III-5 Pretreatment Effect Research - Reaction Studies with 10C Fe/5 Cu/4.2 K/16 SiO$_2$ Catalyst

This catalyst is one of the silicon oxide containing catalysts prepared in our laboratory which has shown desirable properties (activity, selectivity and stability) during a screening test in a fixed bed reactor. Three pretreatment procedures were used to study their effect on subsequent catalyst performance in a stirred tank slurry reactor. Test designations and pretreatment conditions are listed in Table III-5.1.

Table III-5.1   Pretreatment Conditions and Test Designations

Test (ID)	Temp. (°C)	Reductant	Duration (h)	Pressure (MPa)	Flowrate (cm^3/min)
SB-2832	240	H$_2$	2	0.8	7,500
SA-3172	280	H$_2$/CO=0.7	5.5	0.8	280
SB-3362	280	CO	8	0.8	750

SA, SB = Slurry phase reactor test

III-5.1   Experimental Procedure

Test SB-2832

The catalyst with particle size less than 270 mesh (53 μm) was suspended in molten n-octacosane to form a 4.8 wt% slurry and then reduced with H$_2$ at 240°C, 0.8 MPa (150 psig) and flowrate 7,500 cc/min for 2 h. Following the reduction, the catalyst was tested at baseline process conditions of 260°C, 1.48 MPa (200 psig), 1.5 Nl/g-cat/h (2.6 Nl/g-Fe/h) and syngas feed H$_2$/CO = 0.67 during the first 263 h on stream.

The same baseline conditions were employed in all three tests reported in this section. Between 263 and 664 h, the catalyst was tested at 2.17 MPa (300 psig) and gas space velocities of 2.2 Nl/g-cat/h (263 - 526 h) and 1.8 Nl/g-cat/h (526 - 665 h). After testing at higher pressure, the catalyst was regenerated at 666 h with H_2 at 240°C, 1.48 MPa for 1 h, and the baseline conditions were re-established. The test was terminated voluntarily after 720 h on stream.

Test SA-3172

In this test an Ethylflo-164 oil, obtained from Ethyl Corporation, was used as the initial slurry medium. The Ethylflo-164 oil is a hydrogenated 1-decene homopolymer, with a dominant carbon number of C_{30}. Catalyst particles less than 270 mesh were loaded into the reactor, resulting in slurry concentration of about 6 wt%. The catalyst was activated using syngas ($H_2/CO=0.68$) at 280°C, 0.8 MPa, and 2 Nl/g-Fe/h. During the pretreatment, the tail gas composition was continually analyzed by on-line gas chromatography. The pretreatment was stopped after 5.5 h when the two consecutive tail gas analyses showed no change in composition (Figure III-5.1). After the pretreatment, the catalyst was tested under the baseline conditions over a 105 h period. Between 106 and 197 h on stream, the reaction pressure and gas space velocity were increased to 2.17 MPa and 2.1 Nl/g-cat/h, respectively. The baseline conditions were re-established at 198 h on stream. At 223 h the catalyst was regenerated with H_2 at 250°C, 1.48 MPa, 2,000 cc/min for 4 h. After that, the testing continued at the baseline conditions for additional 100 h. The test was terminated at 340 h on stream, and six mass balances were completed during the test.

Test SB-3362

The Ethylflo - 164 oil was used as the initial liquid medium, and the catalyst loading was about 5.5 wt%. The catalyst was pretreated with CO at 280°C, 0.8 MPa
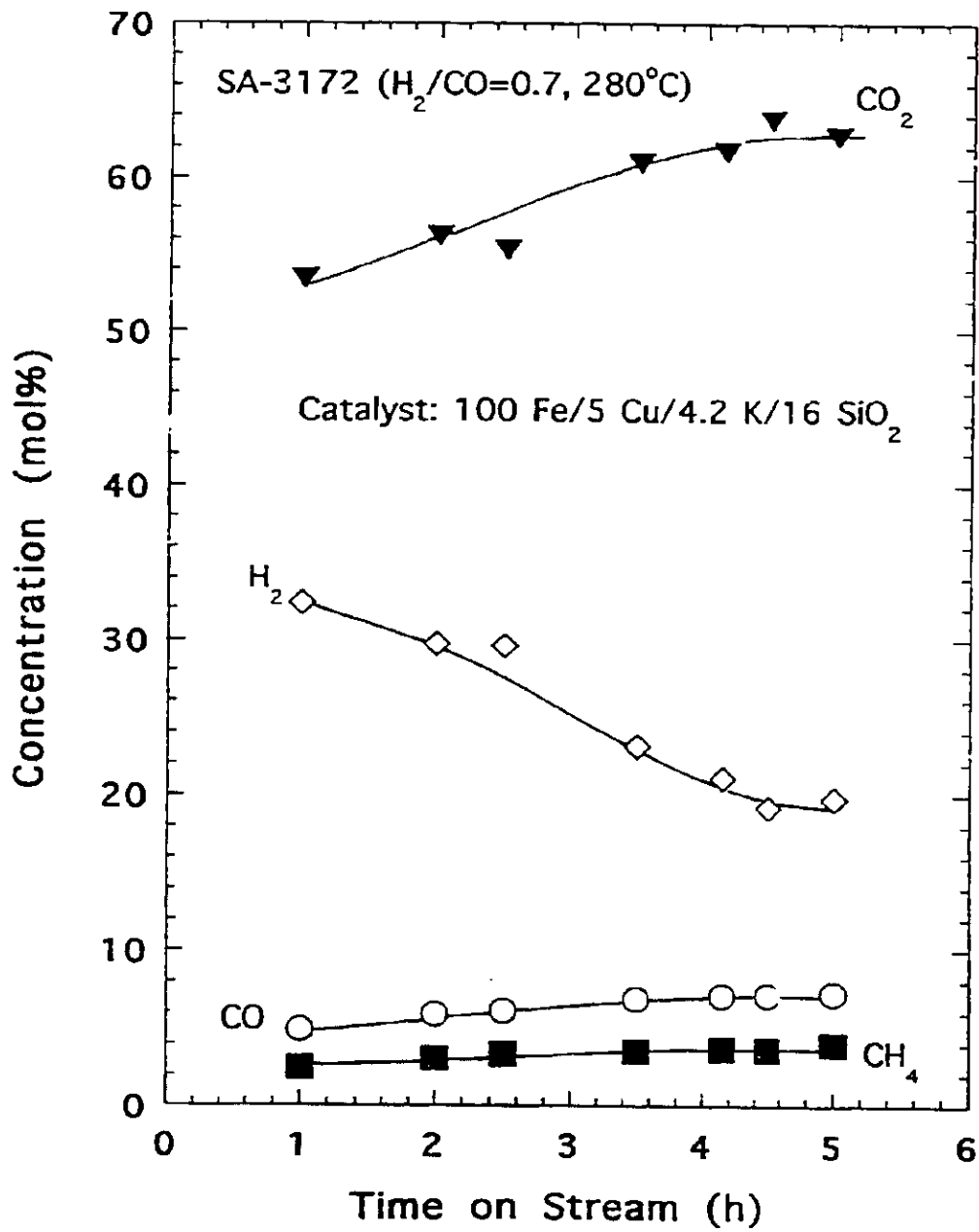
Figure III-5.1   Tail gas composition change during the syngas pretreatment.

and 3.0 Nl/g-cat/h (5.3 Nl/g-Fe/h) for 8 h. During the preparation and pretreatment periods, a substantial amount of slurry medium was lost from the reactor as a result of operational accident and oil evaporation. The catalyst activity at the baseline process conditions was found to be very low (about 11 % syngas conversion) during the first 10-20 h of testing following the pretreatment. This was attributed to low slurry level inside the reactor, i.e. inefficient gas - catalyst contact in the slurry. The test was interrupted and additional Ethylflo oil was added under high purity nitrogen atmosphere into the reactor. The synthesis was then resumed at 39 h on stream under the baseline conditions. Between 235 and 406 h, the catalyst was tested at higher pressure and gas space velocity, 2.17 MPa and 2.2 Nl/g-cat/h, respectively. The baseline conditions were then re-established, and the test continued for additional 70 h to check the catalyst activity after exposure to higher pressure. The test was terminated after 478 h on stream, during which period six mass balances were completed.

III-5.2   Results and Discussion

III-5.2.1 Catalyst Characterization Results

The elemental catalyst composition was determined by AA and/or ICP spectroscopy at our Laboratory, Sandia National Laboratory, DOE PETC and UOP Inc. Results are as follows (in parts per 100 parts of Fe): TAMU (5.6 Cu/6.3 K/18.5 SiO_2); Sandia (5 Cu/4.3 K/18 SiO_2); PETC (5.6 Cu/3.9 K/14.2 SiO_2); UOP (5.2 Cu/3.7 K/13.1 SiO_2). The results from different Laboratories are in a reasonable agreement with each other (except for high potassium content at TAMU), as well as with the intended catalyst composition.

The BET surface area and pore volume of a calcined sample (Air at 300°C for 5 h) were: 234 m^2/g and 0.61 cm^3/g, respectively. The pore size distribution was very broad with local maximum at about 2 nm.

After the reduction with H_2 at 240°C the catalyst had nearly amorphous structure (small crystallites). The magnetite (Fe_3O_4) and $\alpha - Fe_2O_3$ were identified by XRD. During FT synthesis there is an increase in crystallinity (larger particles are formed) and the catalyst is partially carburized. At 665 h on stream the used catalyst sample consisted of Fe_3O_4 and iron carbide phases (Run SB-2832).

