VI   Pretreatment Effect Research

Studies at PETC (Pennline et al., 1987; Zarochak and McDonald, 1986, 1987) and in our laboratory with several precipitated iron catalysts (Bukur et al., 1989; 1995a-d; 1996) have shown that pretreatment procedure may have a marked effect on subsequent catalyst performance during Fischer-Tropsch synthesis in fixed bed and slurry bed reactors. Pretreatment conditions (nature of reductant, temperature, duration and gas flow rate) can be used to alter catalyst activity, hydrocarbon products selectivities and/or to provide a long term stability. The knowledge acquired during these studies was utilized to select the baseline pretreatment conditions in the STSR tests of catalysts B and C. However, the pretreatment conditions chosen were not necessarily the optimal ones. Further improvements in the catalyst performance could be potentially achieved through the use of a better pretreatment procedure.

The effect of different pretreatment procedures on the performance of catalyst C (100 Fe/3 Cu/4 K/16 SiO$_2$, batch-4) was studied in a STSR, and results from these tests are described in Section VI-2. In addition to STSR tests, the reduction behavior of catalysts B (100 Fe/5 Cu/6 K/24 SiO$_2$, batch-3) and C was studied by thermogravimetric analysis (TGA). Iron phases in the pretreated catalysts and catalysts withdrawn from slurry reactor tests were determined by XRD and Mössbauer effect spectroscopy (Section VI-1)

VI-1   Catalyst Characterization Studies

In order to simulate the actual pretreatment conditions followed in Fischer-Tropsch synthesis, isothermal reduction/or pretreatment experiments were conducted with catalysts B, C and Ruhrchemie (100 Fe/5 Cu/4.2 K/25 SiO$_2$). After each isothermal pretreatment the catalysts were passivated (see Appendix 2) and characterized by XRD, and in some cases their surface areas were determined by single point BET measurements (Micromeritics Pulse Chemisorb 2705 unit). Iron phases in pretreated and used catalysts from slurry reactor tests were determined by XRD and Mössbauer effect spectroscopy (MES).

Surface Areas and XRD Analysis of Pretreated Catalysts

Table VI-1.1 summarizes results from surface area and XRD analysis measurements of pretreated and passivated catalysts C and B. The high surface area (~ 290 m^2/g) of calcined catalysts C or B is reduced to 50-115 m^2/g when they are subjected to different reducing gases such as H_2, CO or syngas. The loss in surface area is due to the collapse of pore structure during iron oxide reduction to metallic iron or to iron carbides.

Metallic iron (α-Fe) was the only crystalline phase found in hydrogen reduced catalysts B, C and Ruhrchemie (reductions at 240°C to 280°C for 8 h). Catalyst B reduced in hydrogen first at 250°C for 4 h (baseline reduction procedure), and then exposed to syngas at 260°C (H_2/CO = 0.67) for 4 h, contains ϵ'-Fe$_{2.2}$C. This phase was also found in the catalyst C reduced in hydrogen first at 240°C for 2 h (baseline reduction procedure), and then exposed to syngas at 260°C (H_2/CO = 0.67) for 6 h. These two pretreatments simulate pretreatment conditions employed in slurry reactors, followed by F-T synthesis at 260°C (baseline reaction temperature in slurry reactor tests). Results show that ϵ'-Fe$_{2.2}$C phase is formed rapidly under these conditions. On the other hand, when the catalysts B and C are exposed to syngas directly at 260°C (or at 280°C) for 8 h, the χ-carbide (χ-Fe$_5$C$_2$) phase is formed instead (Table VI-1.1).

After the pretreatment of catalysts B and C with CO or syngas (H_2/CO = 0.67) at either 260°C or 280°C for 8 hours the χ-Fe$_5$C$_2$ phase was the only phase detected by XRD.

TGA Measurement Results

In isothermal reductions conducted in the TGA unit, the catalyst sample was purged with helium (40 ml/min) and the temperature was ramped at a rate of 5°C/min from room temperature to a desired pretreatment temperature. Then the helium flow was switched to reductant gas (hydrogen, carbon monoxide or synthesis gas with H_2:CO molar ratio of 2:3) and the temperature was maintained constant for a fixed period of time (up to 8 h). The degree

VI-2

Table VI-1.1   BET Surface Area and XRD Measurement Results of Reduced and Passivated Samples of Catalyst C (100 Fe/3 Cu/4 K/16 SiO$_2$, batch-4) and Catalyst B (100 Fe/5 Cu/6 K/24 SiO$_2$, batch-3)*

Catalyst Id	Reduction Conditions	Single-Point BET** Surface Area, m^2/g	Iron Phases found in the Reduced and Passivated Samples			
			α-Fe	Fe$_3$O$_4$	ε'-Fe$_{2.2}$C	χ-Fe$_5$C$_2$
100 Fe/3 Cu/4 K/16 SiO$_2$	H$_2$, 240°C for 8 h	-	+			
100 Fe/3 Cu/4 K/16 SiO$_2$	H$_2$, 250°C for 8 h	116	+			
100 Fe/5 Cu/6 K/24 SiO$_2$	H$_2$, 250°C for 8 h	109	+			
Ruhrchemie catalyst	H$_2$, 280°C for 8 h	-	+			
100 Fe/3 Cu/4 K/16 SiO$_2$	H$_2$, 240°C for 2 h, then syngas, 260°C for 6h	-			+	
100 Fe/5 Cu/6 K/24 SiO$_2$	H$_2$, 250°C for 4 h, then in syngas at 260°C for 4 h	-			+	
100 Fe/3 Cu/4 K/16 SiO$_2$	syngas, 280°C for 8 h	53				+
100 Fe/5 Cu/6 K/24 SiO$_2$	syngas, 280°C for 8 h	83				+
100 Fe/3 Cu/4 K/16 SiO$_2$	syngas, 260°C for 8 h	-				+
100 Fe/5 Cu/6 K/24 SiO$_2$	syngas, 260°C for 8 h	-				+
100 Fe/3 Cu/4 K/16 SiO$_2$	CO, 250°C for 8 h	-				+
100 Fe/5 Cu/6 K/24 SiO$_2$	CO, 250°C for 8 h	-				+
100 Fe/3 Cu/4 K/16 SiO$_2$	CO, 280°C for 8 h	-				+
100 Fe/5 Cu/6 K/24 SiO$_2$	CO, 280°C for 8 h	82				+

*   Passivated under controlled conditions at room temperature.
**   Degassed the samples at 200°C for 1.5 h prior to the N$_2$ adsorption measurements.

of reduction was calculated from experimental weight loss vs. time data, and the theoretical weight loss based on the known composition and mass of a sample.

Figure VI-1.1 shows the effect of reduction temperature (240 to 280°C) on the reduction behavior of catalyst C in the TGA unit in pure hydrogen under isothermal conditions. The degree of reduction of catalyst C at 240 and 250°C in hydrogen increased gradually with time and after 8 hours was about 60%. During reduction at 280°C the degree of reduction increased rapidly during the first 100 minutes of hydrogen exposure and then leveled off with further exposure to hydrogen. The degree of reduction was about 65% after the first 100 minutes of reduction period, and about 80% at the end of reduction period (after ~450 minutes in hydrogen). These results show that the reduction of iron catalysts increases with the increase of reduction temperature. Even though these results indicate that the reduction is not complete, the XRD analysis of passivated samples revealed only the presence of metallic iron.

Figure VI-1.2 shows the effect of reduction temperature (250 and 280°C) on the reduction behavior of catalyst B (100 Fe/5 Cu/6 K/24 SiO_2, batch-3) in hydrogen. As expected the final degree of reduction is higher at higher reduction temperature (80% at 280°C vs. 60% at 250°C). From Figures VI-1.1 and VI-1.2 it appears that the reduction behavior of catalysts C and B is similar at both reduction temperatures of 250°C and 280°C. However, the reduction behavior of the Ruhrchemie catalyst at 280°C is similar to that of catalyst B or C reduced at 250°C. Apparently, the catalysts B and C (synthesized in our laboratory) are easier to reduce than the Ruhrchemie catalyst.

Figure VI-1.3 illustrates the effect of temperature (250 and 280°C) on the weight changes of catalyst C during CO pretreatment. Note that the catalyst had lost about 3-4% of initial sample weight during the heating in helium (from room temperature to a reduction temperature) due to removal of adsorbed moisture. The weight loss is rapid during the first 100 minutes of exposure to CO. The resulting weight loss may be due to three different reactions occurring simultaneously on the catalyst surface/or in the bulk. The possible reactions are reduction of iron oxide to metallic iron or magnetite, carbon deposition (via
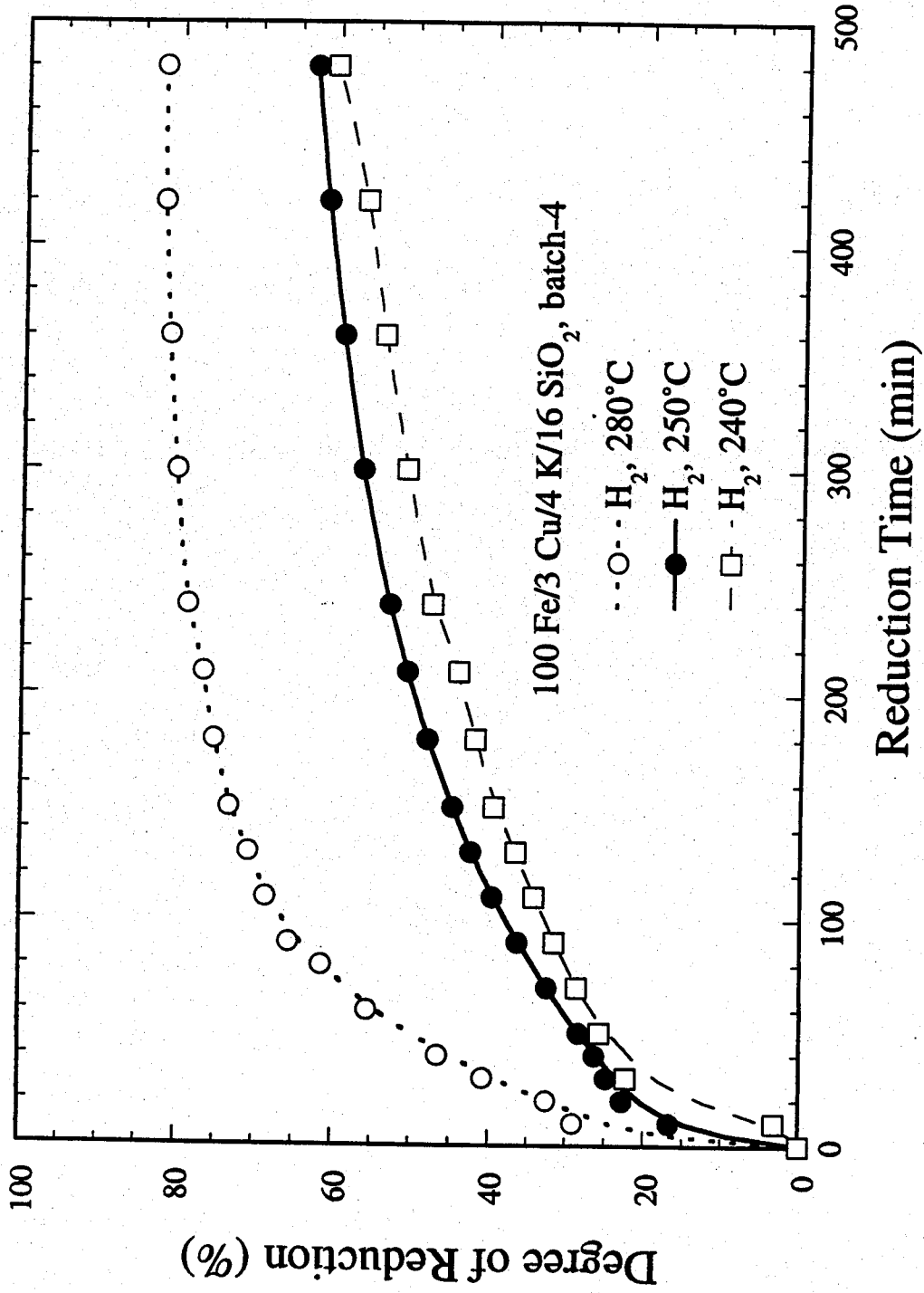
VI-4

