RESULTS AND DISCUSSION

III   Testing of Previously Synthesized Catalysts

The objective of this task is to verify repeatability of results obtained in stirred tank slurry reactor (STSR) tests of two catalysts designated B (100 Fe/5 Cu/6 K/24 SiO_2 containing 55.4 wt% of iron) and C (100 Fe/3 Cu/4 K/16 SiO_2 containing 59.7 wt% of iron) during the previous DOE Contract DE-AC22-89PC89868. These two catalysts were chosen due to good performance (high syngas conversion and low methane and gaseous hydrocarbons selectivities) in slurry reactor tests. The catalysts from the same preparation batch and the same pretreatment and process conditions, were employed as in the previous slurry reactor tests of these two catalysts.

III-1   Catalyst Characterization Studies

Catalysts B and C (both from the first preparation batch) synthesized in our laboratory, and commercial precipitated iron catalyst (LP 33/81) synthesized by Ruhrchemie AG (Oberhausen-Holten, Germany) were characterized after calcination in air at 300°C for 5 h by elemental chemical analysis, BET surface area (SA), total pore volume (PV) and pore size distribution (PSD). Ruhrchemie catalyst was used initially in fixed bed reactors at Sasol in South Africa, and it represents an useful reference catalyst.

Bulk iron phases in catalysts B and C after the Fischer-Tropsch synthesis in a slurry reactor, were determined by X-ray diffraction (XRD) analysis and/or by Mössbauer effect spectroscopy (MES). The Mössbauer spectra were obtained and analyzed at the University of Kentucky (The Consortium for Fossil Fuel Liquefaction Science). A description of the catalyst synthesis procedure is given in Appendix 1, whereas the catalyst characterization equipment and experimental procedures employed are described in Appendix 2.

<u>Catalyst Composition and Physical Characterization</u>

The catalyst composition and textural properties of catalysts calcined at 300°C are summarized in Table III-1.1. The catalyst compositions were calculated based on the

Table III-1.1   Catalyst Composition and Structural Properties of Fischer-Tropsch Catalysts

Catalyst Code	Amount Prepared, (g)	Composition 100 Fe/x Cu/y K/z SiO$_2$	BET Surface Area, m^2/g	Pore Volume, cm^3/g
100 Fe/3 Cu/4 K/16 SiO$_2$ S3416-1	40	3.5/5.8/17 3.0/6.7/16 [a] 3.0/5.9/16 [b]	257 245 [a]	0.66 0.65 [a]
100 Fe/5 Cu/6 K/24 SiO$_2$ S5624-1	67	5.4/6.2/24 5.1/8.1/26 5.5/6.6/24 [c]	235 222 [a]	0.71 0.68 [a]
100 Fe/5 Cu/4.2 K/24 SiO$_2$ Ruhrchemie	n/a	5.6/5.1/31 [a] 5/4/27 [d]	290	0.62

[a]:   Bukur (1994).
[b]:   Analysis conducted at Universal Oil Products Inc.
[c]:   Analysis conducted at Pittsburgh Energy Technology Center.
[d]:   Analysis conducted at Sandia National Laboratory.

elemental analysis by atomic absorption spectroscopy (AAS). The results of elemental analysis of all three catalysts show that numerical values for iron, copper and silica are fairly consistent with the corresponding nominal (intended) values, whereas the potassium contents are slightly higher than the nominal values. The BET surface areas were between 222 and 290 m^2/g, whereas the pore volume varied from 0.62 cm^3/g (Ruhrchemie LP 33/81) to 0.71 cm^3/g (catalyst B). Multiple measurements of the same property with the same catalyst indicate good reproducibility of results. Ruhrchemie catalyst has similar composition as our catalyst B, and its surface area is about 20% higher than that of the catalyst B.

Figure III-1.1 shows the differential pore volumes of catalysts B and C as a function of pore diameter. The data show that the pore volume contribution from larger pores (>10 nm) is very small.

Iron phases in calcined and used catalysts B and C

XRD patterns of calcined catalysts B and C did not exhibit crystallinity, i. e. they are either amorphous or the crystallites are too small (less than 5 nm) to be detected by XRD. The iron phases present in catalysts samples withdrawn from the slurry reactor at the end of several tests are summarized in Table III-1.2. Mössbauer spectroscopy analysis indicates the presence of a significant fraction (38-73%) of iron phase(s) exhibiting superparamagnetic behavior at a room temperature. Kündig et al. (1966) have found that the critical diameter of iron oxide particles for superparamagnetic relaxation at room temperature is about 13.5 nm. In runs SB-0045 and SA-0075 magnetite (Fe_3O_4) was identified by XRD analysis, but not by MES analysis. It is likely that at least a portion of superparamagnetic phase is magnetite. Fe_xC_y designates either a single iron carbide phase (ε'- or χ- carbide) or a mixture of these two carbides. The precise identification of these two types of carbides by XRD analysis is difficult when the signal intensities are low, and other compounds with overlapping peaks are present, such as magnetite and wax. In this report χ-carbide (Fe_5C_2) refers to the so-called
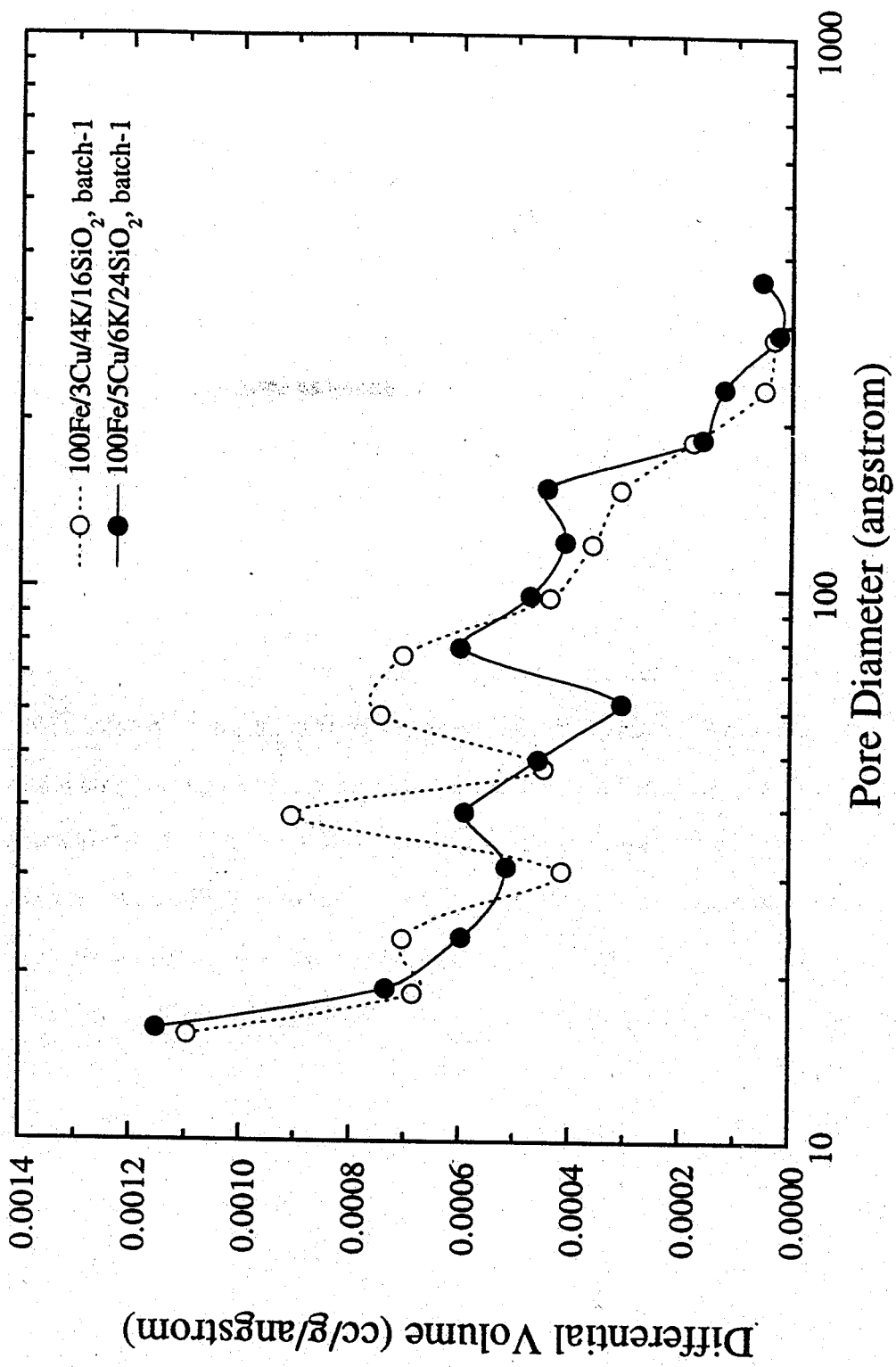
Figure III-1.1 Pore size distributions of catalysts B and C from batch-1.