After the pretreatment with syngas (Run SA-3172) the following bulk iron phases were identified: magnetite, iron oxide and iron carbides. After 223 h on stream, in addition to these phases an iron carbonate (siderite) was also detected. After hydrogen regeneration at 223 h, the peaks associated with iron carbonate have disappeared (227 h, and 340 h on stream), whereas magnetite and iron carbides were present in these samples.

Magnetite and siderite were the only phases identified by XRD in the used catalyst sample at the end of Run SB-3362 (CO pretreatment) .

III-5.2.2 Reaction Results

Selected results obtained from all the mass balances, both at the baseline and higher pressure conditions, are summarized in Table III-5.2 for test SB-2832, Table III-5.3 for SA-3172 and Table III-5.4 for SB-3362, respectively.

Activity and Stability

The catalyst activity following the pretreatment is compared in Figures III-5.2 and III-5.3 for the three tests. Results from testing at the baseline conditions and at higher pressure are included. It can be seen that after H_2 reduction (SB-2832) the initial (H_2+CO) conversion was high (84 % at 17 h on stream). The syngas conversion gradually decreased with time to 77 % at 263 h, for a loss in conversion of about

Table III-5.2 Summary of Slurry Reactor Test Results for Pretreatment Effect Study with
100 Fe/5 Cu/4.2 K/16 SiO$_2$ Catalyst (Hydrogen Reduction)

Test designation		SB-2832				
Temperature, °C	260	260	260	260	260	260
Pressure, MPa	1.48	1.48	1.48	1.48	2.17	2.17
SV, Nl/g-cat/h	1.50	1.50	1.50	1.50	2.20	2.20
Time-on-stream, h	41	92	139	210	308	355
CO conversion, %	87.5	86.4	85.5	83.1	78.0	77.9
(H$_2$+CO) conversion, %	81.1	80.3	79.5	78.7	74.6	74.1
STY, mmol/g-cat/h	54.1	54.2	53.3	53.1	73.0	73.2
k, mmol/g-Fe/h/MPa	268	265	260	277	254	244
(H$_2$/CO) usage ratio	0.58	0.58	0.58	0.59	0.59	0.58
(H$_2$/CO) exit ratio	1.59	1.46	1.40	1.12	0.93	0.95
$K_p = P_{CO_2}P_{H_2}/P_{CO}P_{H_2O}$	37.4	36.9	28.4	20.4	22.2	18.5
mmol CH$_4$/g-Fe/h	1.28	1.33	1.34	1.25	1.79	1.67
Hydrocarbon selectivity, wt%						
CH4	4.5	4.7	4.7	4.5	4.8	4.4
C2-C4	15.2	15.2	15.3	16.6	17.1	17.1
C5-C11	25.5	21.8	20.6	22.6	29.8	22.6
C12+	54.8	58.3	59.4	56.3	48.3	55.9
Chain growth parameter, α_{1-10}[a]	0.73	0.70	0.71	0.72	0.74	0.71
Olefin content, wt%						
C2-C4	66.3	68.0	66.9	69.6	69.9	71.7
C5-C11	69.8	72.0	73.6	74.5	72.8	73.7

H$_2$/CO=0.67 for all tests. a: Parameter estimated from products with carbon number in the range C$_1$-C$_{10}$.

Table III-5.2 (cont'd) Summary of Slurry Reactor Test Results for Pretreatment Effect Study with 100 Fe/5 Cu/4.2 K/16 SiO$_2$ Catalyst (Hydrogen Reduction)

Test designation	SB-2832				
Temperature, °C	260	260	260	260	260[b]
Pressure, MPa	2.17	2.17	2.17	2.17	1.48
SV, Nl/g-cat/h	2.20	2.20	1.80	1.80	1.46
Time-on-stream, h	427	498	570	641	713
CO conversion, %	74.4	71.3	79.8	76.5	71.3
(H$_2$+CO) conversion, %	70.9	68.7	75.7	72.9	67.4
STY, mmol/g-cat/h	69.0	67.0	60.9	59.2	44.1
k, mmol/g-Fe/h/MPa	221	214	203	192	199
(H$_2$/CO) usage ratio	0.60	0.62	0.61	0.60	0.59
(H$_2$/CO) exit ratio	0.91	0.83	1.03	0.93	0.91
$K_p = P_{CO_2}P_{H_2}/P_{CO}P_{H_2O}$	18.4	15.4	20.6	20.6	24.6
mmol CH$_4$/g-Fe/h	1.59	1.52	1.43	1.55	1.02
Hydrocarbon selectivity, wt%					
CH$_4$	4.4	4.3	4.7	5.3	4.5
C2-C4	16.3	16.0	15.8	17.4	15.9
C5-C11	23.1	22.5	21.3	24.7	23.6
C12+	56.2	57.2	58.2	52.6	55.9
Chain growth parameter, α_{1-10}[a]	0.73	0.72	0.69	0.71	0.72
Olefin content, wt%					
C2-C4	72.1	73.9	70.8	71.1	76.3
C5-C11	73.1	73.2	72.9	73.3	75.9

H$_2$/CO=0.67 for all tests. a: Parameter estimated from products with carbon number in the range C$_1$-C$_{10}$.

b: Following H$_2$ regeneration

Table III-5.3 Summary of Slurry Reactor Test Results for Pretreatment Effect Study with 100 Fe/5 Cu/4.2 K/16 SiO_2 Catalyst (Syngas Pretreatment)

Test designation	SA-3172					
Temperature, °C	260	260	260	260	260	260[b]
Pressure, MPa	1.48	1.48	2.17	2.17	2.17	1.48
SV, Nl/g-cat/h	1.44	1.44	2.10	2.10	2.10	1.48
Time-on-stream, h	49	95	152	177	215	272
CO conversion, %	89.4	80.9	80.6	79.8	79.1	76.9
(H_2+CO) conversion, %	85.6	77.9	78.9	78.6	77.1	75.3
STY, mmol/g-cat/h	55.2	50.1	73.0	72.9	49.0	50.3
k, mmol/g-Fe/h/MPa	372	326	340	345	316	295
(H_2/CO) usage ratio	0.61	0.62	0.63	0.64	0.62	0.63
(H_2/CO) exit ratio	1.29	0.93	0.82	0.77	0.83	0.78
	27.0	31.4	14.3	11.9	22.5	22.5
$K_p = P_{CO_2}P_{H_2}/P_{CO}P_{H_2O}$	2.58	2.81	4.01	3.71	2.62	3.74
mmol CH_4/g-Fe/h						
Hydrocarbon selectivity, wt%						
CH4	9.5	11.3	11.1	10.4	10.8	15.4
C2-C4	17.0	19.4	18.8	17.6	18.3	21.3
C5-C11	19.3	20.3	14.3	15.8	18.2	19.9
C12+	54.2	49.0	55.8	56.2	52.7	43.4
Chain growth parameter, α_{1-10}[a]	0.59	0.61	0.58	0.60	0.60	0.58
Olefin content, wt%						
C2-C4	53.5	55.8	59.1	60.8	61.8	55.5
C5-C11	77.8	77.8	79.6	79.4	79.3	78.2

H_2/CO=0.67 for all tests. a: Parameter estimated from products with carbon number in the range C1-C10.

b: Following H_2 regeneration.

Table III-5.4 Summary of Slurry Reactor Test Results for Pretreatment Effect Study with 100 Fe/5 Cu/4.2 K/16 SiO₂ Catalyst (CO Pretreatment)

Test designation			SB-3362			
Temperature, °C	260	260	260	260	260	260
Pressure, MPa	1.48	1.48	1.48	2.17	2.17	1.48
SV, Nl/g-cat/h	1.50	1.50	1.50	2.20	2.20	1.50
Time-on-stream, h	95	144	193	265	384	432
CO conversion, %	77.5	76.1	78.1	69.4	67.6	72.9
(H₂+CO) conversion, %	74.6	72.9	74.0	67.7	66.1	69.9
STY, mmol/g-cat/h	50.1	49.0	50.0	67.2	65.1	47.3
k, mmol/g-Fe/h/MPa	246	244	247	221	221	225
(H₂/CO) usage ratio	0.60	0.60	0.58	0.63	0.63	0.59
(H₂/CO) exit ratio	0.88	0.89	0.97	0.76	0.74	0.84
$K_p = P_{CO_2}P_{H_2}/P_{CO}P_{H_2O}$	9.16	9.57	12.1	6.39	5.62	11.1
mmol CH₄/g-Fe/h	0.83	0.78	0.81	0.93	0.88	0.71
Hydrocarbon selectivity, wt%						
CH4	3.5	3.5	3.5	3.0	2.8	3.2
C2-C4	16.6	15.6	15.6	14.6	14.2	13.6
C5-C11	22.6	19.5	22.0	17.9	20.1	19.1
C12+	57.3	61.4	58.9	64.5	62.9	64.1
Chain growth parameter, α_{1-10}[a]	0.73	0.71	0.76	0.74	0.77	0.74
Olefin content, wt%						
C2-C4	74.1	75.2	74.2	77.9	79.2	76.8
C5-C11	80.5	80.3	79.2	80.3	80.3	80.5

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

0.68% per day. During testing at 2.17 MPa and 2.2 Nl/g-cat/h (same absolute pressure to gas space velocity ratio, which results in the same contact time as at the baseline conditions), the syngas conversion continued to decrease gradually with time. For example, at 284 h and 480 h on stream, the syngas conversion was 74 and 69 %, respectively. Regeneration with H_2 at 666 h on stream could not recover the activity. After the regeneration, the (H_2+CO) conversion was only 68 % at the baseline conditions (not shown in Figure III-5.2).