Figure VI-1.1   Effect of reduction temperature on the reduction behavior of catalyst C (100 Fe/3 Cu/4 K/16 SiO$_2$, batch-4) in hydrogen under isothermal conditions in TGA apparatus.
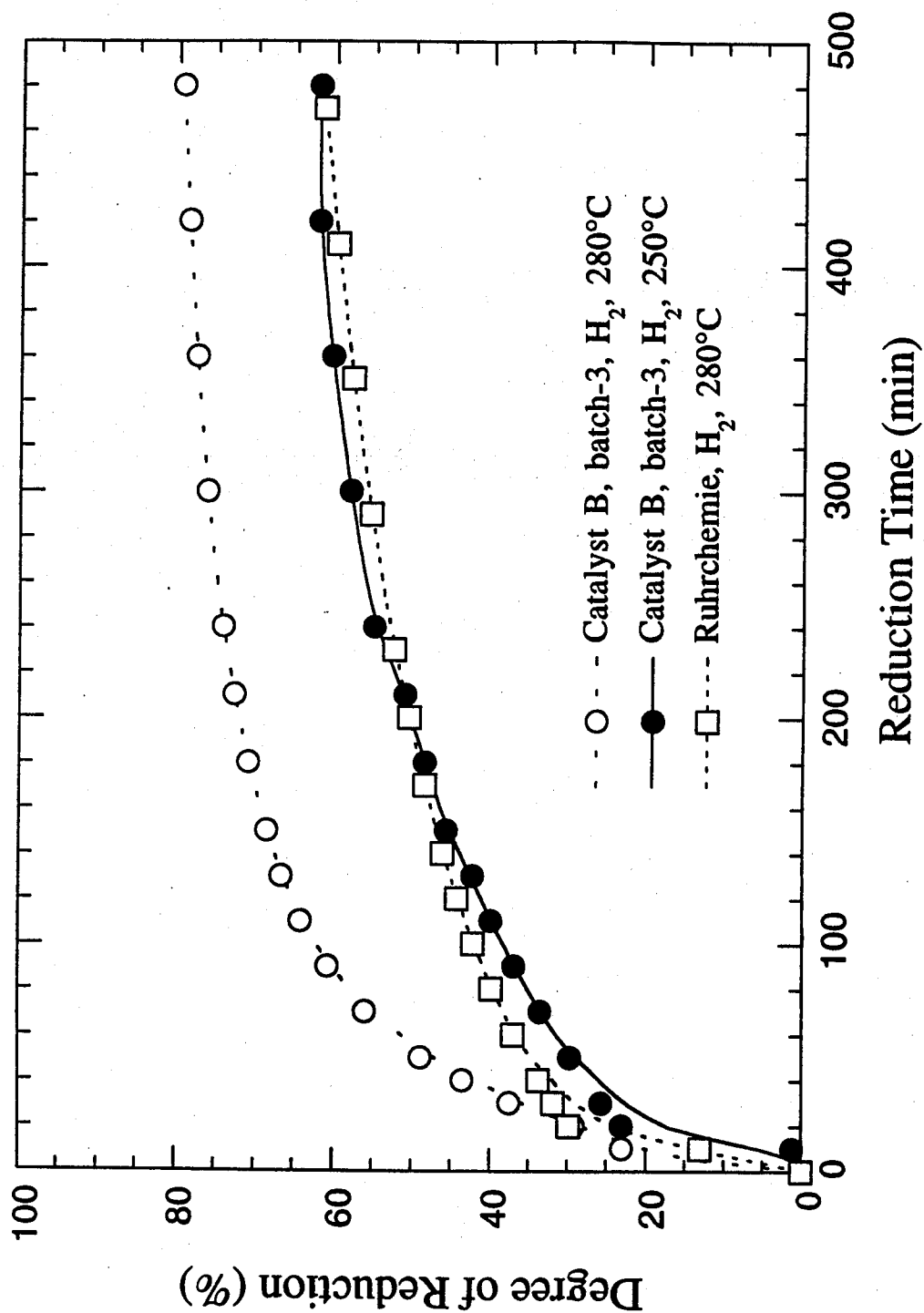
Figure VI-1.2   Effect of reduction temperature on the reduction behavior of catalyst B(100 Fe/5 Cu/6 K/24 SiO$_2$, batch-3) and the Ruhrchemie catalyst in hydrogen under isothermal conditions in TGA apparatus.
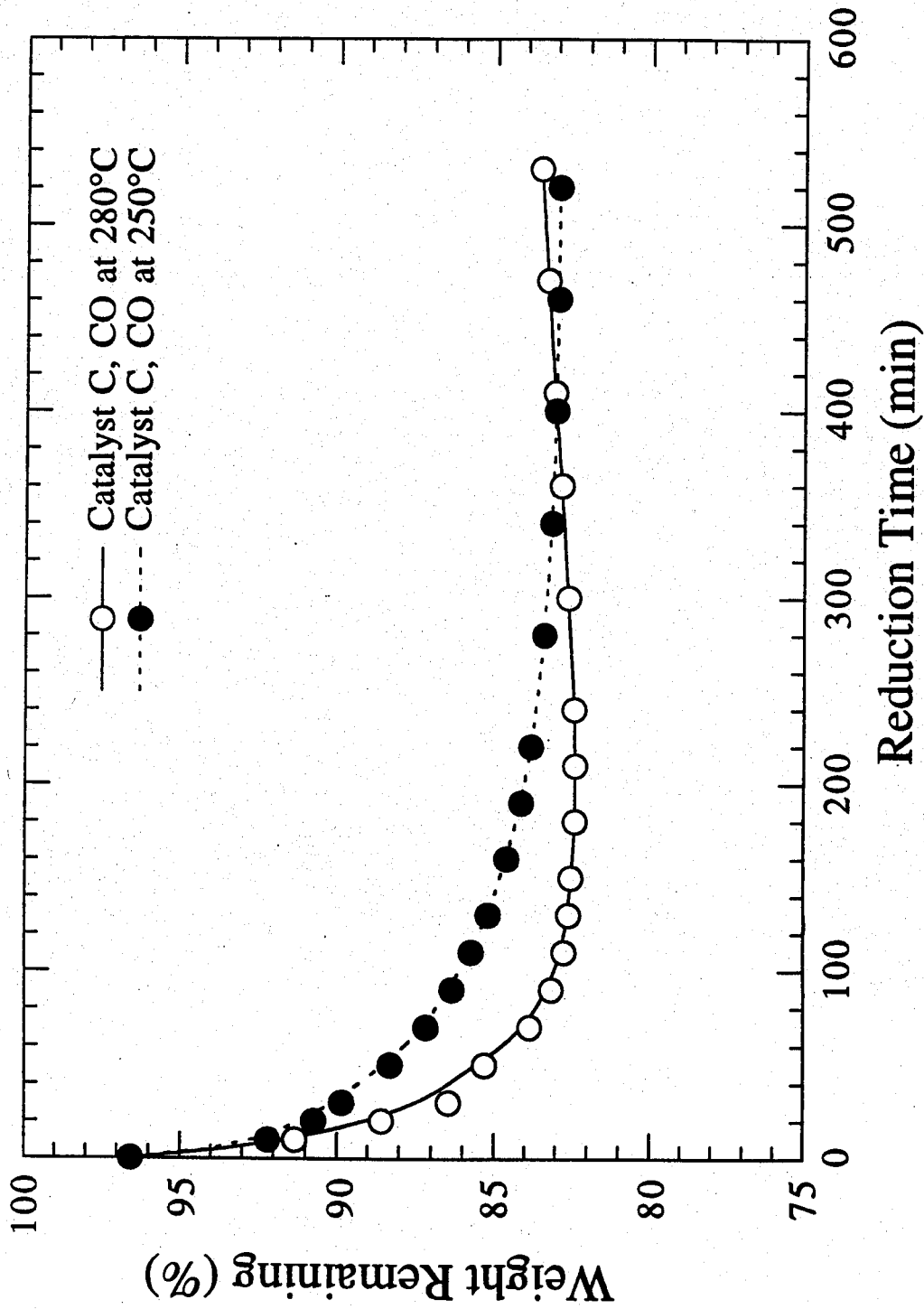
Figure VI-1.3   Effect of reduction temperature on the reduction behavior and weight changes of catalyst C (100 Fe/3 Cu/4 K/16 SiO$_2$, batch-4) in CO under isothermal conditions in TGA apparatus.