Legend:
- ···O··· 100Fe/3Cu/4K/16SiO$_2$, batch-1
- ●—— 100Fe/5Cu/6K/24SiO$_2$, batch-1

X-axis: Pore Diameter (angstrom)

Y-axis: Differential Volume (cc/g/angstrom)

Table III-1.2   Summary of XRD and MES Results of Used Catalyst Samples

Run Number	Catalyst	Time on Stream (TOS), h	Phases Identified by Mössbauer	Phases Identified by XRD	(H_2+CO) (%) Conversion	CH_4 (mol%)
SB-0045	100 Fe/3 Cu/4 K/16 SiO$_2$ S3416-1	400 (EOR)	40% (Spm) and 60% (χ-Fe$_5$C$_2$)	Fe$_3$O$_4$, Fe$_x$C$_y$, and FeCO$_3$	78 - 81	2.2 - 2.4
SA-0705	100 Fe/3 Cu/4 K/16 SiO$_2$ S3416-1	526 (EOR)	38% (Spm) 10% (FeCO$_3$) and 52% (χ-Fe$_5$C$_2$)	Fe$_3$O$_4$, Fe$_x$C$_y$, and FeCO$_3$	76 - 78	2.9 - 3.1
SB-3064	100 Fe/5 Cu/6 K/24 SiO$_2$ S5624-1	54 (EOR)	73% (Spm) and 27% (Fe$_3$O$_4$)	-	8 - 14	8.2 - 11.4
SB-0665	100 Fe/5 Cu/6 K/24 SiO$_2$ S5624-1	377 (EOR)	52% (Spm) 46% (ϵ'-Fe$_{2.2}$C) and 2% (χ-Fe$_5$C$_2$)	-	64 - 67	3.5 - 3.7

EOR stands for end of run.

FTS process conditions for 100 Fe/5 Cu/6 K/24 SiO$_2$, batch-1 catalyst testing are: T = 260°C, P = 1.48 MPa, H$_2$/CO = 0.67, SV = 1.6 - 2.2 Nl/g-cat/h; and for 100 Fe/3 Cu/4 K/16 SiO$_2$, batch-1 catalyst testing: T = 260°C, P = 1.48 MPa, H$_2$/CO = 0.67, SV = 1.4 Nl/g-cat/h during the first 260 h on stream, P = 2.17 MPa, SV = 2.05 Nl/g-cat/h until the end of run.

Fe$_x$C$_y$ denotes iron carbide phase(s).

Hägg carbide and its XRD pattern reported by Hoffer et al. (1949). ε'-carbide ($Fe_{2.2}C$) has a pseudo-hexagonal structure and its XRD pattern was first reported by Barton and Gale (1964). The identification of iron phases by Mössbauer spectroscopy was made by utilizing published values of the hyperfine parameters (the isomer shift, the quadruple splitting, and the magnetic hyperfine field) of the Mössbauer spectra.

The following observations are made from results shown in Table III-1.2:

(1)   Syngas conversion was low (8-14%) in run SB-3064; magnetite and superparamagnetic phase (probably iron oxide) were identified at the end of the test. A possible reason for low activity in this test is the presence of impurities (catalyst poisons) in the initial slurry medium. These impurities may have prevented the formation of active iron phases during the reduction and F-T reaction. In all other tests the catalyst was active and the iron carbide phases were identified by Mössbauer and XRD analysis.

(2)   Catalyst B (24 parts of SiO_2 per 100 parts of Fe) contained ε'-carbide (SB-0665), whereas in runs SB-0045 and SA-0705 with catalyst C (16 parts of SiO_2 per 100 parts of Fe) χ-carbide was found in the used catalyst samples at the end of the tests. It is not clear whether this is due to differences in silicon oxide loadings, or due to the use of different process conditions in different tests. Namely, in runs SB-0045 and SA-0705 with catalyst C, the catalyst was tested at both 1.48 MPa and 2.17 MPa, whereas in run SB-0665, the catalyst B was tested at 1.48 MPa, only.

(3)   Methane selectivities were lower in tests where χ-carbide was the dominant iron phase (catalyst C), in comparison to the test SB-0665 with catalyst B were ε'-carbide was present.

III-2   Reaction Studies with Catalysts B and C

Octacosane (n-C$_{28}$ paraffin) was used as a start-up slurry medium in the first three tests with catalyst B (runs SB-2764, SB-3064 and SA-0025), but all of them were unsuccessful (low catalyst activity). In the original test of catalyst B (SB-1931) purified n-octacosane was used as the start-up fluid, and high synthesis gas conversion was obtained.

Before loading to the reactor, the n-octacosane (99 % purity, The Humphrey Chemical Company, North Haven, CT) was extracted with tetrahydrofuran (THF) to remove bromotetradecane, since bromine is known to be the catalyst poison. Samples of fresh n-octacosane (before purification with THF), and from the slurry reactor (after the purification) were sent for trace bromine analysis to two different Laboratories. According to analysis done at Galbraith Laboratories, Inc. (Knoxville, TN) the as received n-octacosane had 530 ppm bromine, and the purified one less than 10 ppm bromine. The VHG Labs Inc. (Manchester, NH), using TOX (total organic halogen) method, detected even higher level of impurities. They reported 0.7 wt-% total halogen (as bromine) in the fresh n-octacosane, and less than 0.005 wt% (50 ppm) in the purified sample. Both results show that the amount of bromine was substantially reduced with THF washing. However, it can not be ruled out that the residual ppm level of bromine had a detrimental effect on the catalyst activity. The trace of sulfur was also detected by Galbraith Laboratories in used octacosane samples. Therefore, we believe that the presence of impurities in n-octacosane had resulted in catalyst poisoning in the three unsuccessful tests with the catalyst B. After these three unsuccessful tests, we decided to abandon n-octacosane as the start-up liquid medium, and we began using the Ethylflo 164 oil (a hydrogenated 1-decene homopolymer liquid - C$_{30}$, obtained from Ethyl Co.). Ethylflo 164 oil was used in all subsequent slurry reactor tests throughout this contract.

III-2. 1   Stirred Tank Slurry Reactor Tests of Catalyst B (100 Fe/5 Cu/6 K/24 SiO$_2$)

Two successful tests of catalyst B designated SB-3354 and SB-0665 were performed in a slurry reactor B. The catalyst was reduced with H$_2$ at 250°C, 0.8 MPa (100 psig), 4000

cm^3/min for 4 h. The same reduction conditions were employed in the original test of this catalyst (SB-1931). In all three tests the process conditions were: 260°C, 1.48 MPa, gas space velocity (SV) of 1.2-2.2 Nl/g-cat/g using synthesis gas with molar feed ratio H$_2$/CO = 0.67-0.69. In each test, 7-10 g of catalyst with particle size less than 53 μm (270 mesh) was suspended in the start-up liquid to form a 2.4-3.6 wt% slurry.

<u>Activity and Stability</u>

Changes in synthesis gas, (H$_2$+CO), conversion and (H$_2$/CO) usage ratio with time-on-stream (TOS) are shown in Figure III-2.1. In the original run SB-1931 (with n-octacosane as the start-up liquid), (H$_2$+CO) conversion was stable with time (Figure III-2.1a). However, in the two recent runs SB-3354 and SB-0665 (with Ethylflo 164 oil as the initial slurry medium) the catalyst deactivated during the first 150 h of testing. Initial conversions in all three tests were similar (H$_2$+CO conversion was between 72 and 78%), but the initial space velocities were different in these tests (2.2 Nl/g-cat/h in run SB-1931, 2.0 Nl/g-cat/h in run SB-0665 and 1.8 Nl/g-cat/h in run SB-3354). Comparison of conversion values at the same gas space velocity (at 1.8 and 1.6 Nl/g-cat/h) reveals that the catalyst was most active in run SB-1931 (the highest conversions) and the least active in run SB-0665 (the lowest conversions).

Comparison of catalyst activity in terms of syngas conversion is not meaningful when the reaction conditions are not the same. In such a case an apparent reaction rate constant provides a better basis for comparison of the catalyst activity. In this study the apparent reaction rate constant was calculated assuming that the rate of (H$_2$+CO) disappearance has a first-order dependence on hydrogen partial pressure :

$$k = \frac{1000 \cdot SV \cdot X_{H_2+CO}}{22.4 \cdot P_{H_2} \cdot w_{Fe}} \quad \text{(mmol (H}_2\text{+CO) converted/g-Fe/h/MPa)}$$

where: SV = gas space velocity (Nl/g-cat/h); X_{H_2+CO} is syngas conversion; P_{H_2} = partial pressure of hydrogen (MPa); w_{Fe} = mass fraction of iron in the catalyst (-).

The apparent rate constant as a function of time-on-stream for three runs with catalyst B is shown in Figure III-2.2. As can be seen from this figure, initial activities in all three tests were about the same, k = 340-350 mmol/g-Fe/h/MPa. In run SB-1931, the apparent rate constant gradually decreased from 350 to 300 mmol/g-Fe/h/MPa over a 400 hour period. However, in run SB-3354, the rate constant decreased from 340 to 250 mmol/g-Fe/h/MPa during the first 150 h of testing. It was stable at this value during the next 150 hours of testing at SV = 1.6 Nl/g-cat/h; and then decreased further to 200 mmol/g-Fe/h/MPa during testing at SV = 1.2 Nl/g-cat/h. In run SB-0665, the initial value of the apparent rate constant was 350 mmol/g-Fe/h/MPa at 20 h, but the rate constant decreased from 350 to 250 mmol/g-Fe/h/MPa in 120 hours, and than stabilized at 220 mmol/g-Fe/h/MPa between 180 and 370 h of testing.

Water gas shift (WGS) activity of the catalyst is related to (H_2/CO) usage ratio (UR), partial pressure quotient $K_P = P_{CO_2} \cdot P_{H_2}/P_{CO} \cdot P_{H_2O}$ and per cent CO conversion to carbon dioxide (CO_2 selectivity). Lower values of the usage ratio, or higher values of K_P or CO_2 selectivity imply higher WGS activity. In runs SB-3354 and SB-0665, the usage ratio was fairly stable at 0.56-0.58 (see Figure III-2.1b) during the entire test. The usage ratio in run SB-1931 was usually above 0.60, and increased to 0.62 at about 500 h on stream, i. e. the catalyst's WGS activity was lower than in runs SB-3354 and SB-0665.