In test SA-3172 (syngas pretreatment) the (H_2+CO) conversion was 84 - 87 % during the first 55 h on stream. At this time the Autoclave reactor head temperature was decreased from 260 to 210°C in an attempt to control the unusually high methane selectivity (about 9.5 wt%). Following this the syngas conversion decreased and stabilized at about 80 % (70 - 105 h on stream). After changing the reaction pressure and gas space velocity to 2.17 MPa and 2.1 Nl/g-cat/h, respectively, the syngas conversion first increased to 83 % at 115 h, then gradually decreased and leveled to about 79 % at 194 h. Upon returning to the baseline conditions at 200 h on stream, the (H_2+CO) conversion stabilized at 78 %. The latter value is comparable to those obtained between 80 -100 h on stream. Regeneration with H_2 at 250°C, 1.48 MPa, 2000 cc/min for 4 h resulted in a temporary increase of conversion followed by a decline to 74% at 336 h on stream.

Catalyst activity immediately after CO pretreatment in test SB-3362 was low (not shown in Figure III-5.2) because of the loss of slurry liquid as stated earlier, and the reaction was temporarily interrupted. The catalyst activity increased quickly after a sufficient amount of liquid was added and synthesis gas flow resumed at 39 h as shown in Figure III-5.2. The (H_2+CO) conversion was fairly stable (71 - 74 %) between 70 and 230 h on stream. During testing at 2.17 MPa and 2.2 Nl/g-cat/h (the same P/SV ratio as at the baseline conditions), the syngas conversion was lower, about 65 - 67 %. Upon returning to the baseline conditions (407-488 h) the (H_2+CO) conversion
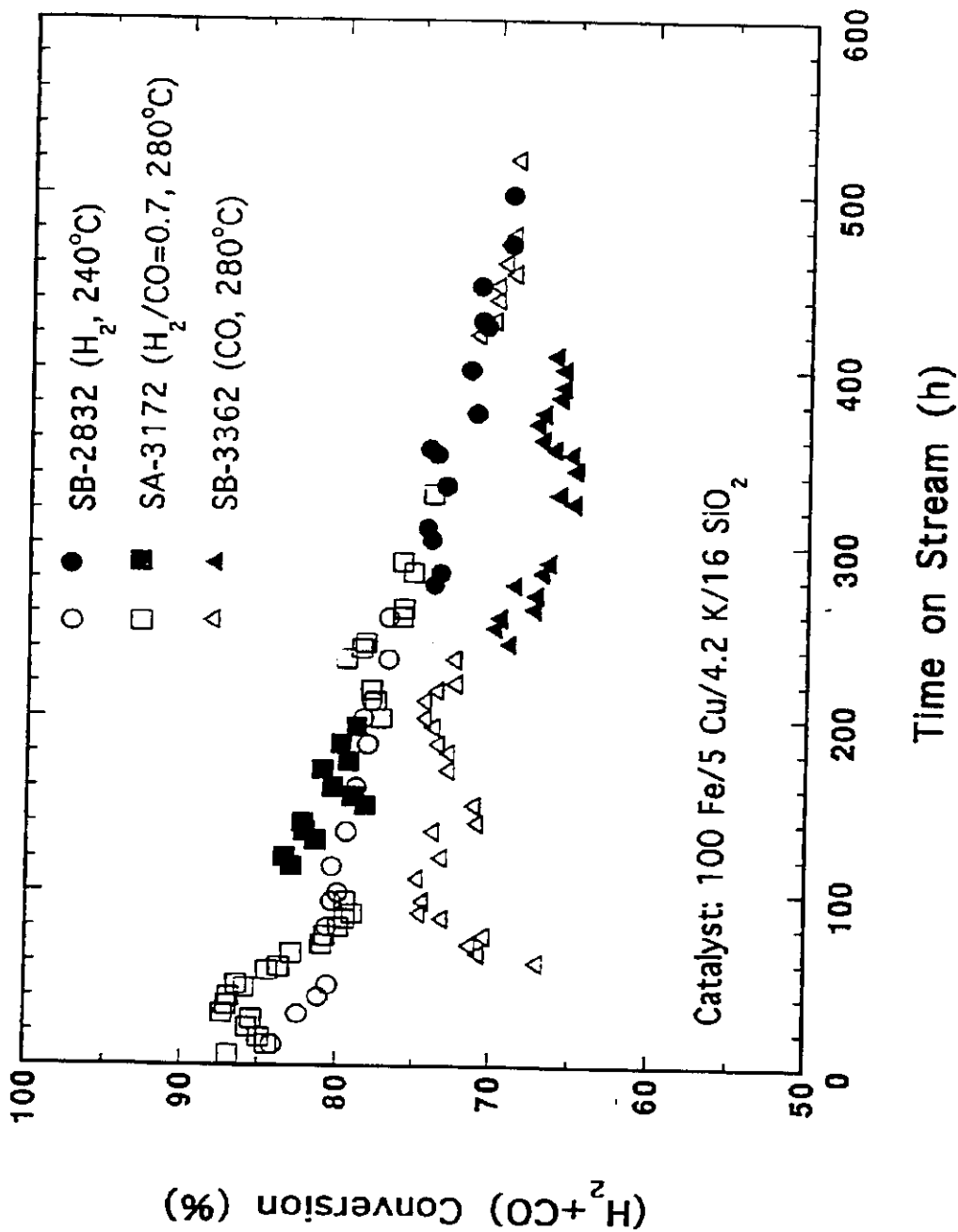
Figure III-5.2 Effect of pretreatment conditions on conversion and catalyst stability (FT synthesis conditions: T=260°C, (H₂/CO)=0.67; open symbol: P=1.48 MPa, SV=1.5 Nl/g-cat/h; closed symbol: P=2.17 MPa, SV=2.2 Nl/g-cat/h).

increased to 70 %. The latter value is comparable to those obtained between 70 and 230 h on stream. The catalyst activity was fairly stable during the test after the initial upset, and the loss of conversion was only 0.24 % per day. However, the catalyst was not properly activated because of the loss of the liquid medium, and interruption of synthesis during the early part of the testing may have had a detrimental effect on catalyst activity.

The effect of pretreatment procedure on catalyst activity, measured by magnitude of the apparent first order reaction rate constant, is shown in Figure III-5.3. The syngas pretreated catalyst was the most active during FT synthesis, whereas activities of hydrogen and carbon monoxide pretreated catalysts were similar to each other.

Following the syngas pretreatment the apparent first order rate constant was 372 mmol/g-Fe/h/MPa, before decreasing the reactor head temperature. After lowering of the reactor head temperature to 210°C, the value of k decreased to 326 mmol/g-Fe/h/MPa at 95 h on stream, and than varied between 316 and 345 mmol/g-Fe/h/MPa up to 215 h on stream. This shows that the catalyst activity was stable, and there was no deactivation during testing under higher pressure. However, some deactivation was noted at 272 h on stream (k = 295 mmol/g-Fe/h/MPa).