Boudoudart reaction: $2 CO \rightarrow CO_2 + CO$); and carbide formation (i.e. carburization). Theoretical weight loss for the total conversion of iron oxide (Fe_2O_3) to: (a) metallic iron is about 25%; (b) χ-Fe_5C_2 is about 20%; and about 3.3% for the formation of magnetite ($Fe_2O_3 \rightarrow$ Fe_3O_4). The observed weight loss (>13%) at 280°C suggests that the reduction and carburization processes are predominant during the first 100 minutes of CO exposure. During the later stages of CO exposure the catalyst weight decreased slowly up to about 200 minutes, and then started to increase with time, which indicates that all three reactions (reduction, carbon deposition and carbide formation) are occurring simultaneously. The observed increase in weight (after ~200 minutes) suggests that the carbon deposition became the dominant reaction, even though the carbide formation and reduction processes were incomplete. The loss of weight during the CO pretreatment at 250°C was more gradual, and it has continued until the end of the reduction period.

Both catalyst B and Ruhrchemie catalyst lost weight rapidly during the initial periods of CO exposure at 280°C (Figure VI-1.4). The weight loss during the first 100 minutes of CO exposure was about 12% for both the catalysts, and the reduction behavior with time was similar with both catalysts. After that, both catalysts started to gain weight slowly with time due to the dominance of carbon deposition reaction. The continued weight loss of catalyst B during the CO pretreatment at 250°C suggests that the reduction of iron oxide and the carbide formation are incomplete (since both reactions are associated with the weight loss).

Changes in weight of catalysts B and C during pretreatments with synthesis gas ($H_2/CO = 0.67$) at 260°C and 280°C are shown in Figure VI-1.5. Both catalysts had lost about 3-4% of the initial sample weight during heating in He flow from room temperature to the pretreatment temperature, due to removal of adsorbed moisture. The weight loss (7-13%) was rapid during the first 100 minutes of exposure to the syngas, suggesting that oxide reduction and carburization reactions are predominant and incomplete. During the later stages of syngas exposure the catalyst weight did not change rapidly, which is an indication that all three
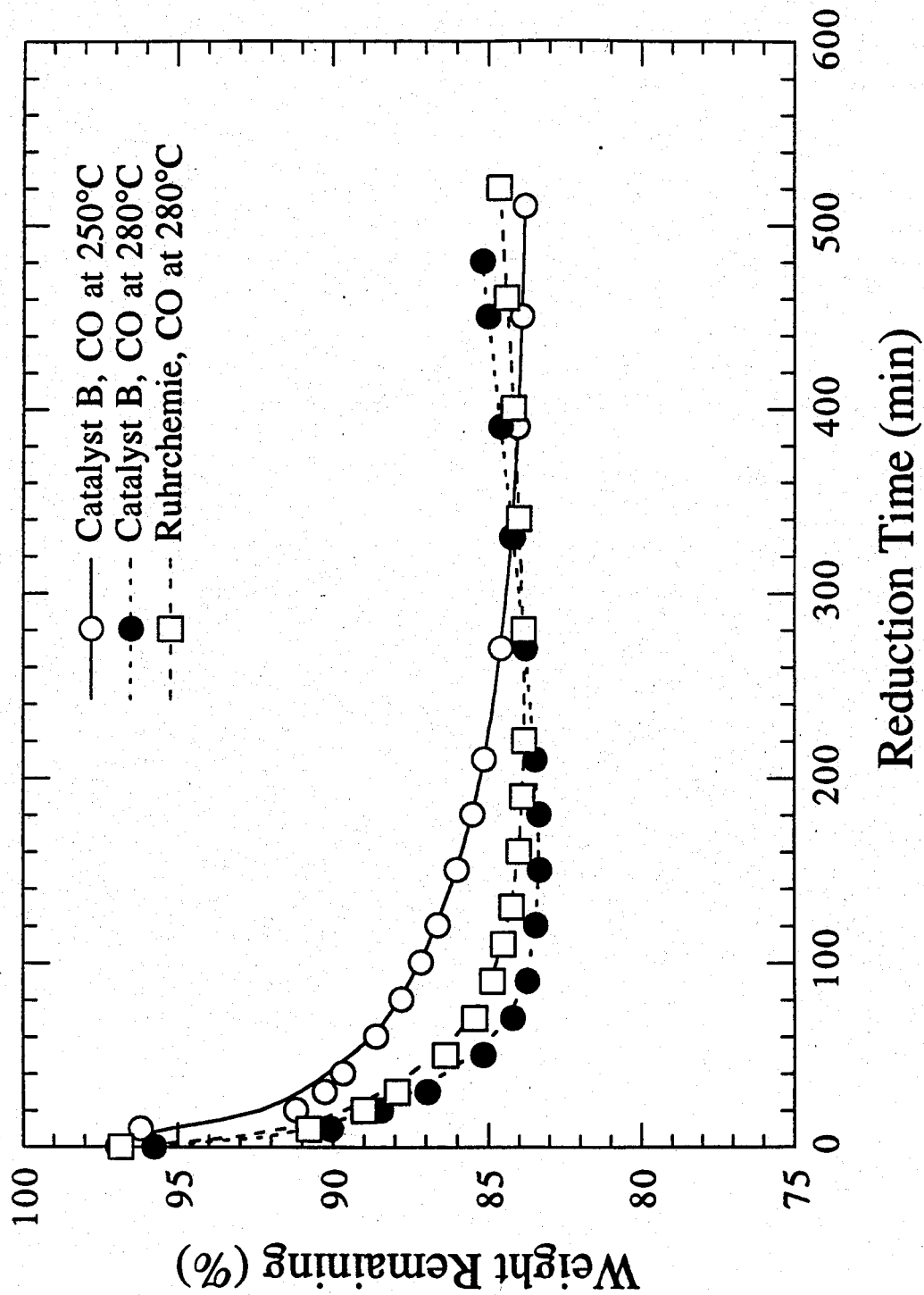
Figure VI-1.4   Effect of reduction temperature on the reduction behavior and weight changes of catalyst B (100 Fe/5 Cu/6 K/24 SiO$_2$, batch-3) and the Ruhrchemie catalyst in CO under isothermal conditions in TGA apparatus.
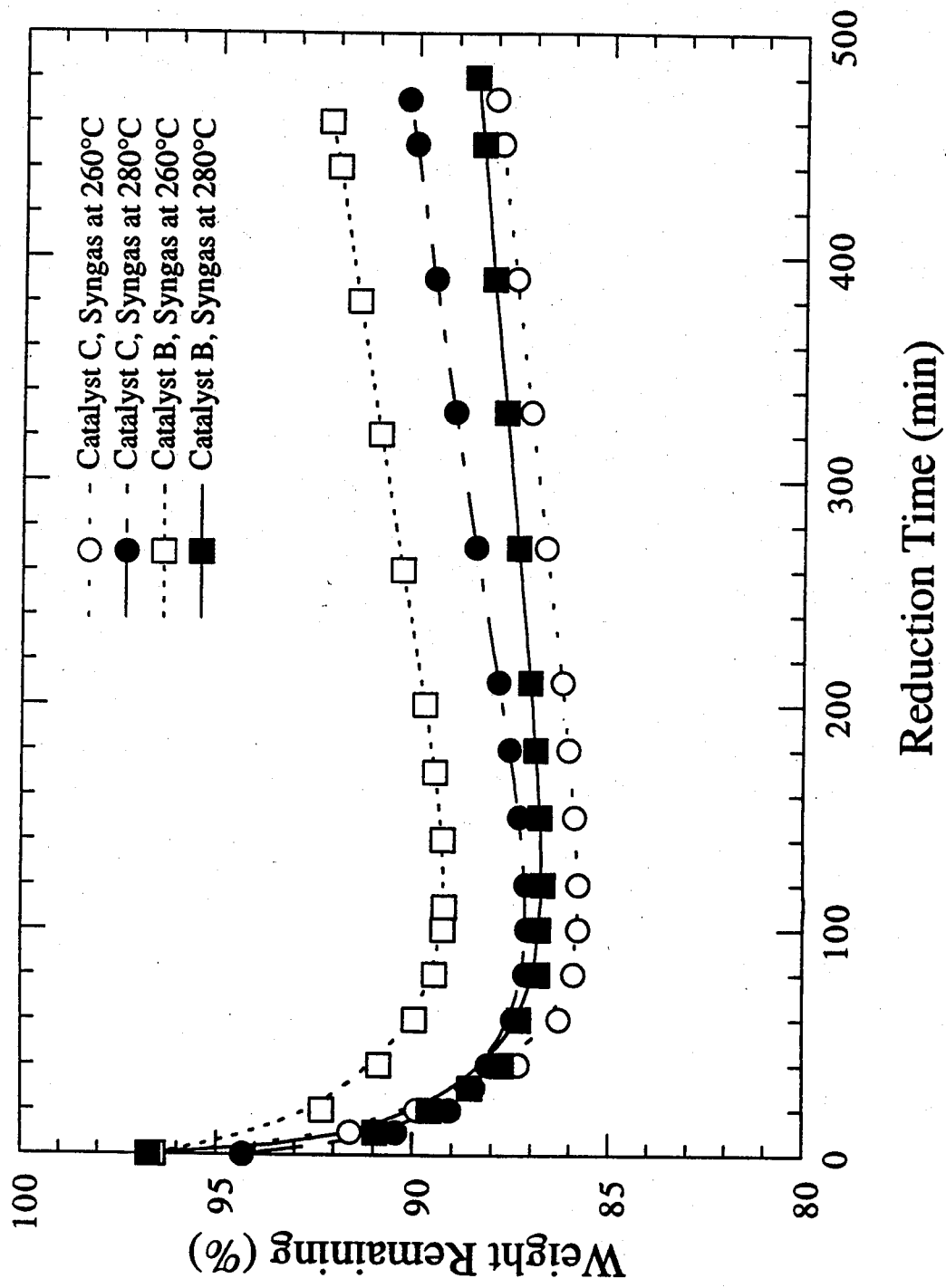
Figure VI-1.5   Comparison of reduction behavior and weight changes of catalyst C (100 Fe/3 Cu/4 K/16 SiO$_2$, batch-4) and catalyst B (100 Fe/5 Cu/6 K/24 SiO$_2$, batch-3) in syngas (H$_2$/CO = 0.67) under isothermal conditions in TGA apparatus.

reactions (reduction of iron oxides; carbon deposition and carbide formation) were occurring simultaneously. However, a gradual increase in weight was observed in all the cases, and this suggests that carbon deposition became the dominant reaction, even though the carbide formation and iron oxide reduction were incomplete.

