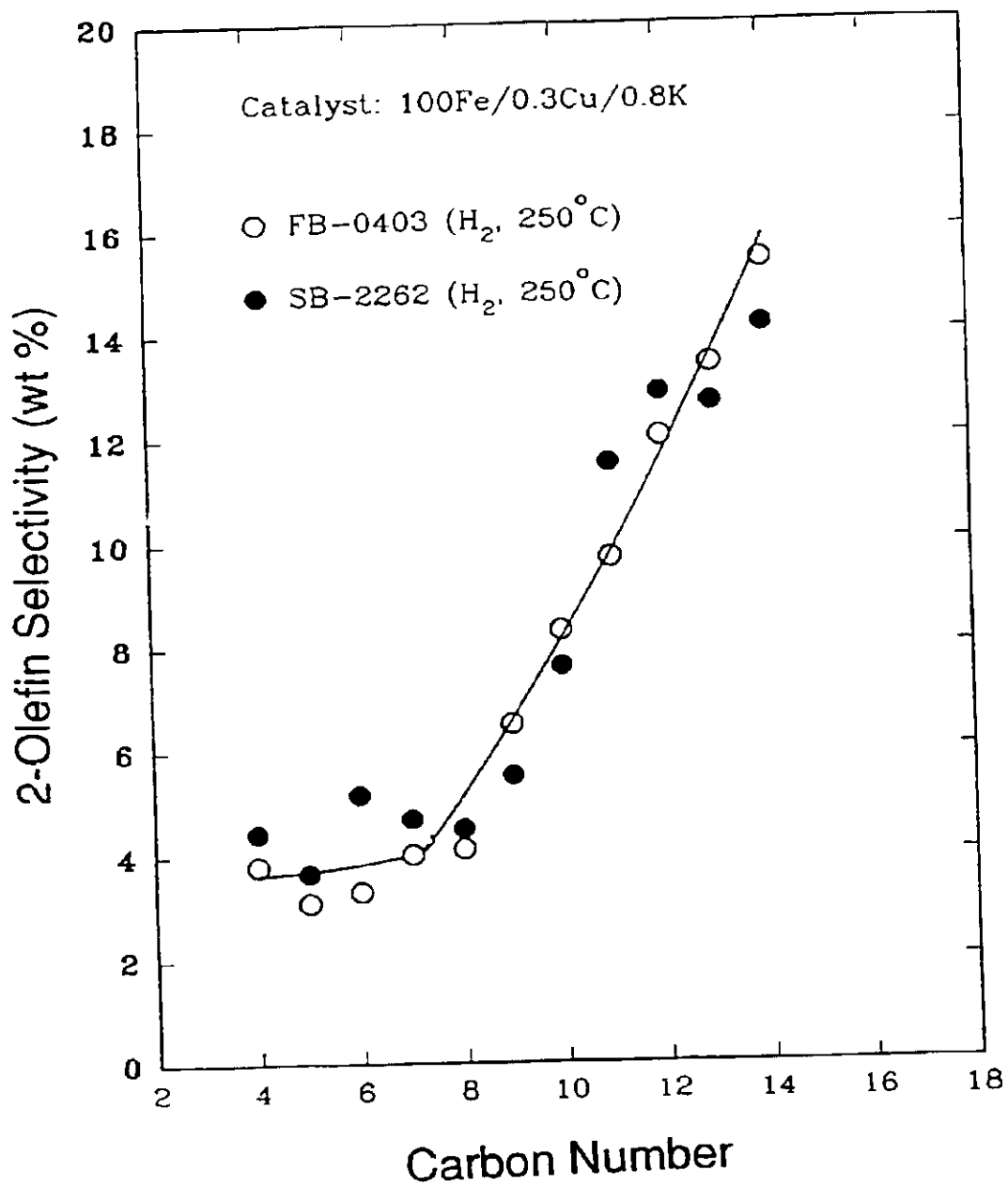


Figure III-2.13 Comparison of 2-olefin selectivities in fixed bed and slurry reactor tests.

The initial (first 100 h) 2-olefin selectivity was also independent of the reactor type, as illustrated in Figure III-2.13 for the two tests using H₂ reduction. The 2-olefin selectivity continually increased with time on stream during the slurry reactor test (Figure III-2.10), however, this was not observed in the corresponding fixed bed reactor test during 120 h of testing.

The above results show that the effects of pretreatment procedures on the catalyst performance were similar in both FBR and STSR. This is probably due to the fact that the change in surface structure of catalyst induced by different pretreatment procedures plays a more important role than the reaction environment (reactor type) in influencing the catalytic activity and selectivity.

III-2.6 Summary

The effects of pretreatment conditions on catalyst performance (activity, selectivity and stability with time) during Fischer-Tropsch synthesis were studied in fixed bed (five different 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 result in stable or increasing catalyst activity with time on stream. Hydrogen reduced catalyst produces more methane and gaseous hydrocarbons than CO or syngas pretreated catalyst. Secondary reactions (olefin hydrogenation and isomerization) were more pronounced in tests in which hydrogen reductions were employed. Pretreatment conditions (temperature, duration and/or gas flow rate) have a strong effect on the subsequent catalyst activity. Differences in activity may be attributed to formation of different iron phases, variations in crystallite sizes (or surface areas) and migration of sulfur impurities to the surface of the catalyst during the reduction.

Pretreatments with carbon monoxide and syngas result in formation of Hägg χ - carbide, which is very active for FT synthesis. However, the catalyst deactivates fairly rapidly with time 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. The CO or syngas pretreated catalyst favors production of high molecular weight hydrocarbons, and suppresses the secondary reactions.

The above results suggest that the surface hydrogen concentration is higher after hydrogen reductions, which results in higher hydrogenation activity, production of low molecular weight hydrocarbons and better stability with time on stream.

The same qualitative trends were observed in two STSR tests, in which hydrogen and syngas pretreatments were used, with the exception that methane selectivity was higher in the test with syngas pretreated catalyst than with H₂ reduced one.

III-2.7 References

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