Hydrogen reduced catalyst was rather stable during the first 210 h of testing at the baseline conditions. The apparent rate constant varied between 265 and 277 mmol/g-Fe/h/MPa during this time period, but it decreased significantly during testing at higher pressure (263-526 h). The rate constant decreased to 214 mmol/g-Fe/h/MPa at 498 h, and further to 192 mmol/g-Fe/h/MPa at 641 h on stream (not shown in Figure III-5.3). After the regeneration the rate constant increased slightly to 199 mmol/g-Fe/h/MPa at 713 h. Catalyst deactivation rate, during 641 h of testing, was about 1% per day. Here, the deactivation rate is expressed as a percent loss of initial k value (at 41 h on stream).
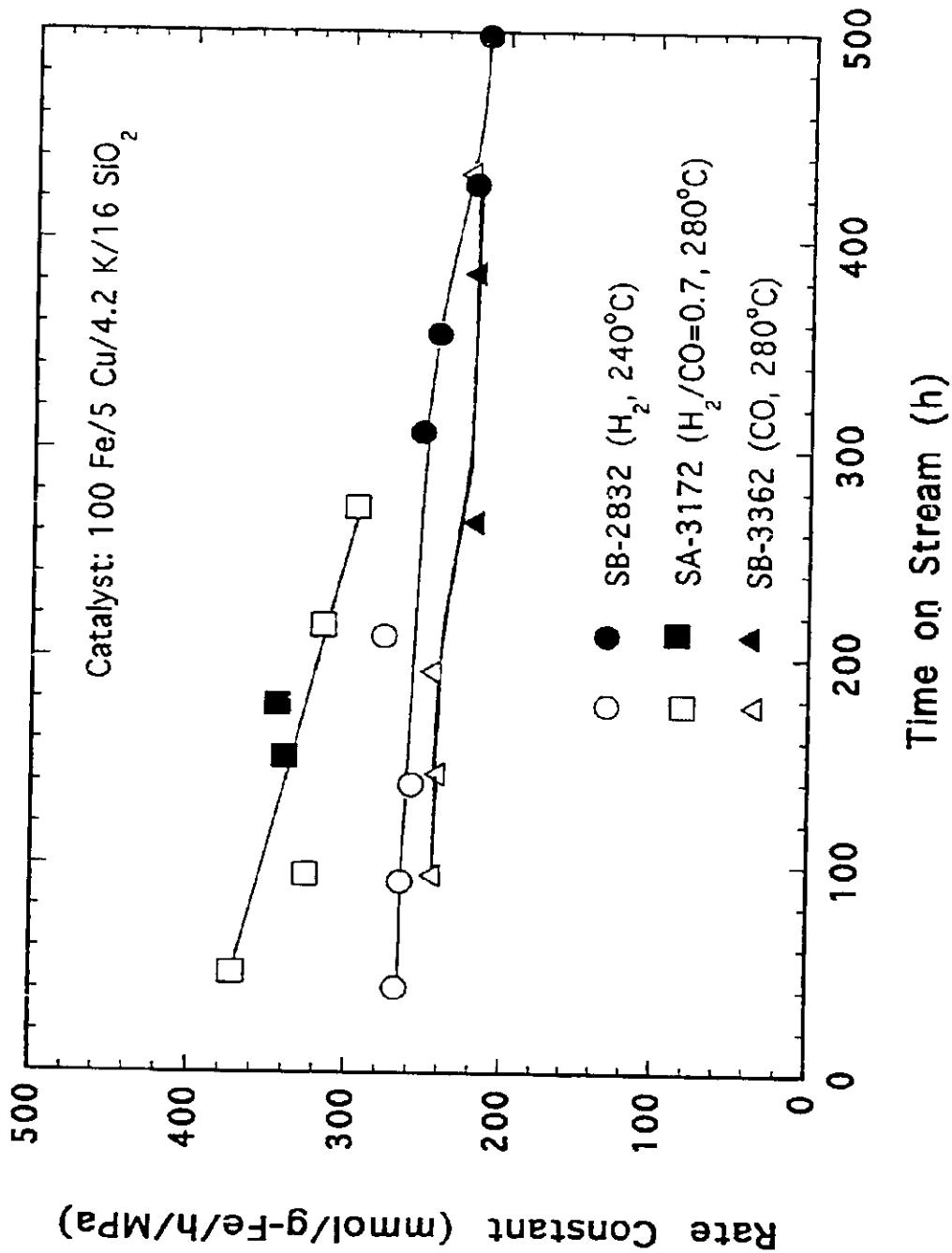
Figure III-5.3 Effect of pretreatment conditions on the apparent first order reaction rate constant (FT synthesis conditions: T=260°C, (H₂/CO)=0.67; open symbol: P=1.48 MPa, SV=1.5 Nl/g-cat/h; closed symbol: P=2.17 MPa, SV=2.2 Nl/g-cat/h).

The CO pretreated catalyst was very stable during the first 200 h at the baseline conditions, and the apparent reaction rate constant was about 245 mmol/g-Fe/h/MPa. Some deactivation occurred during testing at higher pressure, and k decreased to about 220 mmol/g-Fe/h/MPa during testing at 2.17 MPa (250 - 400 h). The rate constant was 225 mmol/g-Fe/h/MPa after returning to the baseline conditions (432 h). This corresponds to 8% loss in activity over 337 h of testing, or deactivation rate of 0.57% per day.

The reactor productivity increased in all three tests during testing at higher pressure (Tables III-5.2 to III-5.4). An increase in reaction pressure of 46.5% (from 1.48 to 2.17 MPa) accompanied by simultaneous equivalent increase in gas space velocity (from 1.5 to 2.2 Nl/g-cat/h) resulted in increase of the space-time-yield (STY) ranging from 32% (H_2 reduced catalyst) to 47% (syngas pretreated catalyst). Obviously, these results provide a strong incentive for carrying FT synthesis at higher reaction pressures and gas space velocities. This, however, may result in faster catalyst deactivation and thus shorter catalyst lifetime.

The water-gas-shift (WGS) activity was high after H_2 reduction (SB-2832), and the usage ratio at baseline conditions was about 0.58-0.59 (Figure III-5.4a). Following syngas pretreatment (SA-3172) the usage ratio was 0.61-0.63 at the same conditions, which indicates that WGS activity was lower (higher usage ratio) in comparison with SB-2832. Due to differences in WGS activities the partial pressure of H_2 was significantly lower in run SA-3172 than in run SB-2832. The apparent rate constant was about 25 % higher after syngas pretreatment than after H_2 reduction, even though the total syngas conversion was approximately the same (~80 %) in these two tests. The usage ratio after CO pretreatment was about 0.58 - 0.60 at the baseline conditions. After increasing reaction pressure to 2.17 MPa, the usage ratio increased in all three tests, i.e. the WGS activity decreased. This may be attributed to catalyst deactivation (Runs SB-2832 and SB-3362) or higher FT activity (Run SA-3172).
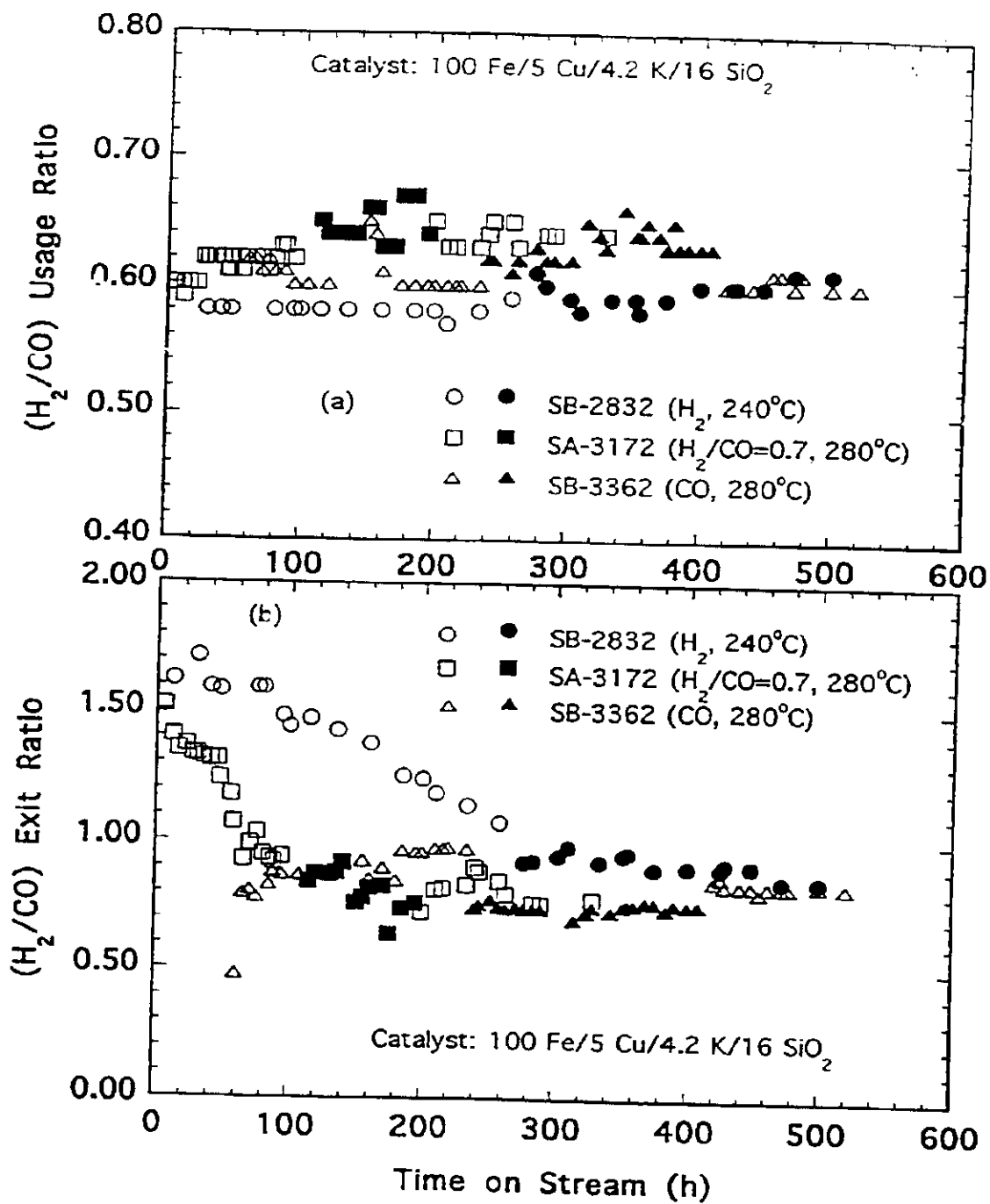
Figure III-5.4 Effect of pretreatment conditions on: (a) (H_2/CO) usage ratio; (b) (H_2/CO) exit ratio (FT synthesis conditions: T=260°C, (H_2/CO)=0.67; open symbol: P=1.48 MPa, SV=1.5 Nl/g-cat/h; closed symbol: P=2.17 MPa, SV=2.2 Nl/g-cat/h).

Since the H_2/CO usage ratio was less than the feed ratio, the exit H_2/CO ratio was greater than the H_2/CO feed ratio. The exit ratio was high initially after H_2 and syngas pretreatments (1.3 - 1.6), but decreased in both tests to 0.8 - 0.9 as the conversion decreased with time. The values of the exit H_2/CO ratio were lower, between 0.7 and 1, in Run SB-3362 (CO pretreatment) as shown in Figure III-5.4b.