Figure VI-1.6 illustrates the weight loss behavior of catalysts B and C exposed first to hydrogen (at 250°C for 4 h - catalyst B; or at 240°C for 2 h - catalyst C), and then to syngas ($H_2/CO = 0.67$) at 260°C. These two pretreatments simulate pretreatment conditions employed in slurry reactors (reduction in hydrogen), followed by F-T synthesis at 260°C. Again, the initial weight loss of about 3%, is due to loss of moisture during heating in helium from room temperature to the reduction temperature. During the reduction in hydrogen, the weight loss was very rapid during the first 20 minutes, and then continued to increase gradually reaching approximately 10% (catalyst C at 120 minutes) and 13% (catalyst B at 240 minutes). Theoretical weight losses for reduction of Fe_2O_3 to Fe_3O_4, and Fe, are approximately 3.3% and 22%, respectively. Experimental weight losses at the end of hydrogen reduction imply that both catalysts, at this reduction stage, were not completely reduced to metallic iron. Upon the catalysts exposure to syngas, the weight remaining of catalyst B began to increase rapidly (about 2.5% in 100 minutes), and then more slowly, while the catalyst C continued to loose weight initially (about 1% in 100 minutes), but eventually its weight also started to increase slowly with time. The sharp increase in weight remaining of the catalyst B after exposure to syngas suggests that carburization and carbon deposition were the predominant reactions. In the case of catalyst C, reduction of magnetite was the dominant reaction during the first 100 minutes in syngas, whereas the carbide formation and the carbon deposition were dominant reactions afterwards.

Iron Phases in Pretreated and Used Catalyst C from Slurry Reactor Tests

XRD and MES results of pretreated and used catalyst C (batch-4) samples from stirred tank slurry reactor in tests are summarized in Table VI-1.2 and Figures VI-1.7 to VI-1.9.
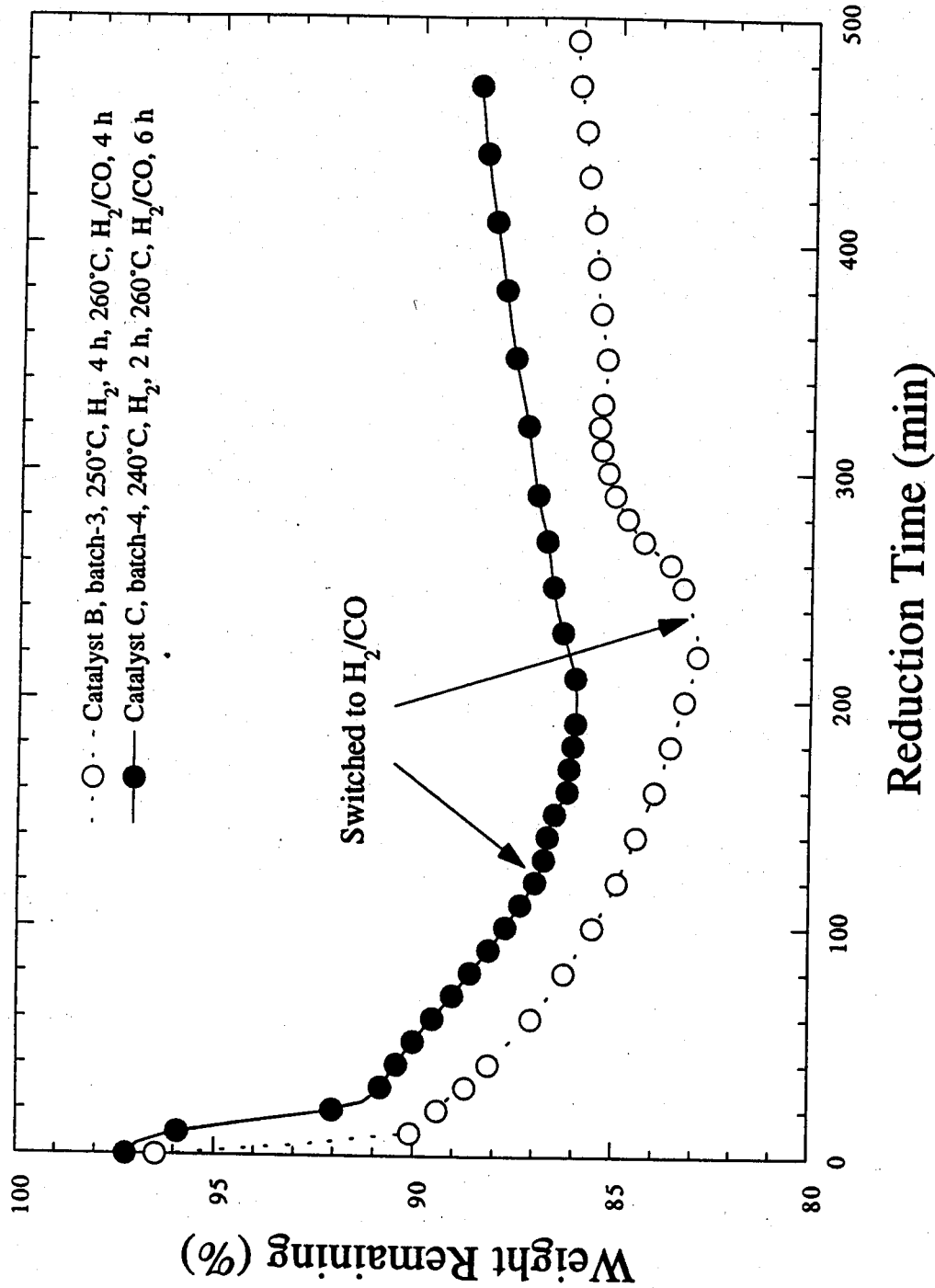
Figure VI-1.6 Reduction behavior and weight changes of catalysts B and C in TGA unit Reduction conditions: catalyst B in H_2 at 250°C for 4 h then switched to syngas at 260°C; catalyst C in H_2 at 240°C for 2 h then switched to syngas at 260°C for 6 h.

Iron phases, determined by XRD, after hydrogen reductions at different temperatures and durations are shown in Figure VI-1.7. After the reduction at 240°C for 2 hours (run SB-2145) the catalyst was reduced to magnetite (Fe_3O_4) (Figure VI-1.7A). After the reductions at 250°C for 4 hours (SB-3425), and at 280°C for 8 hours (SA-0376) both magnetite and metallic iron were found in the reduced sample (Figures VI-1.7B and VI-1.7C). MES results in Table VI-1.2 indicate that the extent of reduction increases with increase in the reduction temperature and duration.

Figure VI-1.8 illustrates XRD patterns of catalyst C withdrawn from the reactor immediately after different pretreatments (TOS = 0 h). The catalyst C which was not pretreated (run SB-2486) does not have crystallinity (amorphous XRD pattern). The catalyst pretreated in CO at 280°C for 8 hours (SA-0946) contains χ-carbide (Fe_5C_2) and magnetite, whereas the syngas pretreated catalyst (at 280°C for 8 hours) contains magnetite, ε'-carbide ($Fe_{2.2}C$) and possibly χ-carbide (SA-1626).

Figures VI-1.9 illustrate the changes of bulk iron phases with time on stream (TOS) with catalyst C (after different pretreatments) from different slurry tests. During F-T synthesis in run SB-2486 both magnetite and ε'-carbide were found in samples withdrawn from the reactor between TOS = 51 and 315 hours (Figure VI-1.9a). During this time period the catalyst activity decreased with time-on-stream (Section VI-2 of the report).

During run SB-3425 (hydrogen reduction at 250°C for 4 hours) both magnetite (Fe_3O_4) and ε'-carbide ($Fe_{2.2}C$) were found in samples withdrawn from the reactor (Figure VI-1.9B, TOS = 111 to 384 h). The MES results of these samples show that the fraction ε'-$Fe_{2.2}C$ phase increased from 37 to 48%, while the fraction of superparamagnetic iron phase(s) (Spm) decreased from 63 to 41% between 111 and 384 h on stream. At 384 on stream magnetite was also detected by MES analysis. Catalyst activity decreased with time during this test, even though the fraction of iron carbide increased with time.

VI-13

Table VI-1.2   X-ray Diffraction and MES Results of Pretreated and Used Samples (Catalyst C:100 Fe/3 Cu/4 K/16 SiO_2, batch-4)