Hydrocarbon Selectivity and Carbon Number Distribution

Methane and $C_1 + C_2$ hydrocarbons (methane + ethane + ethylene) selectivities are shown in Figure III-2.3. Low selectivities of methane and $C_1 + C_2$ hydrocarbons obtained in run SB-1931 were also observed in runs SB-3354 and SB-0665. For example, selectivities to methane and $C_1 + C_2$ hydrocarbons during run SB-3354, were similar to those obtained in run SB-1931 (2.5-3 mol% and 5-6 mol%, respectively); whereas the corresponding values in
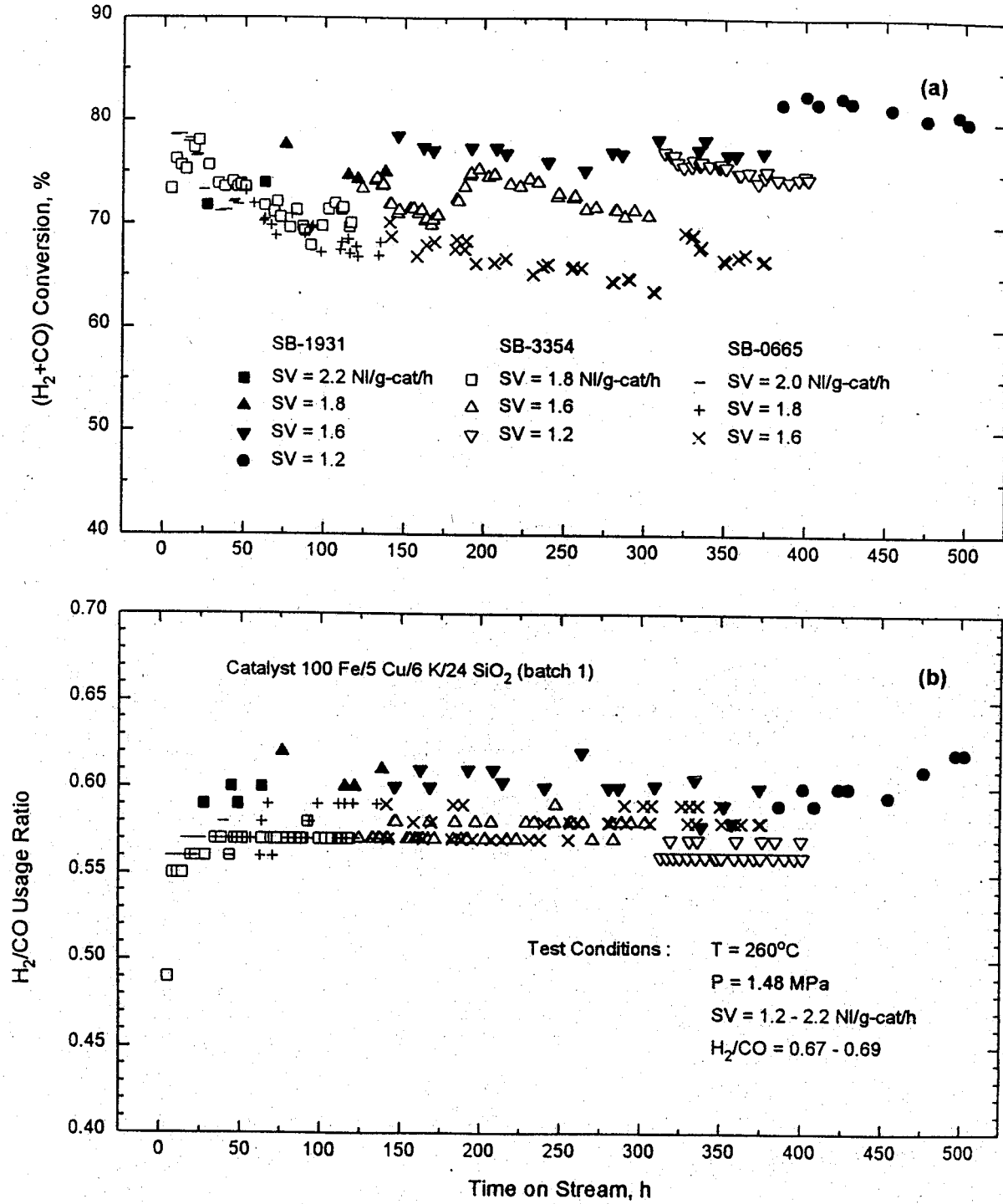
Figure III-2.1 Changes in (a) (H$_2$+CO) conversion and (b) H$_2$/CO usage ratio with time and

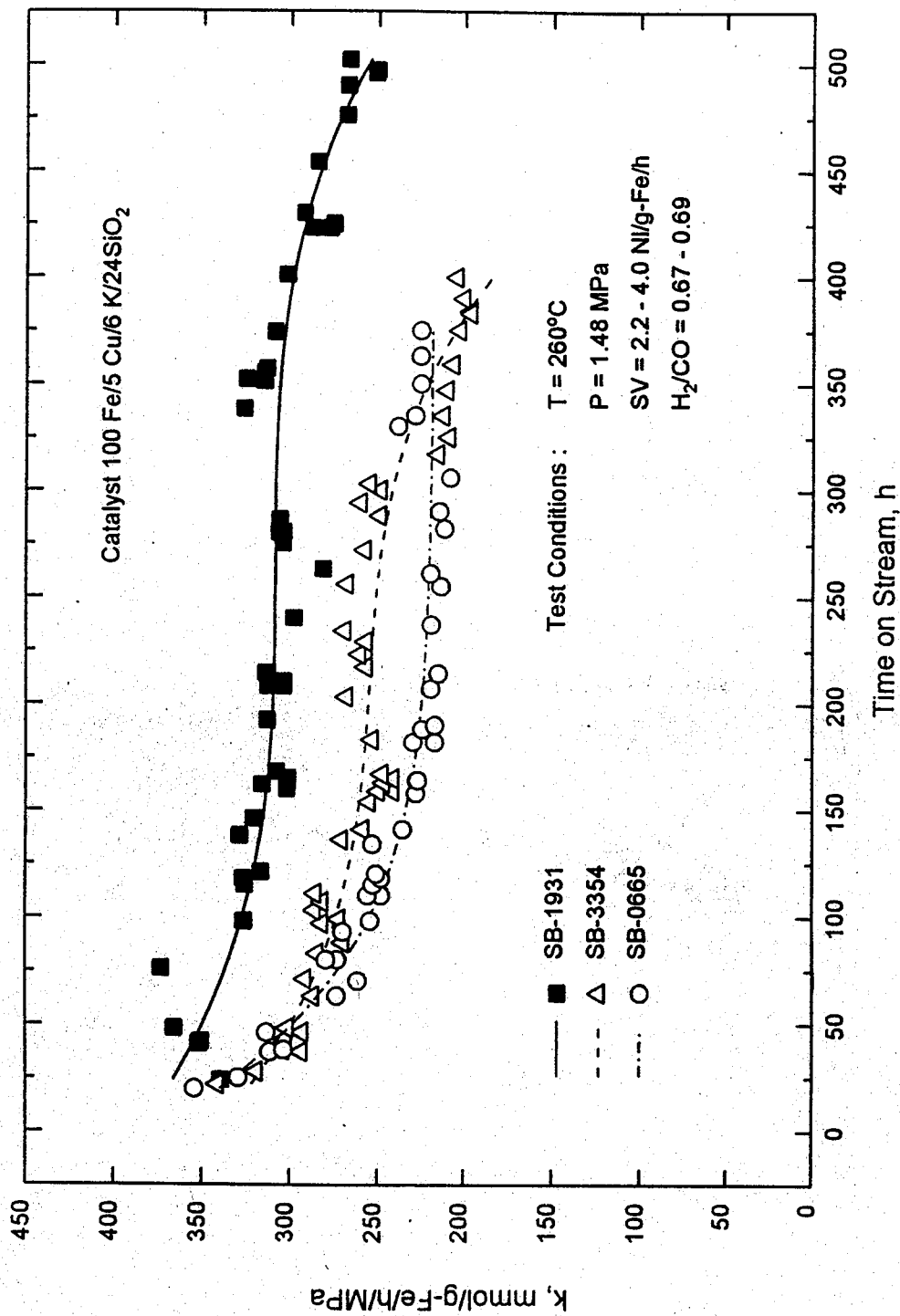process conditions in STSR tests of the 100 Fe/5 Cu/6 K/24 SiO$_2$ catalyst.