Selectivity

Hydrocarbon and Carbon Number Product Distributions

Hydrocarbon selectivities as a function of TOS for each of the pretreatment procedures are shown in Figure III-5.5. In these figures, cumulative values are shown for lumped product distributions of selected product groups: methane, C_1-C_4, and C_1-C_{11}. Distances between numerical values for these groups show mass percentages of: methane, C_2-C_4 (light gases), C_5-C_{11} (gasoline) and C_{12+} (diesel and wax) hydrocarbon products. There were no significant changes in hydrocarbon product distributions during testing at the baseline conditions in all three tests. An increase in reaction pressure, from 1.48 to 2.17 MPa, either had no effect on hydrocarbon product distribution (SB-2832) or resulted in slight decrease of low molecular products (Runs SA-3172 and SB-3362) and the corresponding increase of C_{12+} products. The effect of pressure was the most pronounced in run SB-3362 (CO pretreatment), in which methane selectivity decreased from 3.5 to 2.9 wt% whereas C_{12+} increased from 59.5 to 63.7 %. In runs SB-2832 and SA-3172, the catalyst was also regenerated with H_2 during the test. In run SB-2832 hydrocarbon selectivity did not change after regeneration with H_2 at 240°C for 1 h (at 666 h on stream). However, hydrocarbon selectivity shifted significantly toward gaseous hydrocarbons in run SA-3172 after regeneration with H_2 at 250°C for 4 h (at 223 h on stream), as shown in Figure III-5.5b. Regeneration conditions were more severe in the latter case, which is probably the reason for the observed change in hydrocarbon selectivity.
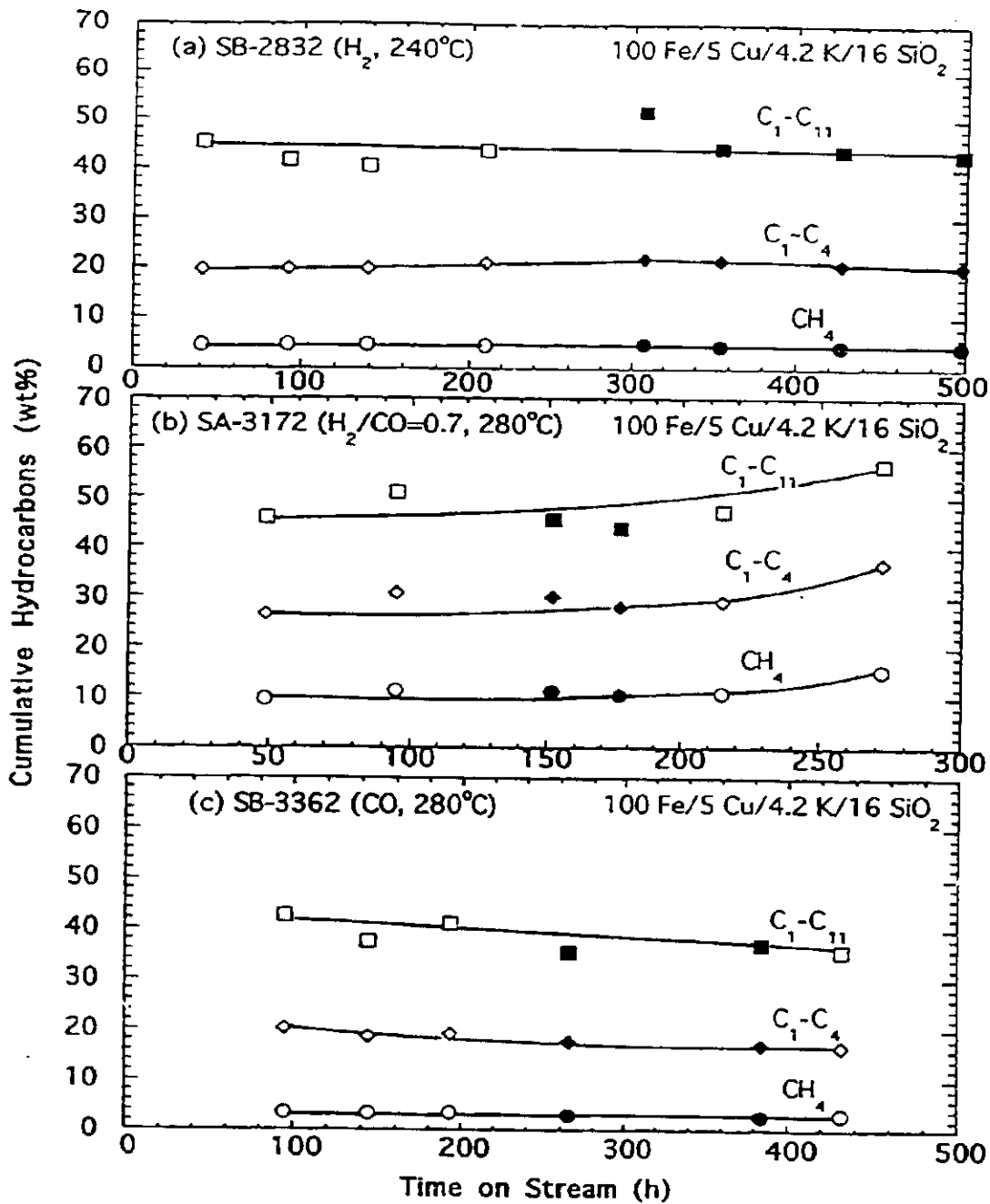
Figure III-5.5 Effect of time-on-stream on hydrocarbon product distribution following different pretreatment precedures: (a) SB-2832; (b) SA-3172; (c) SB-3362 (FT synthesis conditions: T=260°C, (H₂/CO)=0.67; open symbol: P=1.48 MPa, SV=1.5 Nl/g-cat/h; closed symbol: P=2.17 MPa, SV=2.2 Nl/g-cat/h).

The effect of pretreatment procedure on hydrocarbon selectivity is shown in Figure III-5.6. In this figure the average values from mass balances at the baseline conditions (up to 240 h on stream) are used for comparison. The catalyst had low methane and high C_{12+} selectivity after either CO or H_2 pretreatment. The average hydrocarbon product distribution at the baseline conditions after CO pretreatment was: CH_4 = 3.5 wt%, (C_2-C_4) = 15.8 %, (C_5-C_{11}) = 21.2 % and C_{12+} = 59.5 %; whereas after H_2 reduction it was: CH_4 = 4.6 wt%, (C_2-C_4) = 15.5 %, (C_5-C_{11}) = 22.0 % and C_{12+} = 57.9 %. Hydrocarbon selectivities were similar after these two pretreatment procedures. On the other hand, in run SA-3172, following syngas pretreatment, the catalyst produced significantly more methane and light gases. In this test the average hydrocarbon product distribution at the baseline conditions was: CH_4 = 10.4 wt%, (C_2-C_4) = 18.2 %, (C_5-C_{11}) = 19.8 % and C_{12+} = 51.6 %. This is completely unexpected, based on our previous studies with several precipitated iron catalysts. The syngas pretreated catalysts normally do not produce high yields of methane and gaseous hydrocarbons (e.g. see Bukur et al., 1989a, and Sections III-2 and III-4 of this report).