Run Number	Pretreatment Conditions	Time on Stream (TOS), h	Phases Identified by Mössbauer	Phases Identified by XRD
SB-2145	H_2, 240°C, 2 h	0	69 (Spm), and 31% (Fe_3O_4)	Fe_3O_4
		67	48 (Spm), 24% (Fe_3O_4), 14% (ϵ'-$Fe_{22}C$) and 14% (Fe_5C_2)	Fe_3O_4, and ϵ'-$Fe_{22}C$
		145	63 (Spm) and 37% (ϵ'-$Fe_{22}C$)	Fe_3O_4, and ϵ'-$Fe_{22}C$
		213	65 (Spm) and 35% (ϵ'-$Fe_{22}C$)	Fe_3O_4, and ϵ'-$Fe_{22}C$
		401	55 (Spm) and 45% (ϵ'-$Fe_{22}C$)	Fe_3O_4, and ϵ'-$Fe_{22}C$
		402 (EOR)	54 (Spm), 3% (Fe_3O_4), 39% (ϵ'-$Fe_{22}C$) and 4% (Fe_5C_2)	Fe_3O_4, and ϵ'-$Fe_{22}C$
SB-3425	H_2, 250°C, 4 h	0	76%(Spm) and 22% (α-Fe)	Fe_3O_4, and α-Fe
		111	63% (Spm) and 37% (ϵ'-$Fe_{22}C$)	Fe_3O_4, and ϵ'-$Fe_{22}C$
		233	52% (Spm) and 48% (ϵ'-$Fe_{22}C$)	Fe_3O_4, and ϵ'-$Fe_{22}C$
		330	53% (Spm) and 47% (ϵ'-$Fe_{22}C$)	Fe_3O_4, and ϵ'-$Fe_{22}C$
		384	41% (Spm), 11%(Fe_3O_4) and 48% (ϵ'-$Fe_{22}C$)	Fe_3O_4, and ϵ'-$Fe_{22}C$
SA-0376	H_2, 280°C, 8 h	0	69%(Spm) and 31% (α-Fe)	Fe_3O_4, and α-Fe ϵ'-$Fe_{22}C$
		134	48% (Spm), 42% (ϵ'-$Fe_{22}C$) and 10% (Fe_5C_2)	
		230	54% (Spm), 25% (ϵ'-$Fe_{22}C$) and 21% (Fe_5C_2)	Fe_3O_4, and ϵ'-$Fe_{22}C$
		350	34% (Spm), 7% (Fe_3O_4), 50% (ϵ'-$Fe_{22}C$) and 9% (Fe_5C_2)	Fe_3O_4, and ϵ'-$Fe_{22}C$
SB-2486	No Pretreatment	0		-
		51		Fe_3O_4, and ϵ'-$Fe_{22}C$
		100		Fe_3O_4, and ϵ'-$Fe_{22}C$
		147		Fe_3O_4, and ϵ'-$Fe_{22}C$
		260		Fe_3O_4, and ϵ'-$Fe_{22}C$
		315		Fe_3O_4, and ϵ'-$Fe_{22}C$
SA-0946	CO, 280°C, 8 h	0	58% (Spm) and 42% (Fe_5C_2)	Fe_3O_4, and Fe_5C_2
		113	54% (Spm) and 46% (Fe_5C_2)	Fe_3O_4, and Fe_5C_2
		229	55% (Spm) and 45% (Fe_5C_2)	Fe_3O_4, and Fe_5C_2
		354	45% (Spm) and 55% (Fe_5C_2)	Fe_3O_4, and Fe_5C_2
		427	41% (Spm) and 59% (Fe_5C_2)	Fe_3O_4, and Fe_5C_2
		563	37% (Spm), 24% (Fe_3O_4), 27% (ϵ'-$Fe_{22}C$) and 12% (Fe_5C_2)	Fe_3O_4, and Fe_5C_2
SA-1626	H_2/CO, 280°C, 8 h	0		Fe_3O_4, and ϵ'-$Fe_{22}C$
		137		Fe_3O_4, and ϵ'-$Fe_{22}C$
		258		Fe_3O_4, and ϵ'-$Fe_{22}C$
		403		Fe_3O_4, and ϵ'-$Fe_{22}C$

EOR stands for end of the run sample which was exposed to air; TOS = 0 h means reduced sample.

FTS process conditions for the slurry tests with catalyst C (100 Fe/3 Cu/4 K/16 SiO_2, batch-4) were: T = 260°C, P = 1.48 - 2.17 MPa, H_2/CO = 0.67, SV = 1.4 - 2.6 Nl/g-cat/h.
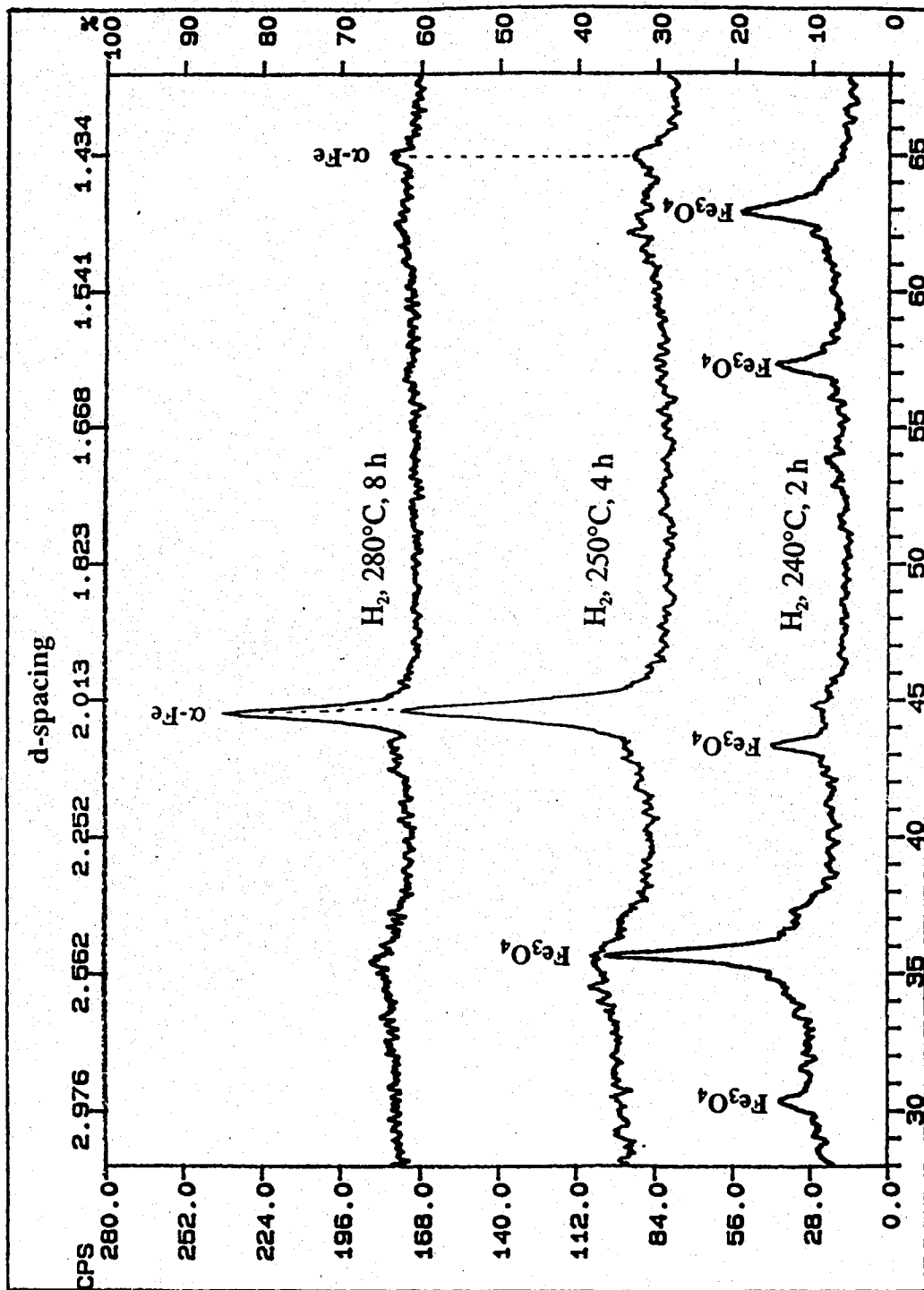
Figure VI-1.7   XRD patterns of catalyst C (100 Fe/3 Cu/4 K/16 SiO$_2$, batch-4) after pretreatment with hydrogen at different conditions in a slurry reactor.
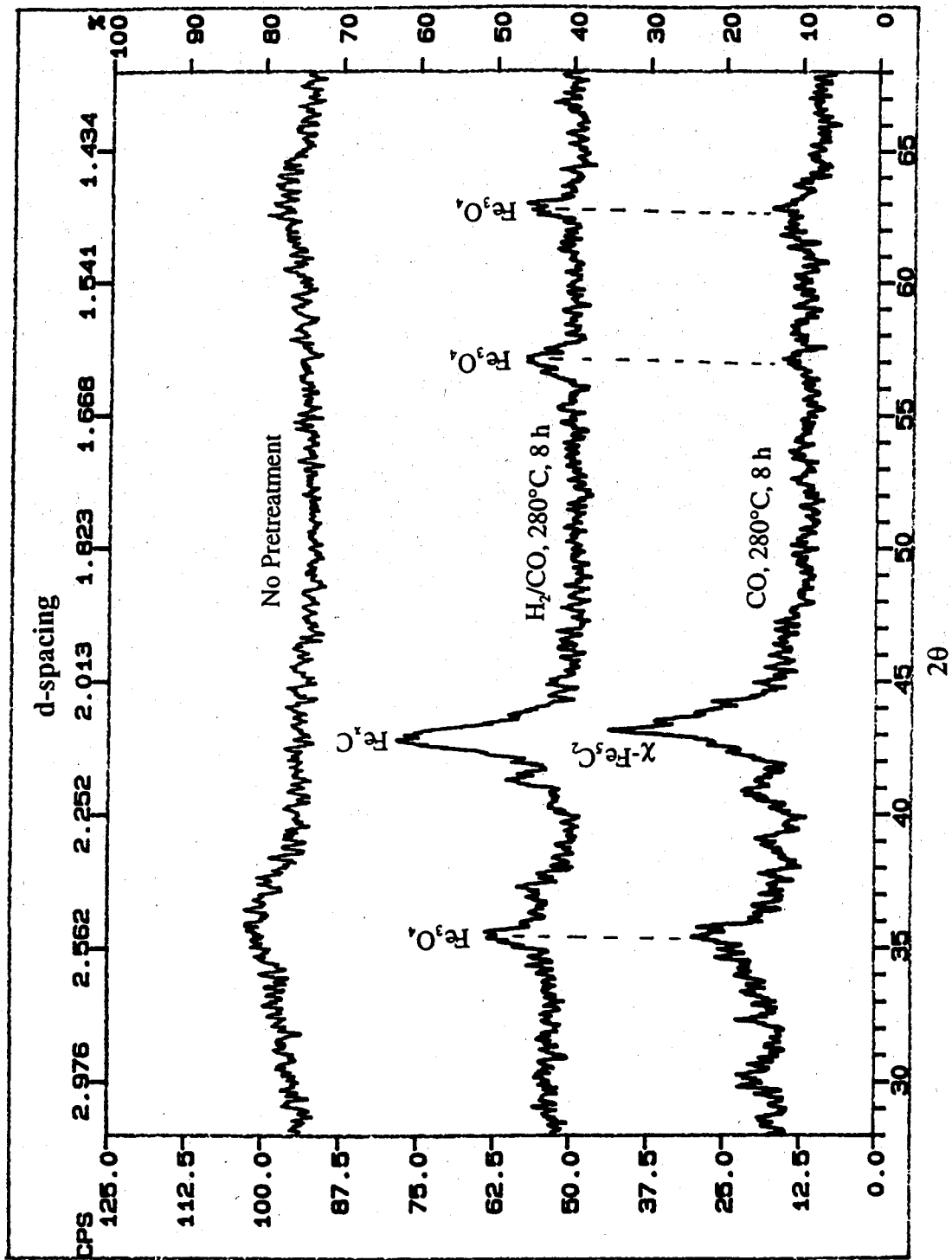
Figure VI-1.8   XRD patterns of catalyst C (100 Fe/3 Cu/4 K/16 SiO$_2$, batch-4) after different pretreatments in a slurry reactor.
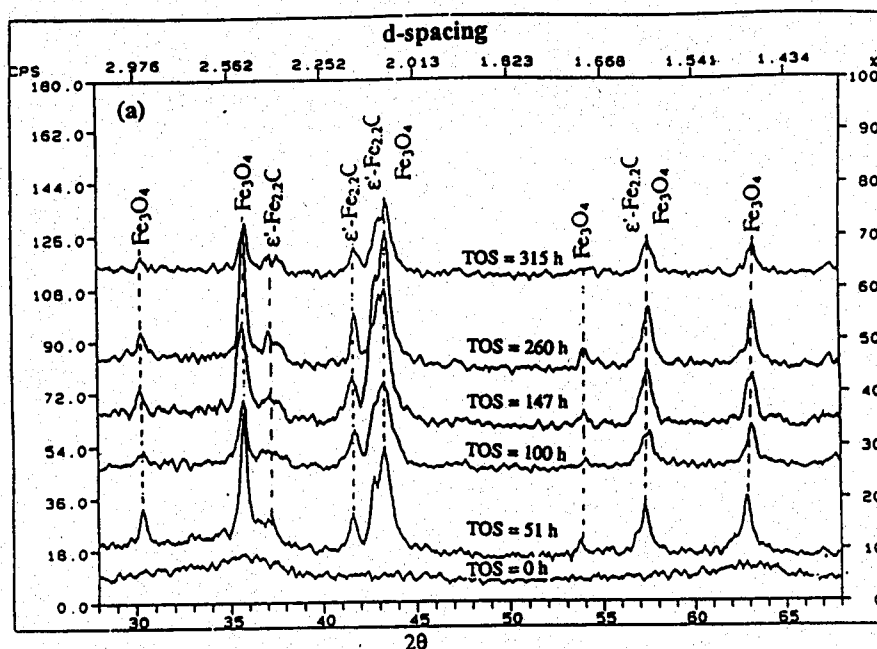
Figure VI-1.9a   Changes in bulk iron phases with time on stream in a slurry reactor (catalyst C, run SB-2486, No pretreatment).
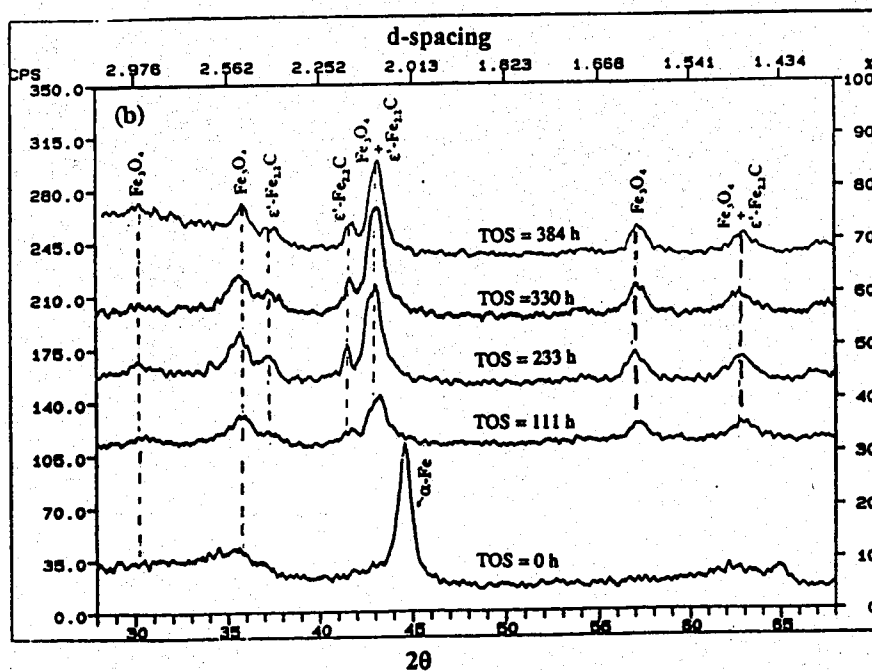