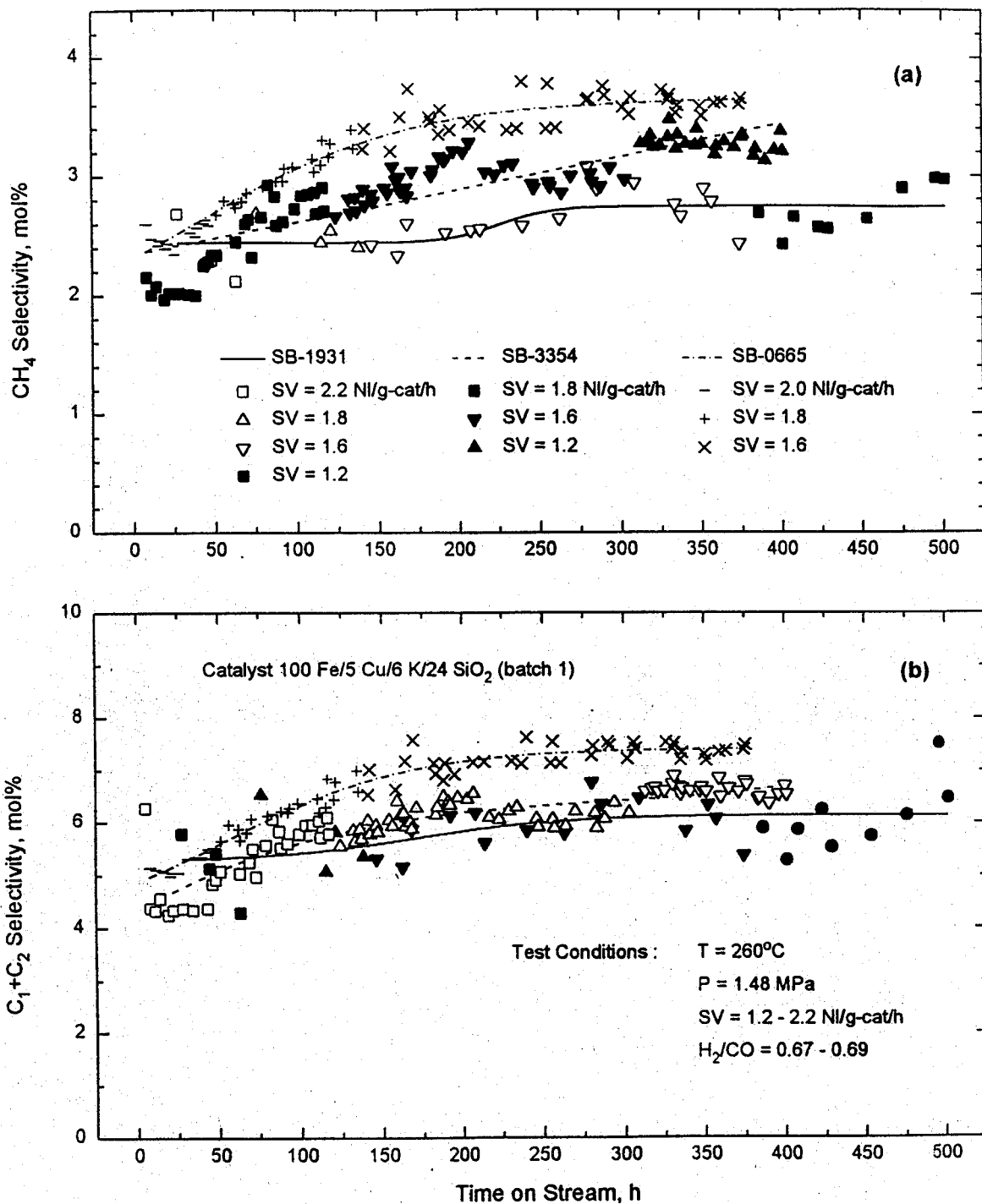Figure III-2.2 Apparent first order reaction rate constant as a function of time (100 Fe/5 Cu/6 K/24 SiO₂ catalyst).

Figure III-2.3 Methane (a) and (C_1+C_2) hydrocarbon selectivity (b) as a function of time

(100 Fe/5 Cu/6 K/24 SiO_2 catalyst).

run SB-0665 were slightly higher (e. g. 2.5-3.6 mol% and 5-7 mol%, respectively). Gaseous hydrocarbon selectivities (C_2 - C_4) (Table III-2.1) varied between 10 and 12.5 wt% in runs SB-1931 and SB-3354, but were higher in run SB-0665 (12-15 wt%).

In run SB-1931, hydrocarbon product distribution shifted gradually toward lower molecular weight products with time (see Table III-2.1). For example, methane selectivity increased from 2.5 wt% (42 h) to 3.7 wt% (496 h), while C_2 - C_4 selectivity increased from 11 to 14.6 wt% (between 98 and 208 hours on stream), whereas $C_{19}+$ selectivity decreased from 58 to 49 wt% (also between 98 and 208 h). In runs SB-3354 and SB-0665, hydrocarbon product distribution during the first 100 h on stream was very similar to that obtained in run SB-1931 (Table III-2.1), but after about 100 h on stream the product distribution in these two tests did not change significantly with time. Some differences in hydrocarbon product distributions were observed in these three runs. For example, gasoline range hydrocarbons (C_5 - C_{11}) selectivity in run SB-1931 was between 13.2 and 19.6 wt%, whereas in run SB-0665 it varied between 16.3 and 23 wt%. The gasoline range hydrocarbons in run SB-3354 varied between 16.9 and 19.2 wt%, which is similar to that obtained in run SB-1931.

Carbon number distributions obtained in tests with catalyst B, are shown in Figure III-2.4 in the form of Anderson - Schulz - Flory (ASF) plots (log of mole fraction vs. carbon number). Data for individual mass balances at SV = 1.6 Nl/g-cat/h and similar TOS were chosen for comparison (The effect of time-on-stream and process conditions on the carbon number distribution was negligible in all three tests). Positive deviations from ASF distribution are noted in all three tests in C_{10} - C_{22} carbon number range. We are not certain whether this is due to the intrinsic catalytic selectivity, or due to experimental errors (e.g. loss of products and/or errors in analysis). The same behavior was obtained in several other mass balances in each of these three tests. Experimental data in Figure III-2.4 were fitted with a three parameter model of Huff and Satterfield (1984):

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

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 2 sites, respectively. The model parameters were estimated by a nonlinear regression (products of carbon number range C_{10}-C_{20} were excluded from calculations). Numerical values of the parameters are as follows:

$\alpha_1 = 0.61$, $\alpha_2 = 0.93$, and $\beta = 0.76$.

Olefin Selectivity

Primary products of Fischer-Tropsch synthesis are 1-olefins and to a smaller extent, n-paraffins. Alpha olefins may undergo secondary reactions, such as hydrogenation, isomerization and readsorption. The olefin content, defined as 100 x olefin/(olefin+paraffin), is a measure of catalyst's hydrogenation activity. Weight percent olefin content variation with carbon number (up to C_{15}) is illustrated in Figure III-2.5a. The ethene content is low, since it readsorbs much more readily than the other low molecular weight olefins resulting in hydrogenation and/or chain growth initiation to higher molecular weight products. The olefin content reaches a maximum at C_3 - C_4, and then decreases with increase in carbon number. The olefin contents were similar in runs SB-1931 and SB-3354, whereas slightly lower values were obtained in run SB-0665.

Ratio of 2-olefins/(1+2)- linear olefins is indicative of catalyst's isomerization activity. This ratio usually increases with carbon number, especially for hydrocarbons in the liquid phase (C_7+). The 2-olefin contents were similar in all three runs (Figure III-2.5b), although the 2-olefin content in run SB-1931 was slightly lower than that obtained in runs SB-3354 and SB-0665.

Table III-2.1 Performance of 100 Fe/5 Cu/6 K/24 SiO_2 (batch-1) Catalyst[a] in Slurry Reactor Tests

Test designation	SB-1931					SB-3354			SB-0665	
Test conditions										
Temperature, °C	260	260	260	260	260	260	260	260	260	260
Pressure, MPa	1.48	1.48	1.48	1.48	1.48	1.48	1.48	1.48	1.48	1.48
Space velocity, Nl/g-cat/h [b]	2.2	1.8	1.6	1.2	1.8	1.6	1.2	2.0	1.8	1.6
Feed H_2/CO ratio	0.67	0.67	0.67	0.67	0.67	0.67	0.67	0.67	0.67	0.67
Time on stream, h	42	98	208	496	97	288	384	38	110	290
CO conversion, %	78.2	78.4	81.4	83.9	76.0	74.4	79.4	76.2	71.1	69.2
(H_2+CO) conversion, %	74.0	75.1	77.3	80.3	71.5	70.6	74.2	71.5	67.0	65.4
STY, mmol (H_2+CO)/g-cat/h [b]	71	68	56	43	57	50	40	63	54	47
k, mmol/g-Fe/h/MPa [c]	346	370	304	280	282	249	226	328	284	215
(H_2/CO) usage ratio	0.60	0.62	0.60	0.60	0.57	0.57	0.56	0.56	0.57	0.58
$K_P = P_{CO_2}\cdot P_{H_2}/P_{CO}/P_{H_2O}$	24	10	11	17	27	22	32	22	20	20
% CO converted to CO_2	47.6	46.4	46.8	45.1	48.6	48.3	48.1	48.3	47.8	48.2
Hydrocarbon selectivity, wt%										
CH_4	2.5	2.8	2.8	3.7	3.2	3.5	3.5	3.0	4.1	4.2
C_2-C_4	10.9	10.2	10.7	14.6	12.4	12.9	12.6	12.3	15.3	15.5
C_5-C_{11}	18.0	13.2	13.5	19.6	18.5	19.2	16.9	16.3	22.9	22.7
C_{12}-C_{18}		14.3	23.7		13.7	18.8	18.1		22.1	17.8
C_{12}^+	68.6	72.8	73.0	62.1	65.9	64.4	67.2	68.4	55.7	57.6
C_1+C_2	5.4	5.7	6.1	8.1	6.4	6.9	6.9	6.1	8.0	8.2
Yield, g/Nm^3(H_2+CO) Converted										
Hydrocarbons	212	217	213	206	207	206	210	209	193	199
Oxygenates	2.5	3.6	4.6	3.1	6.3	5.6	3.8	4.6	9.2	10.0
Catalyst productivity, g HC/g-cat/h [b]	0.34	0.33	0.27	0.20	0.26	0.23	0.19	0.29	0.23	0.21

[a] Iron content of this catalyst (0.554 g-Fe/g-cat)