Typical carbon number distribution at the baseline process conditions, including the analyzed wax withdrawn from the slurry reactor, is presented in Figure III-5.7. Some positive deviations from the ASF distribution are noted in C_{11} to C_{20} carbon number range in two of the tests (SB-2832 and SA-3172). We are not certain whether this is due to the intrinsic catalytic selectivity or some experimental artifacts (e.g. loss of products and errors in analysis). The same trend was obtained in several other mass balances in each of these two tests. Experimental data were fitted with a three parameter model of Huff and Satterfield (1984). The model parameters were estimated by a nonlinear regression, and their numerical values are summarized in Table III-5.5 together with 95% confidence interval limits for these parameters.
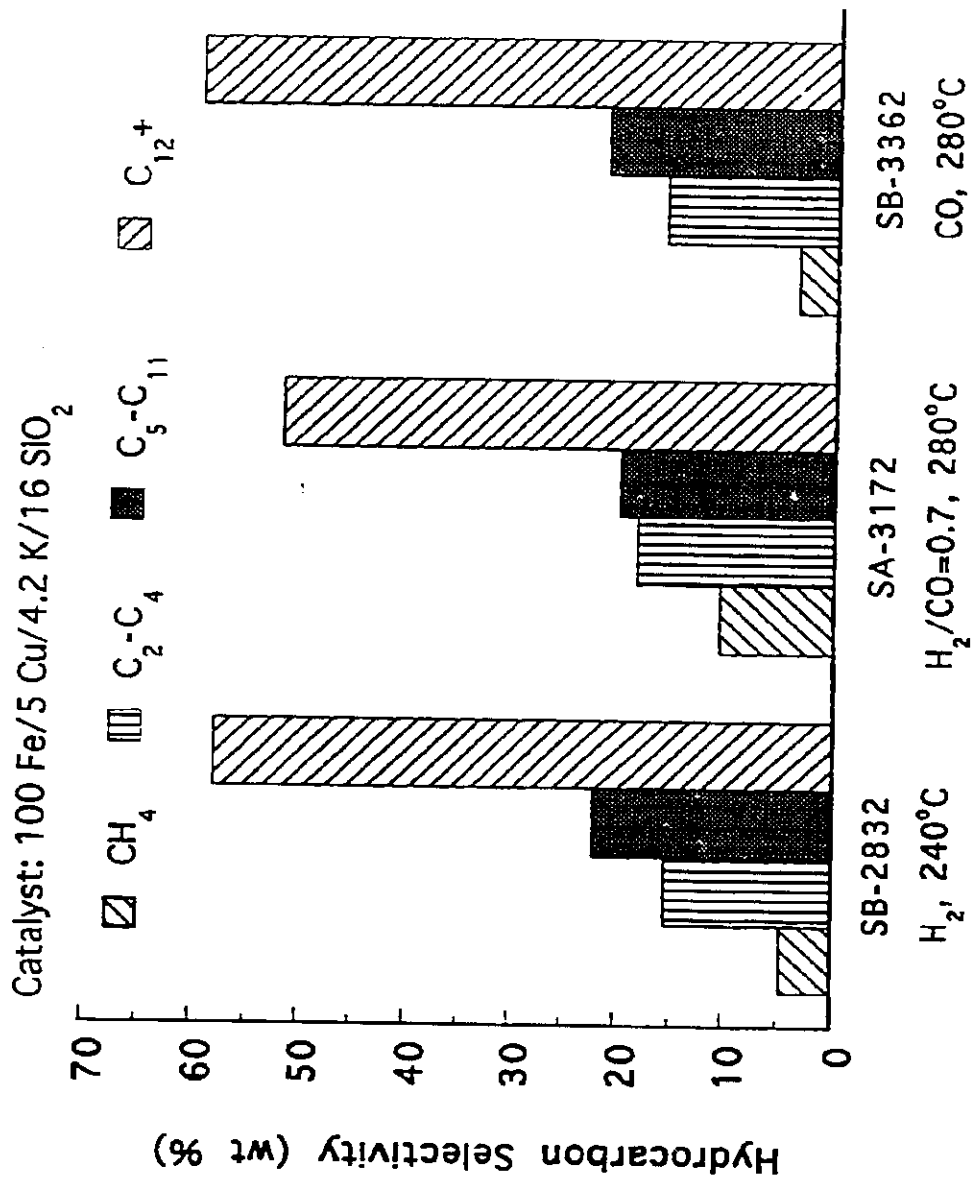
Figure III-5.6   Effect of pretreatment conditions on hydrocarbon selectivity at the baseline conditions: (a) SB-2832; (b) SA-3172; (c) SB-3362.
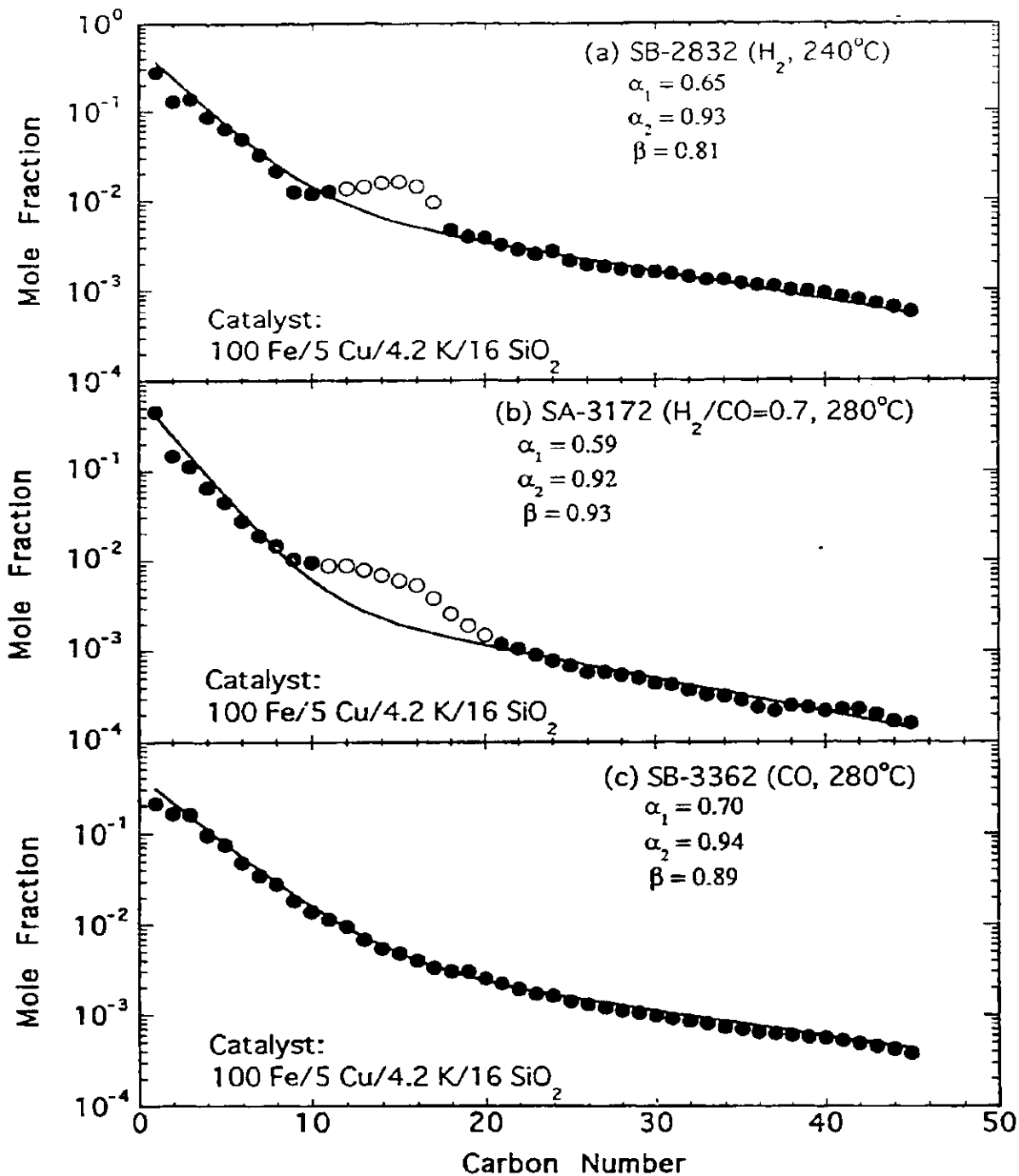
Figure III-5.7   Carbon number product distribution at the baseline conditions: (a) SB-2832; (b) SA-3172; (c) SB-3362. (closed circles: included point; open circles: excluded point for parameter estimation).

Olefin Selectivity

The effects of time-on-stream and reaction pressure on olefin selectivity are illustrated in Figure III-5.8. In general, the olefin selectivity was fairly stable during testing at the baseline process conditions in all three tests. The olefin content exhibited a broad maximum in C_3 - C_7 carbon number range, which is typical for iron FT catalysts. This particular shape is due to high hydrogenation activity of ethylene, and high adsorptivity and long residence time of high molecular weight olefins (C_{8+}). The olefin content was higher in all three tests during testing at higher pressure (2.17 MPa, SV = 2.2 Nl/g-cat/h), which may be attributed to decrease in H_2/CO ratio with increase in pressure.

Table III-5.5 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]
SB-2832	92	0.65 (0.63-0.66)	0.93 (0.92-0.94)	0.81 (0.80-0.83)
	355	0.68 (0.65-0.69)	0.93 (0.93-0.94)	0.82 (0.81-0.84)
SA-3172	95	0.59 (0.57-0.61)	0.92 (0.91-0.93)	0.93 (0.92-0.94)
	152	0.55 (0.52-0.58)	0.92 (0.91-0.93)	0.88 (0.86-0.90)
	272	0.58 (0.56-0.60)	0.93 (0.92-0.93)	0.93 (0.92-0.94)
SB-3362	95	0.70 (0.69-0.71)	0.93 (0.93-0.93)	0.89 (0.88-0.90)
	144	0.67 (0.66-0.68)	0.94 (0.94-0.94)	0.87 (0.86-0.88)
	265	0.65 (0.65-0.65)	0.93 (0.93-0.93)	0.77 (0.76-0.78)
	384	0.70 (0.69-0.71)	0.93 (0.93-0.93)	0.74 (0.73-0.75)