Figure VI-1.9b   Changes in bulk iron phases with time on stream in a slurry reactor (catalyst C, run SB-3425, reduced in H_2, at 250°C for 4 h).

Similar results were obtained in two other tests with hydrogen reduced catalysts (runs SB-3425 and SA-0376). In both of these two tests magnetite and ε'-carbide were identified by XRD analysis, whereas MES analysis revealed the presence of ε'-carbide in both tests, but magnetite was detected only in the samples withdrawn from the reactor near the end of the test (Table VI-1.2). In run SA-0376, a fraction of iron was in the form of χ-carbide (9-21%). In both tests the catalyst deactivated with time, whereas the fraction of iron carbide(s) present remained essentially constant.

Figure VI-1.10 illustrates changes in bulk iron phases with time-on-stream during run SA-0946 (CO pretreatment at 280°C for 8 h) and run SA-1626 (syngas pretreatment at 280°C for 8 h). During F-T synthesis in run SA-0946 both χ-carbide and, to a smaller extent, magnetite were identified by XRD (TOS = 113 to 563 h). MES analysis of these samples showed the increase in the fraction of χ-carbide from 46% at 134 h to 59% at 427 h, during which time period the catalyst activity was stable (Section VI-2). However, near the end of the run (TOS = 563) the fraction of magnetite was 24%, and the fraction of iron carbides (χ-carbide and ε'-carbide) was only 39%. Catalyst deactivated during the last 120 h on stream, upon exposure of the catalyst to CO rich syngas ($H_2/CO = 0.6$).

During run SA-1626 (Figure VI-1.10b) both magnetite and iron carbides were found in used catalyst samples (TOS = 127-403 hours), and the catalyst deactivated slowly with time.
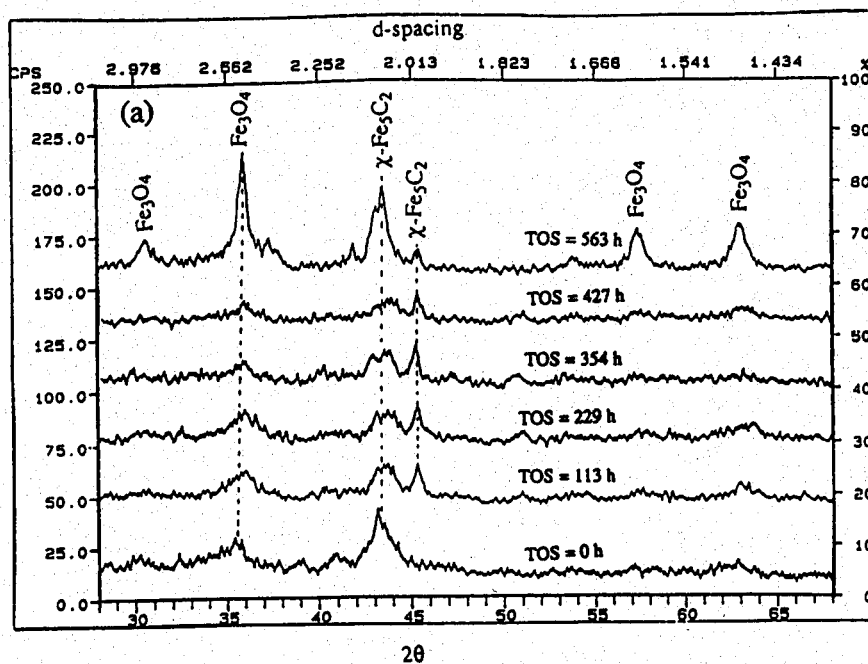
Figure VI-1.10a Changes in bulk iron phases with time on stream in a slurry reactor (catalyst C, run SA-0946, reduced in CO, at 280°C for 8 h).
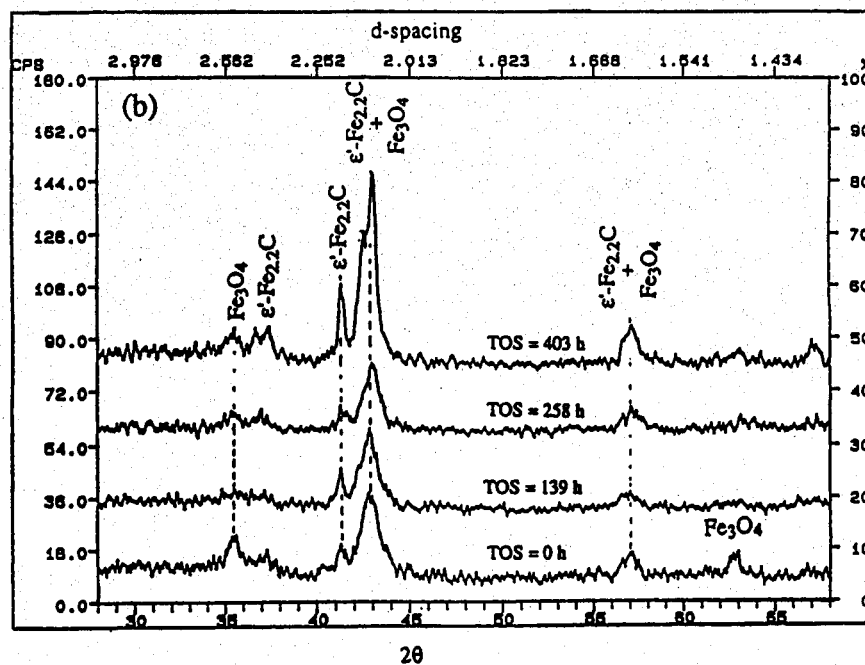

Figure VI-1.10b Changes in bulk iron phases with time on stream in a slurry reactor (catalyst C, run SA-1626, reduced in syngas, at 280°C for 8 h).

VI-2   Reaction Studies - Pretreatment Effect Research

Seven different pretreatment procedures were employed in stirred tank slurry reactor tests. Test identifications and pretreatment conditions are listed in Table VI-2.1. Tests SB-2145 and SA-1665 were completed under task 4 (Reproducibility of Catalyst Preparation), but selected results from these two tests are included here for comparison purposes. Our standard (baseline) reduction conditions for the catalyst C were used in these two tests (i.e. hydrogen reduction at 240°C for 2 hours). The purpose of run SB-1486 was to check reproducibility of results following the CO pretreatment, i.e. to repeat pretreatment conditions used in test SA-0946, and obtain results on catalysts activity and selectivity under the same process conditions.