[b] Based on unreduced catalyst

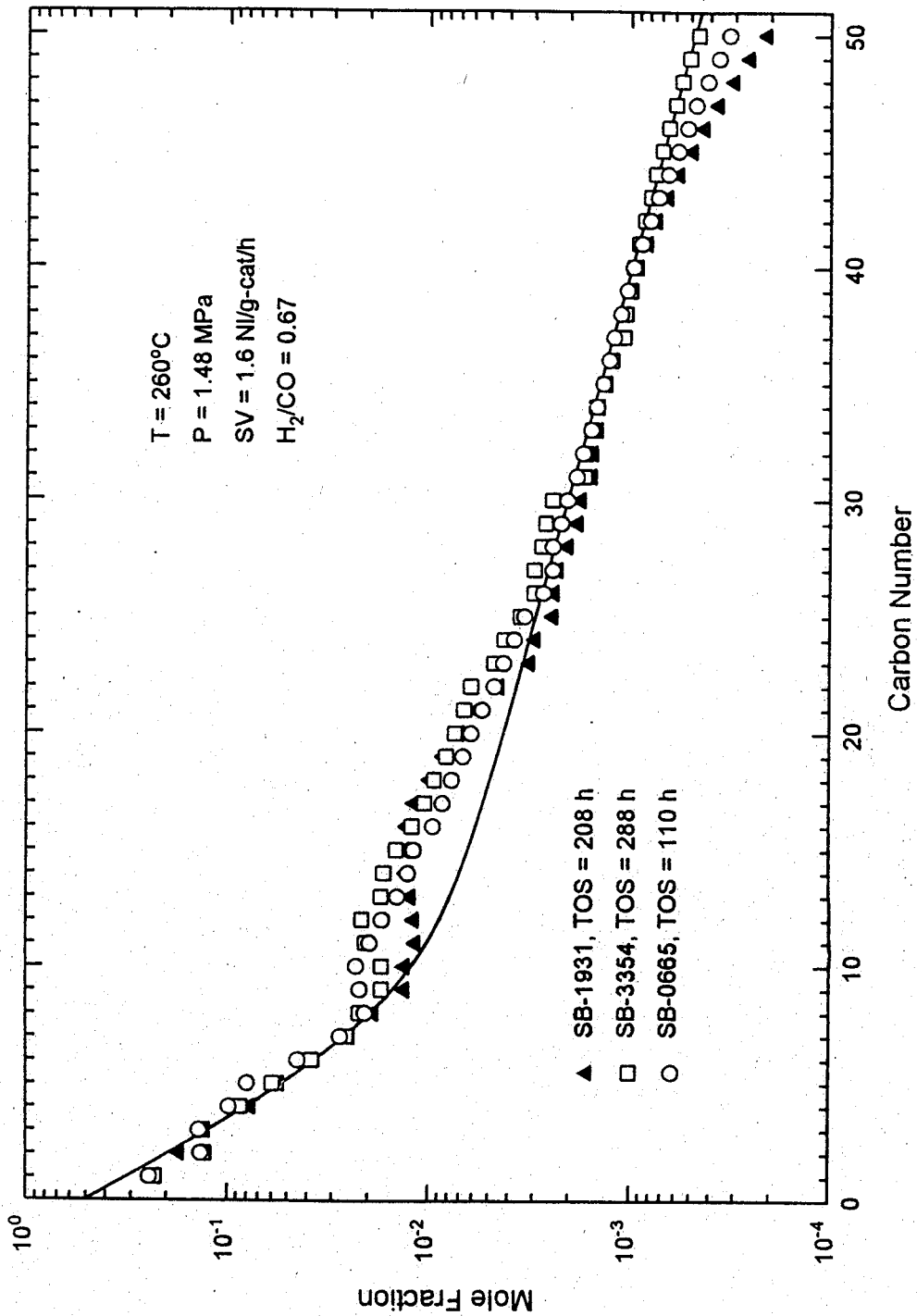[c] Apparent rate constant for a first order reaction in hydrogen

Figure III-2.4 Carbon number product distribution in STSR tests of the 100 Fe/5 Cu/6 K/24 SiO$_2$ catalyst.
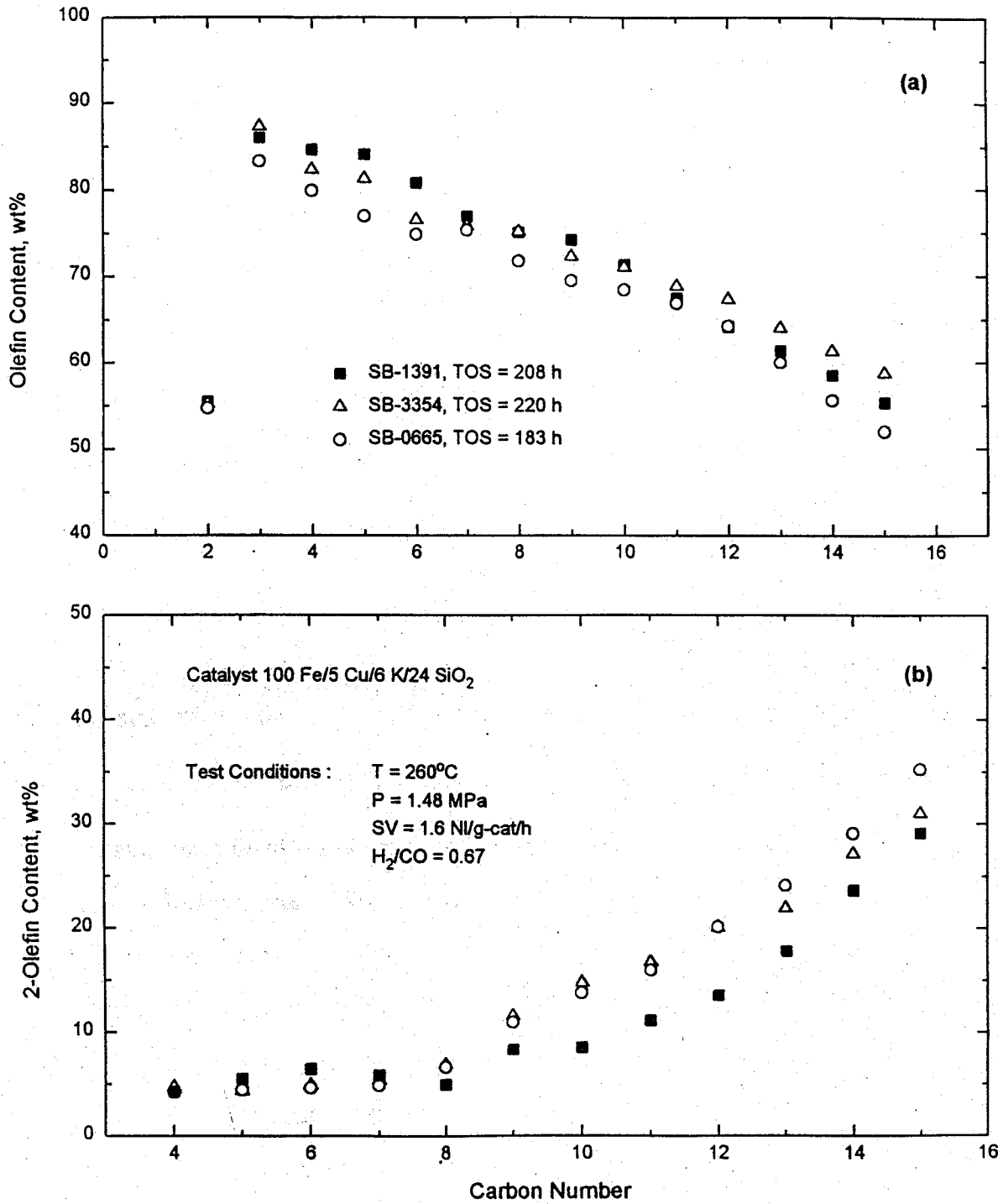
Figure III-2.5 Olefin content (a) and 2-olefin content (b) dependence on carbon number

(100 Fe/5 Cu/6 K/24 SiO$_2$ catalyst).

III-2. 2   Stirred Tank Slurry Reactor Tests of Catalyst C (100 Fe/3 Cu/4 K/16 SiO$_2$)

Two new slurry phase tests were conducted with catalyst C from batch 1. These two runs were carried out in two different reactor systems, run SA-0705 was made in the slurry reactor A and run SB-0045 in the slurry reactor B. The reduction conditions employed in the original test of this catalyst (SB-0261) and in run SA-0705 were the same (H$_2$ at 240°C, 0.8 MPa (100 psig), 7500 cc/min for 2 h). In the test SB-0045 the reduction was carried out at a higher temperature (250°C, instead of 240°C), whereas the remaining conditions were the same. In all three tests the catalyst was tested at: 260°C, 1.48 MPa, 1.4-2.0 Nl/g-cat/h using synthesis gas with molar feed ratio H$_2$/CO = 0.67-0.69. About 7-20 g of catalyst of particle size less than 53 μm (270 mesh) was suspended in the start-up fluid to form a 2.3-7 wt% slurry.