[a] Parameters estimated from products with carbon number in the range C_1-C_{45}.
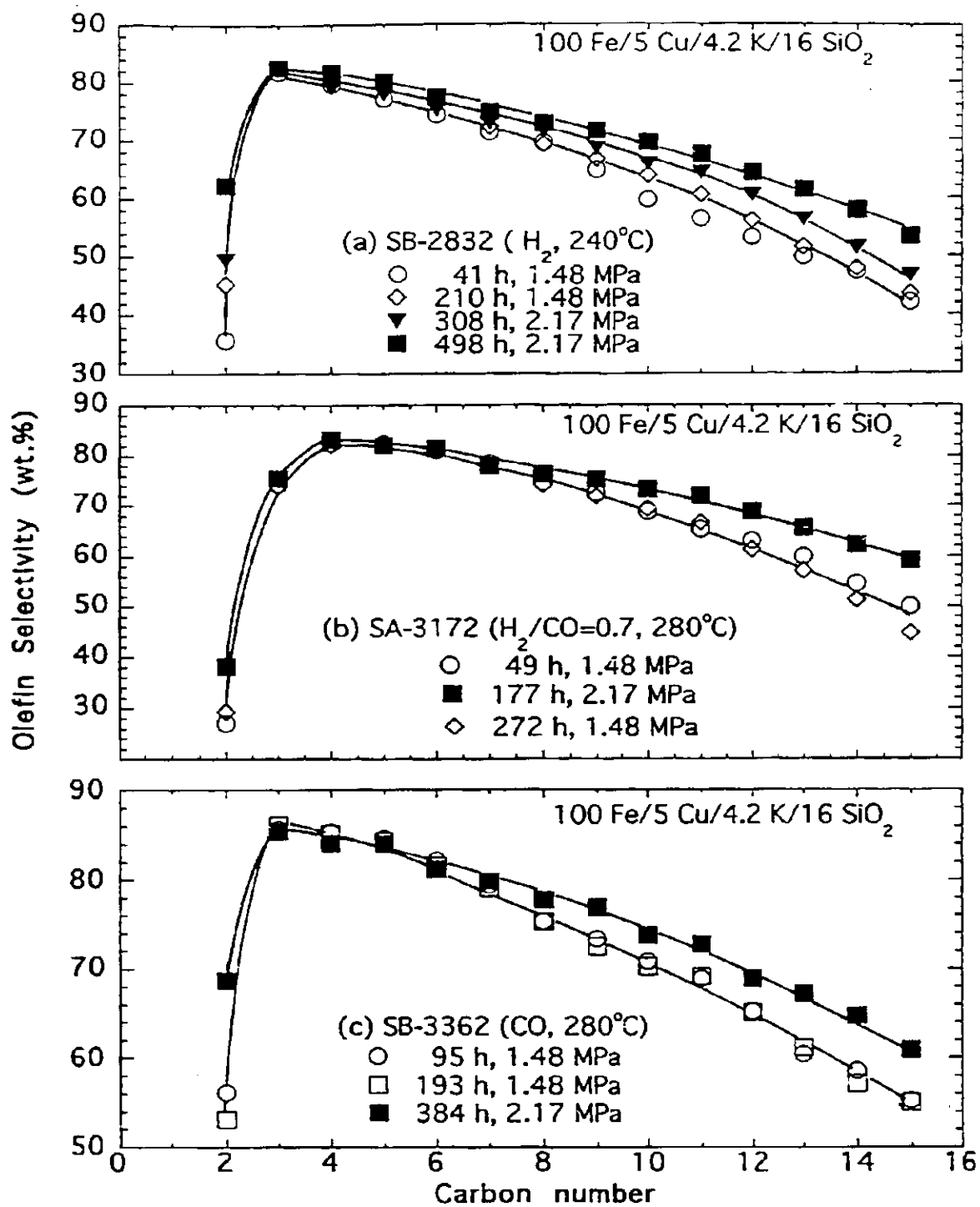
[b] 95% confidence interval.

Figure III-5.8 Effects of time-on-stream and reaction pressure on olefin selectivity: (a) SB-2832; (b) SA-3172; (c) SB-3362.

Since variations in olefin content with time were small during testing under the baseline conditions the average values were used to examine the effect of pretreatment conditions on olefin selectivity (Figure III-5.9). In general, the olefin content was higher when the catalyst was activated with CO or syngas than with H_2, and such a trend is in agreement with results obtained in our studies with other iron FT catalysts. Olefin contents of C_2 - C_4 hydrocarbons were low following the syngas pretreatment, which is consistent with high methane selectivity during this test, but not with the data for C_{5+} hydrocarbons (Figure III-5.9).

2-Olefin Selectivity

Variations in 2-olefin selectivity, which is a measure of catalyst isomerization activity, with time are shown in Figure III-5.10 for all three STSR tests. During testing at the baseline process conditions the 2-olefin selectivity was fairly stable. Upon increasing reaction pressure and gas space velocity to 2.17 MPa and 2.2 Nl/g-cat/h, respectively, the 2-olefin selectivity remained unchanged in run SA-3172 (syngas pretreatment), but decreased slightly in tests SB-2832 (H_2 reduction) and SB-3362 (CO pretreatment). This is consistent with observed trends in olefin selectivity, i.e. secondary hydrogenation and isomerization reactions are less pronounced at higher reaction pressure. Also, in run SB-2832 the 2-olefin selectivity decreased with time during testing at higher pressure (see data at 308 and 498 h on stream in Figure III-5.10a).