Table VI-2.1   Pretreatment Conditions and Test Designations

Catalyst: 100 Fe/3 Cu/4 K/16 SiO_2

Test (ID)	Temp. (°C)	Reductant	Duration (h)	Pressure (MPa)	Flowrate (cm^3/min)
SA-1665	240	H_2	2	0.78	7500
SB-2145	240	H_2	2	0.78	7500
SB-3425	250	H_2	4	0.78	7500
SA-0376	280	H_2	8	0.78	950
SA-0946	280	CO	8	0.78	750
SB-1486	280	CO	8	0.78	750
SA-1626	280	H_2/CO = 0.67	8	0.78	750
SA-2186	280	CO/He=1/10	8	1.48	5500
SB-2486	No pretreatment				

Catalyst loading and particle size in, all new tests, were similar to those employed in previous tests of catalyst C (i.e. 10-20 g of catalyst <270 mesh in size in Durasyn 164 oil,

slurry concentration between 3.4 and 6.7 wt%). In run SB-2486 (no pretreatment) the slurry was heated in helium at 0.78 MPa to the desired reaction temperature (260°C) over a period of 3.5 h, and then exposed to the synthesis gas at 260°C, 1.48 MPa (200 psig), syngas molar feed ratio of $H_2/CO = 0.67$ and space velocity of 2.3 Nl/g-cat/h.

VI-2.1 Hydrogen Reductions

Changes in syngas conversion with time-on-stream and process conditions after hydrogen reductions at different conditions are shown in Figure VI-2.1a. The important observation is that the hydrogen reduced catalyst quickly reaches its steady state activity (within 4-10 h from exposure to synthesis gas). The catalyst was very stable in run SA-1665 (standard reduction procedure) but some deactivation was observed in all other tests.

Catalyst activity, measured in terms of the apparent reaction rate constant, for these four tests is shown in Figure VI-2.1b. The use of apparent rate constant enables one to compare activity of catalysts tested at different reaction pressures, gas space velocities and/or feed compositions, but at a constant reaction temperature. Catalyst reduced at 250°C for 4 h had the highest initial activity (360 mmol/g-Fe/h/MPa), whereas initial activities in runs SA-0376, SB-2145 and SA-1665 were similar (230-260 mmol/g-Fe/h/MPa). The iron phases in reduced catalysts, determined by XRD (see Section VI-1, Figure VI-1.7), were: α-Fe and magnetite (Fe_3O_4), in runs SA-0376 (reduction at 280°C for 8 h) and SB-3425 (reduction at 250°C for 4 h), and magnetite only in run SB-2145 (reduction at 240°C for 2 h). It is important to note that the catalyst reduced to magnetite only (runs SB-2145 and SA-1665) had higher activity than the catalyst which was almost completely reduced to metallic iron (run SA-0376). This demonstrates that the use of more severe reduction conditions does not necessarily result in higher activity. Previous studies in our laboratory with iron based catalysts without silicon oxide (Bukur et al. 1989; 1995a), have shown that the use of more severe reduction conditions may result in low catalyst activity. Catalyst activity in run SA-1665 was nearly constant up to 400 h on stream, whereas catalysts in runs SB-3425 and SA-0376 started to deactivate after about 100 h and 260 h on stream, respectively.
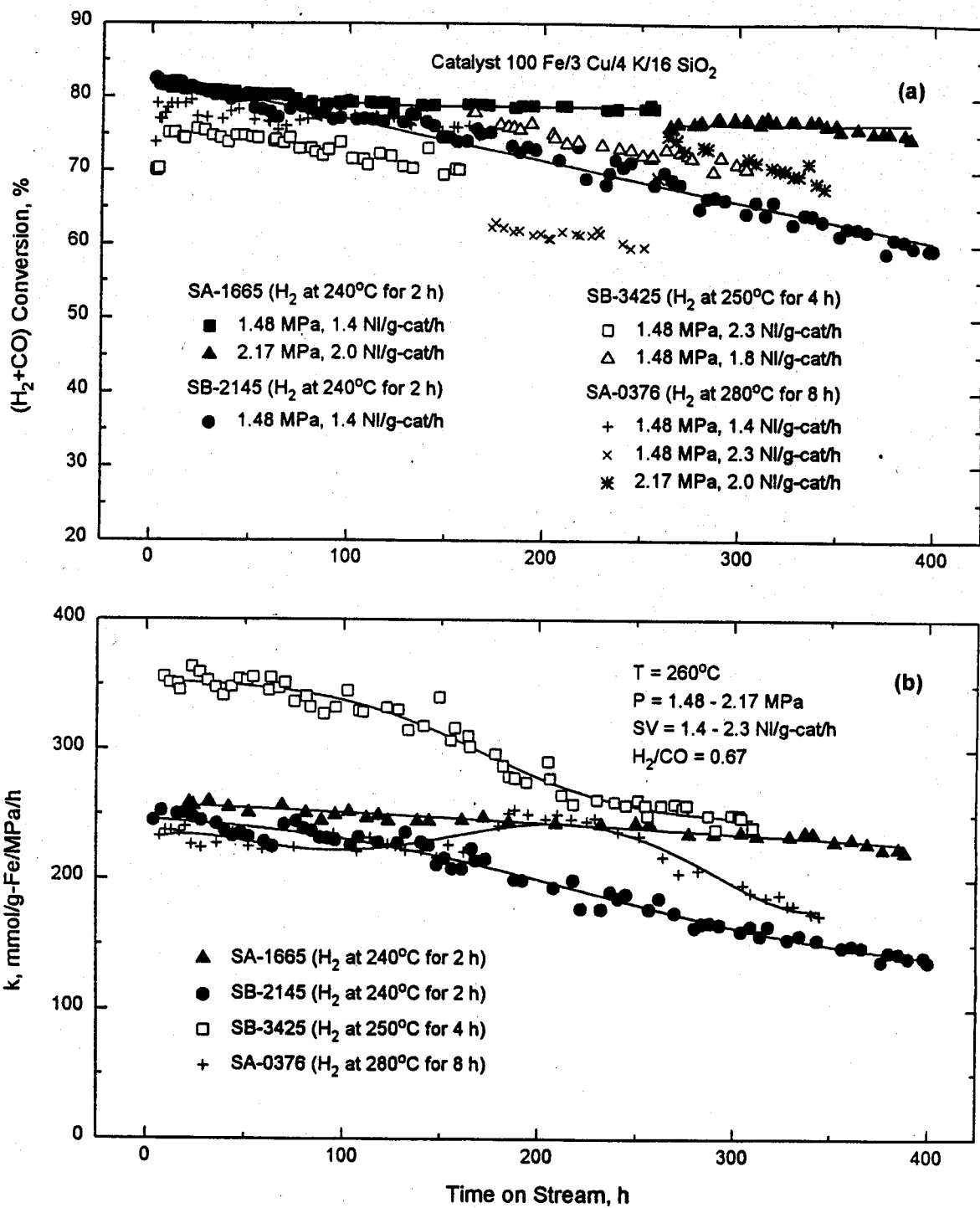
Figure VI-2.1   Synthesis gas conversion (a) and apparent reaction rate constant (b) as a function of time for STSR tests of catalyst C reduced with hydrogen at different temperatures.

Methane and C_1+C_2 gaseous hydrocarbon selectivities in run SA-0376 were similar to those obtained in run SB-3425 (Figure VI-2.2), and slightly higher than those in runs SA-1665 and SB-2145 (standard reduction procedure). This is consistent with results obtained previously in our laboratory, with other iron Fischer-Tropsch catalysts (Bukur et al. 1989; 1995a), which showed that the use of more severe reduction conditions often results in higher gaseous hydrocarbon selectivities.

Total olefin and 2-olefin contents were not affected by differences in reduction conditions employed (Figure VI-2.3). Total olefin content in all three tests decreased from about 85% at C_3 to about 55% at C_{15}, whereas the 2-olefin content increased with increase in carbon number, e.g. it is about 5% for C_4-C_8 hydrocarbons and about 30% at C_{15}.

Lumped hydrocarbon product distributions and product yields obtained in four tests in which hydrogen reductions were employed are summarized in Table VI-2.2, together with results from Mobil's and Rheinpreussen's bubble column slurry reactor tests of precipitated Fe-Cu-K catalysts. Hydrocarbon product distribution in run SA-1665 was similar to that obtained in Mobil's run CT-256-13 (Kuo, 1985). Catalyst productivity (expressed as gHC/g-Fe/h) in this test at reaction pressure of 1.48 MPa was similar to that obtained in Mobil's run, but it was significantly higher during testing at 2.17 MPa. In the other three tests the average molecular weight of hydrocarbon products produced was lower than that in run SA-1665. Catalyst productivity was either higher (run SB-3425) or lower (runs SB-2145 and SA-0376) than that obtained in run SA-1665. Yield of oxygenates was relatively low in all four tests, except in run SA-0376 at 324 hours on stream (testing at 2.17 MPa).