Catalyst Activity and Stability

Changes in (H$_2$+CO) conversion and H$_2$/CO usage ratio with time are shown in Figure III-2.6. During the first 100 hours of testing at the baseline conditions: 260°C, 1.48 MPa, and 1.4 Nl/g-cat/h, the syngas conversions were similar in all three tests. After 100 h, the syngas conversion started to decline in run SB-0261, and reached 76% at 150 h on stream. Between 160 and 240 h on stream the catalyst was tested at 263°C (results not shown), and upon returning to the baseline conditions the conversion was about 67%. After that, the catalyst became stable and the conversion did not change with time. On the other hand, in runs SB-0045 and SA-0705 the catalyst was quite stable up to 250 h, and the syngas conversion was about 81%. After that, in both tests, the reaction pressure and gas space velocity were increased proportionally to 2.17 MPa and 2.05 Nl/g-cat/h, respectively, in order to maintain the constant gas residence time. In both cases, the conversion decreased slightly to about 79%, and in run SA-0705 the syngas conversion decreased from 79 to 75 %
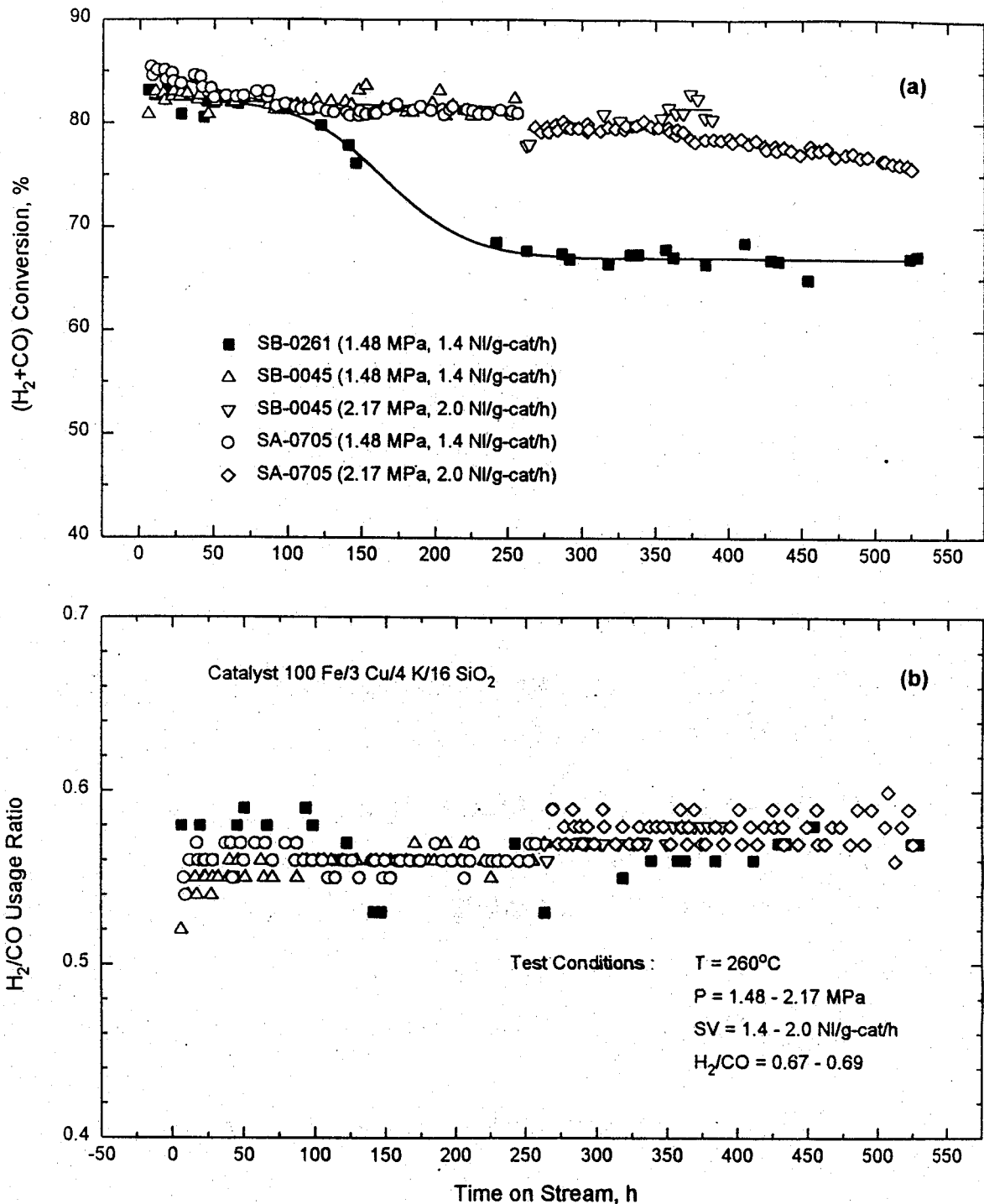
Figure III-2.6 Changes in (a) (H_2+CO) conversion and (b) H_2/CO usage ratio with time and process conditions in STSR tests of the 100 Fe/3 Cu/4 K/16 SiO_2 catalyst.

during the next 260 h of testing at higher reaction pressure. The reactor space-time-yield (STY) increased by about 40% during testing at 2.17 MPa and 2.05 Nl/g-cat/h (Table III-2.2).

Good reproducibility of catalyst activity is also reflected in Figure III-2.7, in which the apparent reaction rate constant in all three tests varied between 250-270 mmol/g-Fe/h/MPa during the initial 100 h on stream. Constant activity and low deactivation rate were observed during the next 150 hours of testing in runs SB-0045 and SA-0705. In the original test (SB-0261), the catalyst began to deactivate after about 100 h on stream. However, it became stable again at about 250 hours (k = 170 mmol/g-Fe/h/MPa).

In the two recent tests (SB-0045 and SA-0705) of catalyst C, the reaction pressure and space velocity were increased to 2.17 MPa and 2.05 Nl/g-cat/h, respectively, at about 250 hours. The apparent rate constant in run SB-0045 remained almost constant (about 255 mmol/g-Fe/h/MPa), whereas in run SA-0705 it decreased from 256 to 240 mmol/g-Fe/h/MPa at 525 hours on stream.

Water gas shift activity in all three tests was high and very reproducible (Figure III-2.6b). The usage ratio was between 0.55 and 0.57 in all three tests.

Hydrocarbon Selectivity and Carbon Number Distribution

Methane and gaseous hydrocarbon selectivities obtained in runs SB-0261 and SB-0045 were similar (Figure III-2.8 and Table III-2.2), whereas slightly higher selectivities of low molecular weight hydrocarbons were obtained in run SA-0705. For example, methane selectivity varied between 2 and 3 mol% in the latter test, whereas in the two tests conducted in the reactor B it was between 1.9 and 2.4 mol%. Also, $C_2 - C_4$ selectivity was between 9.3 - 11.3 wt% (Table III-2.2) in tests conducted in the slurry B system, whereas it was 12.5-14 wt% in the test SA-0705.