There were no significant differences in 2-olefin selectivities after different pretreatment procedures as shown in Figure III-5.11. The average values of 2-olefin selectivities during testing at the baseline conditions were used for this comparison. This catalyst has rather high olefin isomerization activity, especially for C_{9+} hydrocarbons.
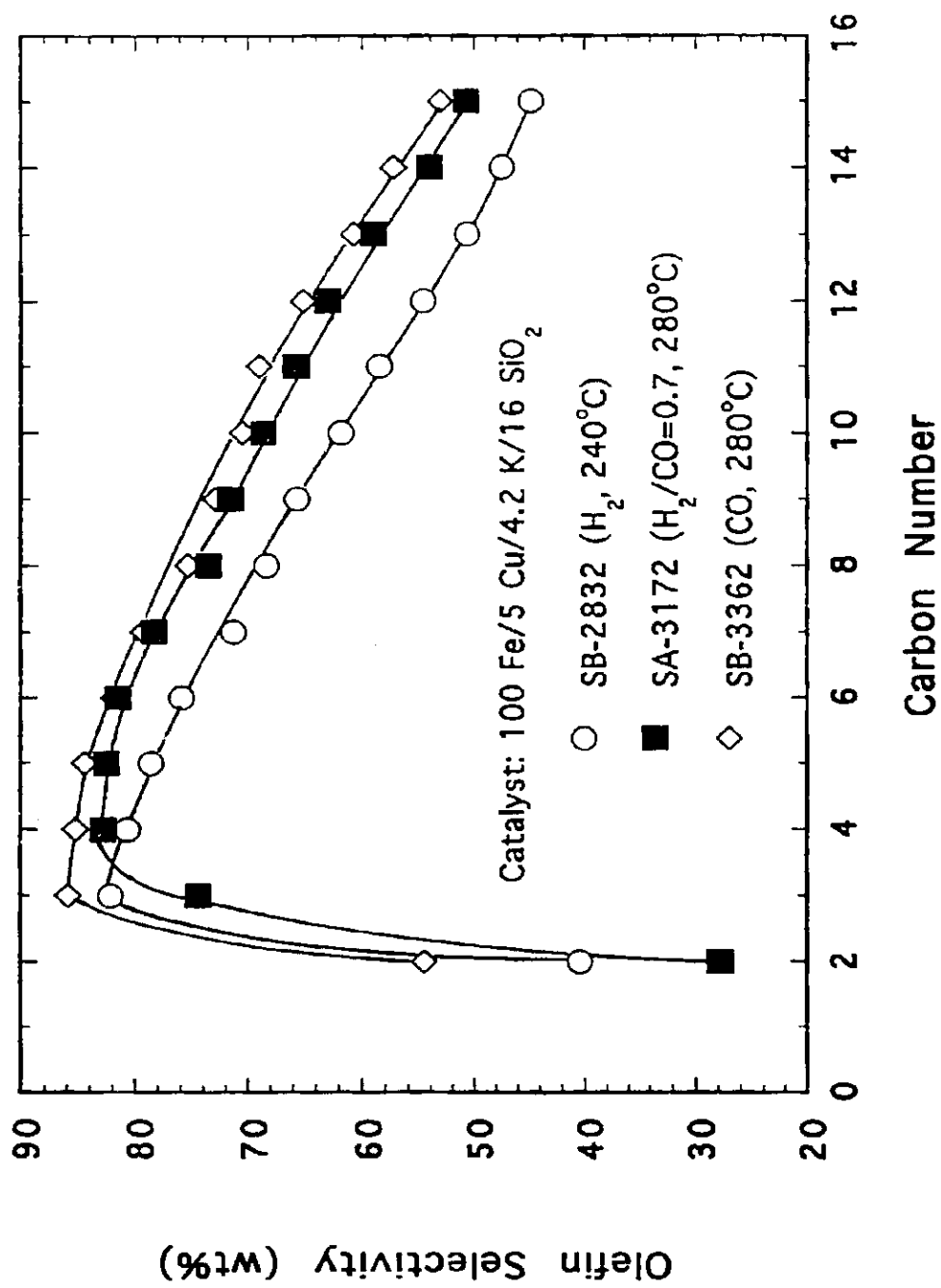
Figure III-5.9   Effect of pretreatment conditions on olefin selectivity at the baseline conditions.
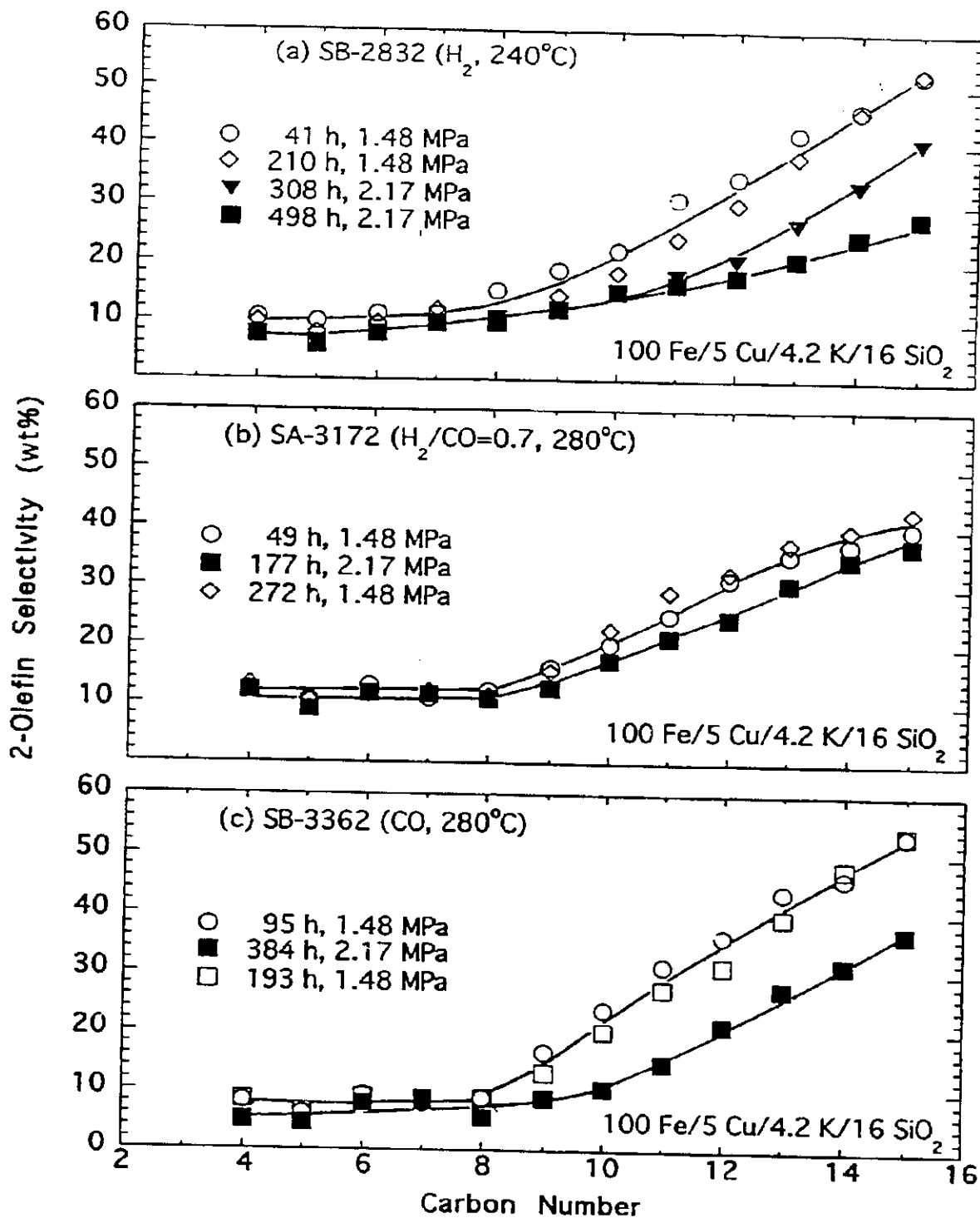
Figure III-5.10 Effect of time-on-stream and reaction pressure on 2-olefin selectivity: (a) SB-2832; (b) SA-3172; (c) SB-3362.
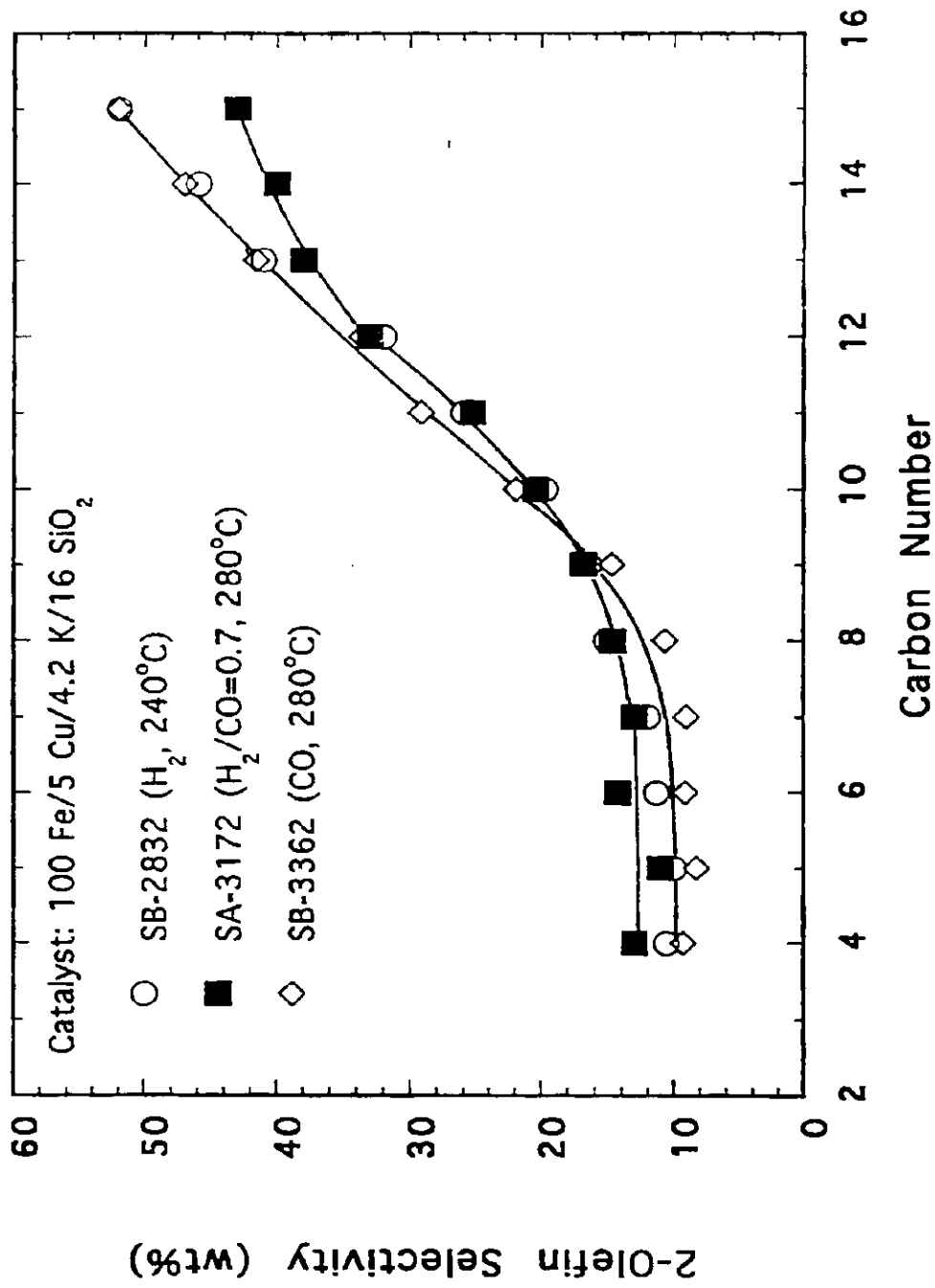
Figure III-5.11 Effect of pretreatment conditions on 2-olefin selectivity at the baseline conditions.

III-5.3 Summary

The effect of three pretreatment procedures, using H_2, CO and $H_2/CO = 0.7$ as reductants, on performance of 100 Fe/5 Cu/4.2 K/16 SiO_2 catalyst during Fischer-Tropsch synthesis was studied in stirred tank slurry reactors. The test duration was between 340 and 720 h of continuous operation.

The synthesis gas conversion was high in all three tests, and varied between 64 and 87%. Deactivation rates were low and the loss of activity was less than 1% per day in all three tests. Activity of the syngas pretreated catalyst was about 25% higher than that of H_2 or CO pretreated catalyst. Beneficial effects of operation at higher reaction pressure on the reactor productivity (space-time-yield) were demonstrated in all three tests. By simultaneously increasing the reaction pressure and the gas space velocity in the same proportion (from 1.48 MPa and 1.5 Nl/g-cat/h to 2.17 MPa and 2.2 Nl/g-cat/h) in order to keep the gas contact time constant as at the baseline conditions, the STY was increased by 32% to 47%. The latter value is proportional to increase in reaction pressure, and confirms some of the earlier literature findings that space-time-yield is proportional to pressure (Hall et al., 1952; Anderson, 1956; Dry, 1981; Bukur and Brown, 1987). Obviously, one would want to operate at as high synthesis pressure as possible, however, the catalyst deactivation rate also increases with pressure, and there is an optimum value of reaction pressure which is largely influenced by process economics.

In general, catalyst selectivity did not vary markedly with time on stream. During the operation at high pressure a slight decrease in secondary olefin hydrogenation and isomerization reactions was observed, as well as a shift in selectivity toward higher molecular weight hydrocarbons. However, the magnitude of these changes was small in all cases. Methane selectivity was low (2.9-4.6 wt%) and C_{12+} selectivity was high (57-64 wt%) after hydrogen and CO pretreatments, whereas the syngas pretreated catalyst had unexpectedly high methane (10-11 wt%) selectivity. The olefin

content was higher after CO and syngas pretreatments, than that of hydrogen reduced catalyst.

III-5.4 References

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