Hydrocarbon product distributions for C_5+ products in all three tests were similar (Table III-2.2). For example, the fraction of gasoline range hydrocarbons ($C_5 - C_{11}$) was generally between 11-14 wt%. Numerical values for diesel range hydrocarbons ($C_{12} - C_{18}$)
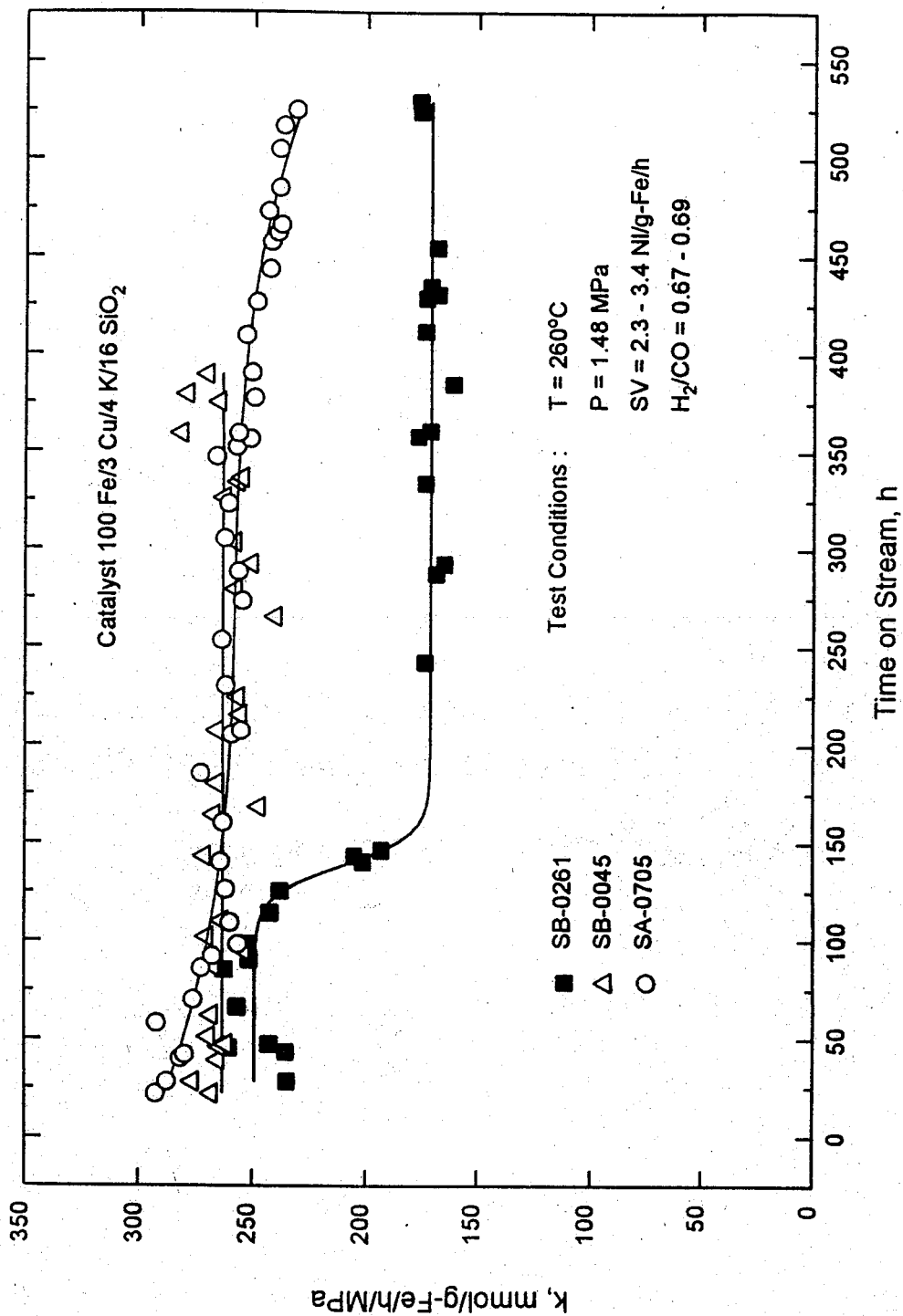
Figure III-2.7   Apparent first order reaction rate constant as a function of time (100 Fe/3 Cu/4 K/16 SiO$_2$ catalyst).
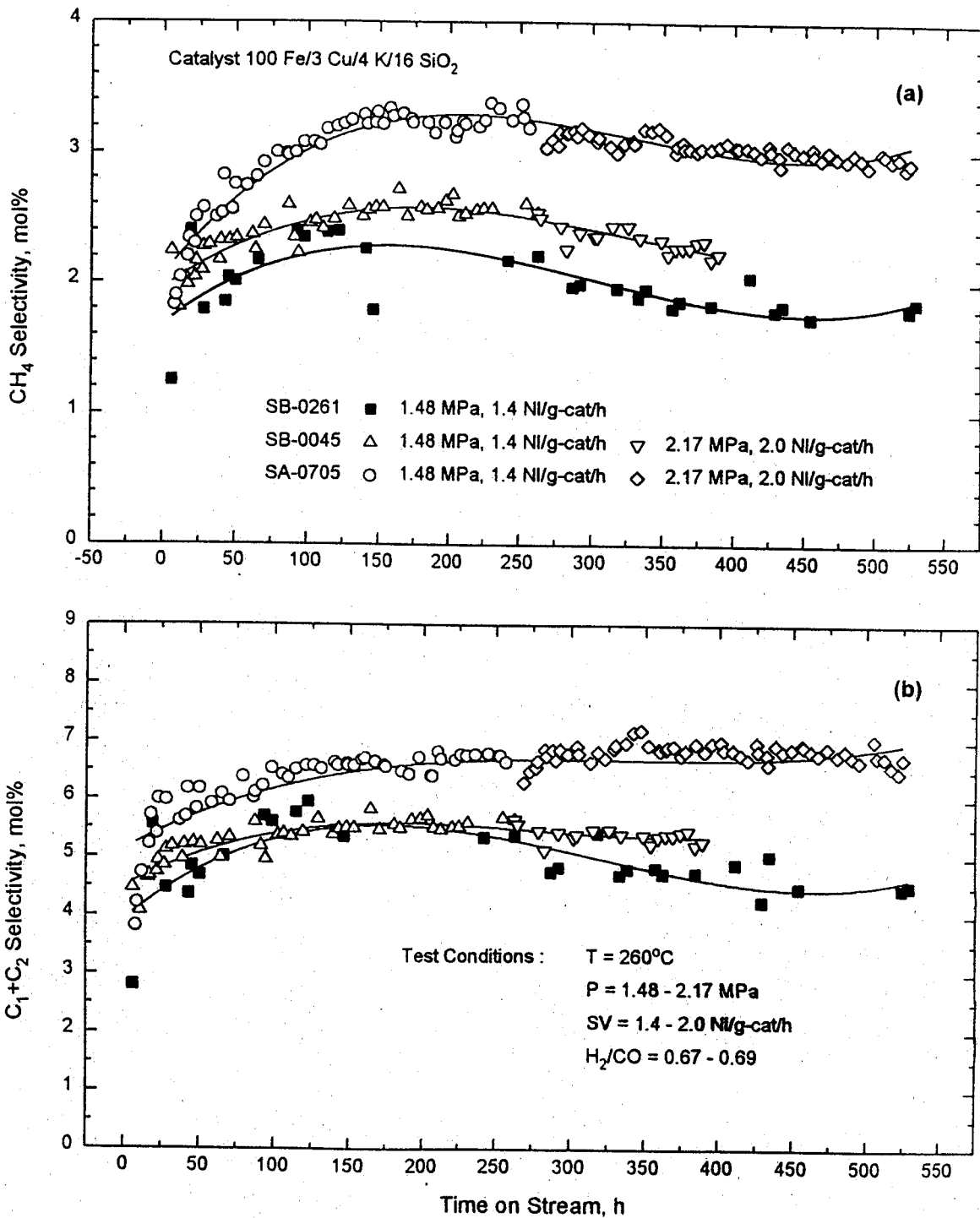
Figure III-2.8 Methane (a) and ($C_1 + C_2$) hydrocarbon selectivity (b) as a function of time

(100 Fe/3 Cu/4 K/16 SiO$_2$).

Table III-2.2 Performance of 100 Fe/3 Cu/4 K/16 SiO_2 (batch-1) Catalyst[a] in Slurry Reactor Tests

Test designation	SB-0261			SB-0045			SA-0705		
Test conditions									
Temperature, °C	260	260	260	260	260	260	260	260	260
Pressure, MPa	1.48	1.48	1.48	1.48	1.48	2.17	1.48	1.48	2.17
Space velocity, Nl/g-cat/h [b]	1.4	1.4	1.4	1.4	1.4	2.0	1.4	1.4	2.0
Feed H_2/CO ratio	0.67	0.67	0.67	0.67	0.67	0.67	0.67	0.67	0.67
Time on stream, h	92	356	523	95	215	336	88	197	364
CO conversion, %	87.4	72.4	72.6	87.1	86.7	85.0	87.5	86.9	83.8
(H_2+CO) conversion, %	81.4	67.4	67.9	81.0	80.8	79.9	81.4	81.1	79.1
STY, mmol (H_2+CO)/g-cat/h [b]	50	42	39	51	51	73	51	51	72
k, mmol/g-Fe/h/MPa [c]	251	165	161	254	256	255	256	255	252
(H_2/CO) usage ratio	0.57	0.56	0.57	0.55	0.56	0.57	0.55	0.56	0.57
$K_p = P_{CO_2} \cdot P_{H_2} / P_{CO} / P_{H_2O}$	24	21	26	41	39	21	36	40	26
% CO converted to CO_2	49.2	48.5	49.4	49.8	49.8	48.5	48.9	48.6	48.5
Hydrocarbon selectivity, wt%									
CH_4	2.7	2.2	2.2	2.7	2.9	2.6	3.5	3.7	3.6
C_2-C_4	11.3	9.7	9.3	10.4	10.4	10.7	12.5	13.0	14.3
C_5-C_{11}	14.0	13.0	8.9	13.2	14.0	14.5	12.3	11.4	12.4
C_{12}-C_{18}	17.9	24.5	20.9	14.8	17.8			18.0	18.2
$C_{12}+$	70.7	75.6	76.2	73.5	72.7	72.3	67.6	71.8	69.7
C_1+C_2	5.2	5.2	4.9	5.7	5.9	5.7	7.1	7.5	7.4
Yield, g/Nm³(H_2+CO) Converted									
Hydrocarbons	196.8	200.8	205.5	197.7	206.9	203.0	203.3	205.8	202.6
Oxygenates	2.2	2.0	1.8	2.5	3.2	3.4	2.6	2.2	2.6
Catalyst productivity, g HC/g-cat/h [b]	0.22	0.19	0.18	0.23	0.24	0.36	0.23	0.24	0.33

[a] Iron content of this catalyst (0.597 g-Fe/g-cat)

[b] Based on unreduced catalyst

[c] Apparent rate constant for a first order reaction in hydrogen

and $C_{19}+$ products were not as reproducible as those for the gasoline range hydrocarbons, but for majority of mass balances the corresponding selectivities were about 18 wt% and 51-55 wt%, respectively.

Typical carbon number distribution obtained in run SB-0045 is shown in Figure III-2.9. Positive deviations from ASF distribution are noted in C_{10} - C_{20} carbon number range. The same type of irregularity was observed in tests with catalyst B (Figure III-2.4). Experimental data were fitted with a three parameter model, and the model prediction is shown as a solid line. The estimated values of parameters are as follows: $\alpha_1 = 0.59$; $\alpha_2 = 0.95$, and $\beta = 0.75$.

Olefin Selectivity

Total olefin and 2-olefin contents as a function of carbon number are shown in Figure III-2.10. Total olefin contents (Figure III-2.10a) were similar in all three runs and small deviations in results may be attributed to experimental errors. Also, 2-olefin contents (Figure III-2.10b) were similar in all three runs up to C_{12}, but significantly higher 2-olefin contents of $C_{13}+$ hydrocarbons were obtained in run SB-0261 than in the other two tests.

Concluding Remarks on Multiple Tests with Catalysts B and C

Three tests were conducted with each of the two catalysts. In the original tests conducted in 1991 (SB-1931 with the catalyst B, and SB-0261 with the catalyst C) n-octacosane was used as the initial medium. In the four tests conducted during the current contract, Ethylflo 164 oil was used as the start-up fluid, due to problems encountered in three initial tests using n-octacosane as the start-up liquid (low activity in all three tests). The effect of reactor set-up (slurry A vs. slurry B reactor system) was investigated in two recent tests with the catalyst C (runs SB-0045 and SA-0705). In general, reproducibility of results in multiple tests of the same catalyst may be regarded as quite satisfactory. The catalyst B (100 Fe/5 Cu/6 K/24 SiO_2) was more stable in the original test (SB-1931) than in the two recent tests (SB-3354 and SB-0665), whereas the opposite trend was observed in tests with
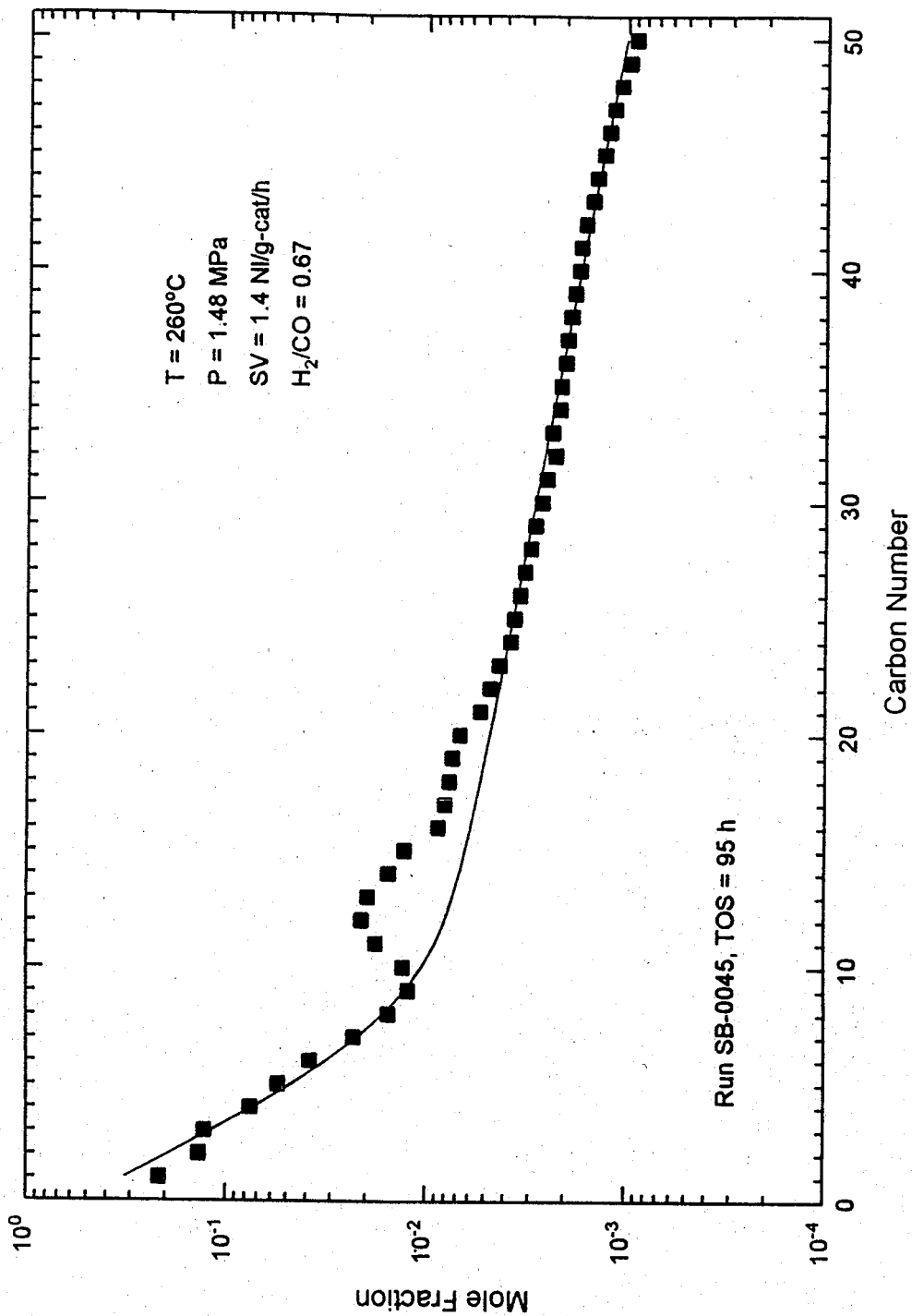
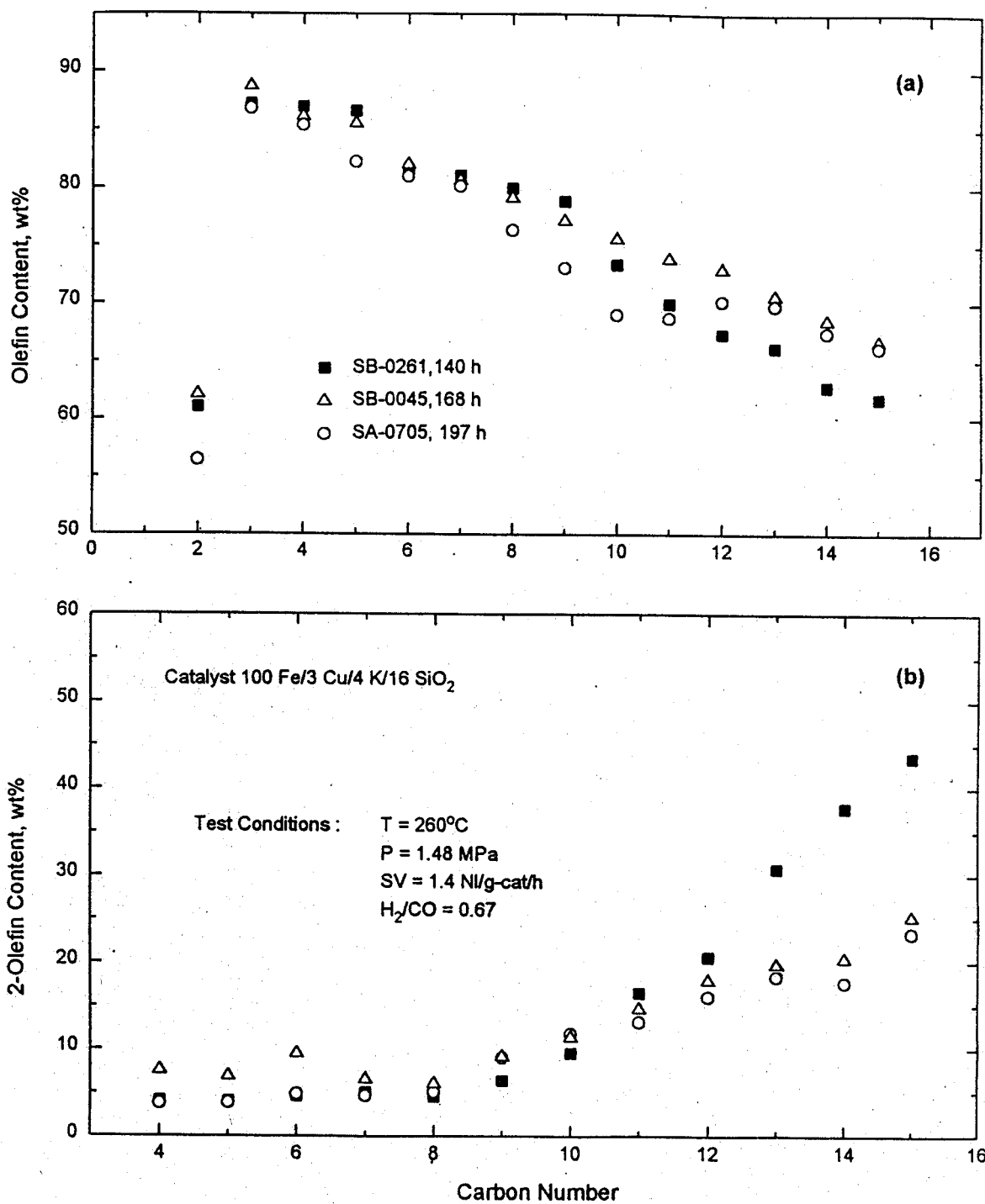Figure III-2.9 Carbon number product distribution in STSR tests of the 100 Fe/3 Cu/4 K/16 SiO$_2$ catalyst.

Figure III-2.10 Olefin content (a) and 2-olefin content (b) dependence on carbon number (100 Fe/3 Cu/4 K/16 SiO₂ catalyst).

the catalyst C (100 Fe/3 Cu/4 K/16 SiO_2). Hydrocarbon product distributions and olefin selectivities in multiple tests with the same catalyst were also reproducible.

Performance of catalysts B and C is comparable to, or exceeds, that obtained in the two most successful bubble column slurry reactor (BCSR) tests conducted by Mobil (Kuo, 1985) and Rheinpreussen (Kölbel et al., 1955). In Mobil's run CT-256-13 at synthesis gas conversion of 82%, methane and $C_1 + C_2$ selectivities were 2.7 and 5.6 wt%, respectively, whereas the catalyst productivity was about 0.26 g HC/g-cat/h (Test conditions: 257°C, 1.48 MPa, 2.3 Nl/g-Fe/h, $H_2/CO = 0.73$). In Rheinpreussen's demonstration plant unit the $C_1 + C_2$ selectivity was 6.8% at the synthesis gas conversion of 89%, and the catalyst productivity was about 0.33 g HC/g-cat/h (Test conditions: 268°C, 1.48 MPa, 3.1 Nl/g-Fe/h, $H_2/CO = 0.67$).

In run SB-3354 with catalyst B (TOS = 97 h) the following results were obtained at 260°C, 1.48 MPa, 3.2 Nl/g-Fe/h, $H_2/CO = 0.67$: Methane and $C_1 + C_2$ selectivities were 3.2 and 5.3 wt%, respectively, and the catalyst productivity was 0.26 g HC/g-cat/h at the synthesis gas conversion of 71.5%. The catalyst performance in the original test of the catalyst B (run SB-1931) was even better (see Table III-2.1), i. e. higher activity and lower methane and gaseous hydrocarbon selectivities were obtained.

The performance of catalyst C in run SB-0045 is illustrated in Table III-2.1. For example, at the reaction pressure of 1.48 MPa and 215 hours on stream, its performance was very similar to that obtained in Mobil's run CT-256-13. However, the performance of catalyst C was better at reaction pressure of 2.17 MPa and gas space velocity of 3.4 Nl/g-Fe/h (TOS = 336 h). Methane and $C_1 + C_2$ selectivities were 2.6 and 5.4 wt%, respectively, and the catalyst productivity was 0.36 g HC/g-cat/h at the synthesis gas conversion of about 80%.

III-3   References

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