VI-2.2   Effect of Reductant Type

In comparison to hydrogen reductions, the time needed to reach a steady state activity was longer when other reductants were used, i.e. about 20 h for the syngas pretreated (SA-1626) or unreduced catalyst (SB-2486), and about 80 h for the CO pretreated catalyst (run SA-0946). Since the process conditions, including the gas space velocity, were the same in runs SB-2486, SA-1626, and SA-0946, the values of syngas conversion can be used as a measure
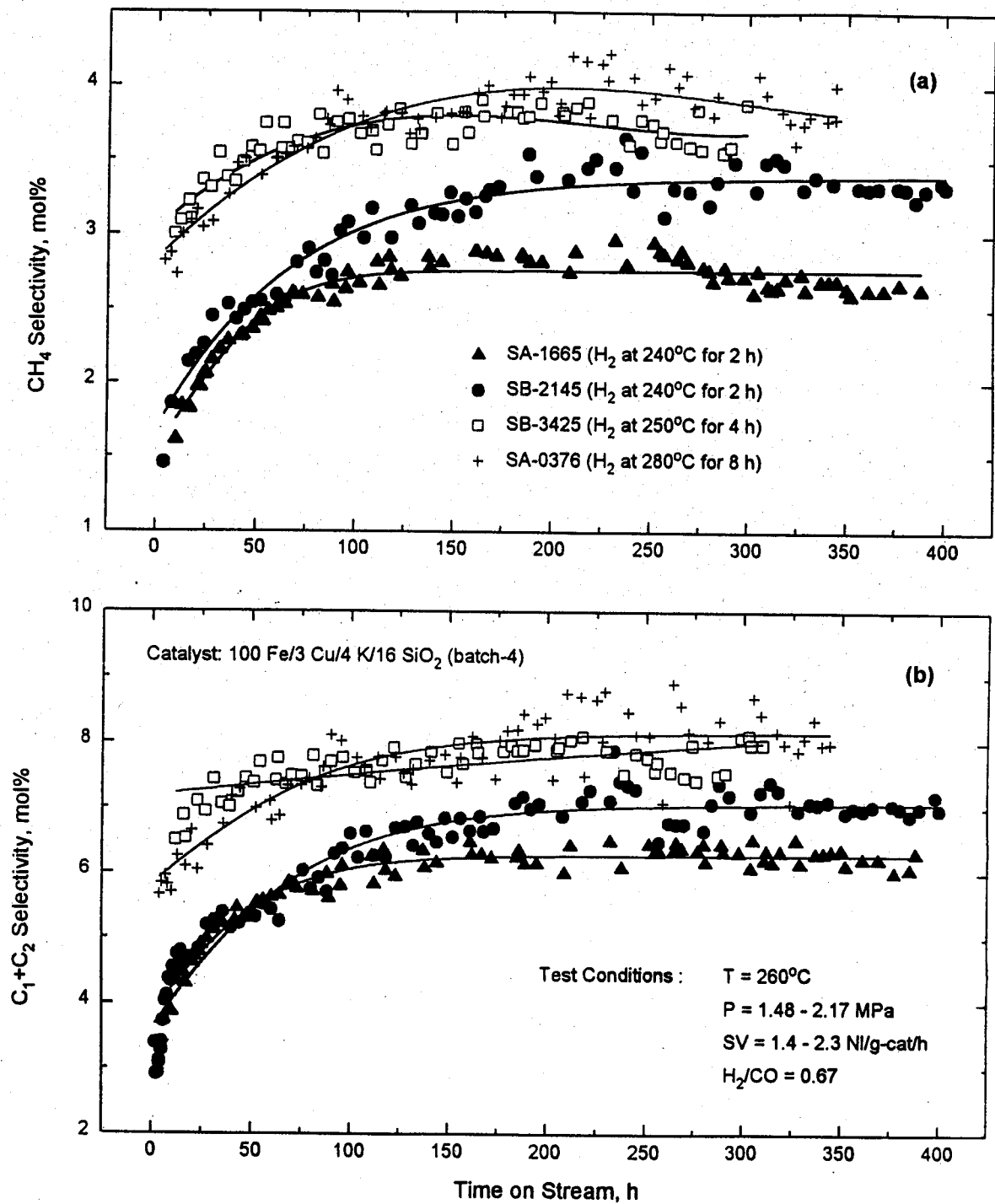
Figure VI-2.2   Methane selectivity (a) and $(C_1 + C_2)$ hydrocarbon selectivity (b) as a function of time for time for STSR tests of catalyst C reduced with hydrogen at different temperatures.
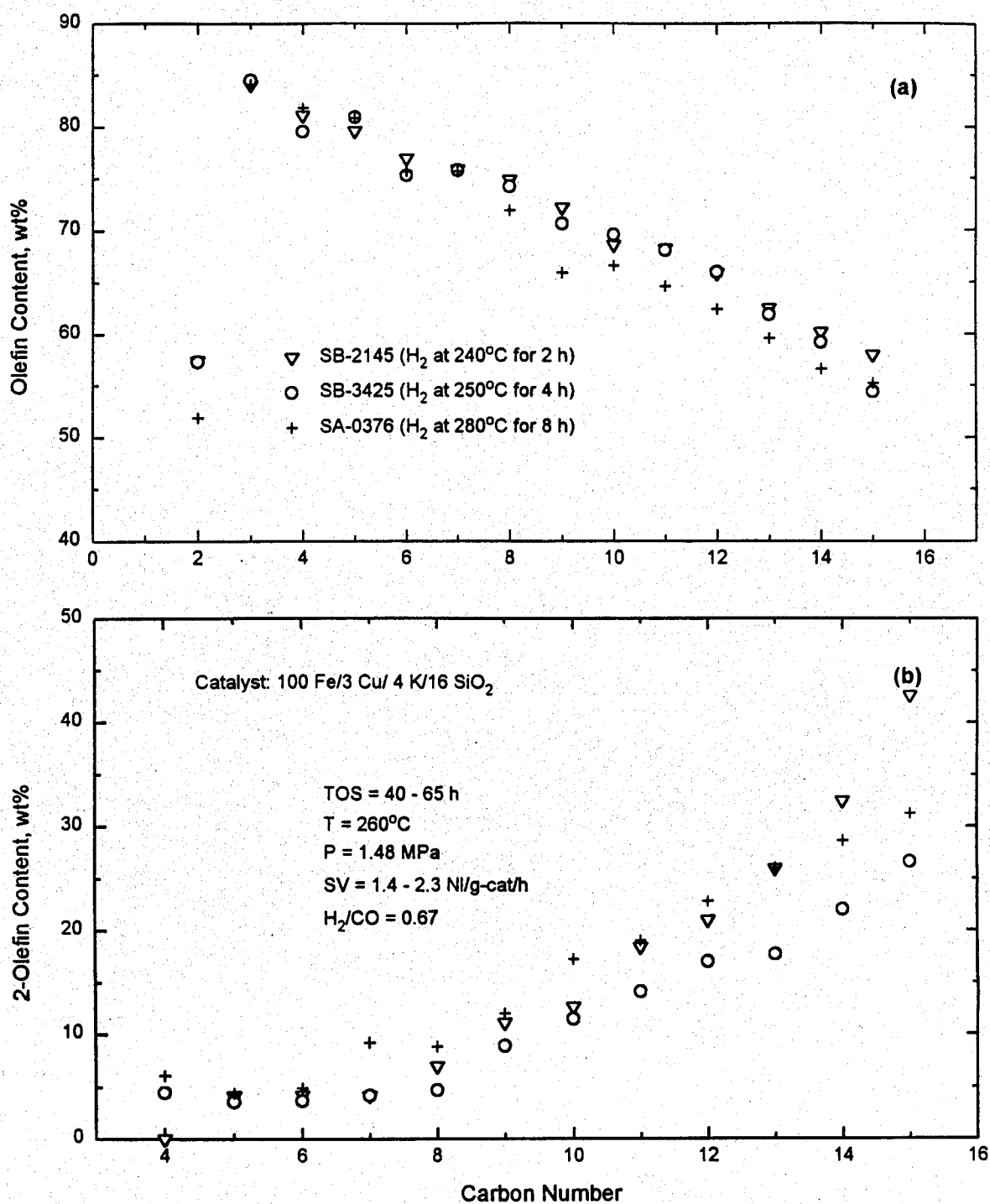
Figure VI-2.3   Olefin content (a) and 2-olefin content (b) dependence on carbon number for catalyst C reduced with hydrogen at different temperatures.

Table VI-2.2 Effect of Pretreatment Procedure on Catalyst Performance in Slurry Reactor Tests

Run ID / Pretreatment	SA-1665 H$_2$, 240°C	SB-2145 H$_2$, 240°C	SB-3425 H$_2$, 250°C	SA-0376 H$_2$, 280°C	Mobil[a] CT-256-13 Kuo (1985)	Rheinpreussen[a] Kölbel et al. (1955)
Test conditions						
Temperature, °C	260	260	260	260	257	268
Pressure, MPa	1.48	1.48	1.48	2.17	1.48	1.20
Space velocity, Nl/g-Fe/h	2.3	2.4	3.0	3.4	2.3	3.1
Feed H$_2$/CO ratio	0.67	0.67	0.67	0.67	0.73	0.67
Time on stream, h	220	310	264	324	475	
CO conversion, %	83.6	69.1	76.9	74.3	90	91
(H$_2$+CO) conversion, %	78.5	64.4	71.9	69.5	82	89
(H$_2$/CO) usage ratio	0.56	0.55	0.56	0.56	0.59	0.63
Hydrocarbon selectivites, wt%						
CH$_4$	3.2	4.1	4.4	4.8	2.7	3.2[b]
C$_2$-C$_4$	12.2	15.0	15.5	18.3	11.1	31.3
C$_5$-C$_{11}$	12.8	20.9	20.4	26.5	18.1	53.6
C$_{12}$+	71.9	60.0	59.7	50.4	68.1	11.9
C$_1$+C$_2$	6.6	8.3	8.2	9.6	5.6	6.8
Yields						
Nm^3/kg-Fe/h	1.8	1.5	2.2	2.4	1.9	2.8
g HC/Nm^3(H$_2$+CO)	205	194	196	187	206	178
g C$_3$+/Nm^3(H$_2$+CO)	191	178	179	169	195	166
g Oxy/Nm^3(H$_2$+CO)	2.8	10.7	9.6	18.2		
g HC/g-Fe/h	0.38	0.29	0.43	0.44	0.39	0.49

[a] Slurry bubble column reactor test.

[b] CH$_4$ + C$_2$H$_6$

of relative catalyst F-T activity (Figure VI-2.4a). Initial activity of the unreduced catalyst (SB-2486) was the lowest, but at approximately 20 h on stream it was the same as that of the CO pretreated catalyst (SA-0946). After 20 h on stream the conversion (activity) of unreduced catalyst started to decline, whereas that of the CO pretreated catalyst continued to increase up to 80 h, and then became stable at about 76%. Initially, the conversion of the syngas pretreated catalyst was higher than that of the unreduced and the CO pretreated catalyst, and it reached its steady state value of ~70% at about 20 h. The steady state activity of the syngas pretreated catalyst was lower than that of the CO pretreated catalyst. Although, the syngas conversion of the hydrogen reduced catalyst (SB-2145) up to 80 h on stream was higher than those obtained in the other tests, this does not imply the highest catalyst activity, since the gas space velocity in run SB-2145 (1.4 Nl/g-cat/h) was significantly lower than in the other three tests (2.3 Nl/g-cat/h).

Activity comparison, in terms of the apparent reaction rate constant for first order reaction in hydrogen, is given in Figure VI-2.4b. Initially, the CO and syngas activated catalysts had the highest activity (k = 280 mmol/g-Fe/h/MPa) , whereas the catalyst reduced with hydrogen at 280°C for 8 h and the catalyst which was not pretreated were the least active (k = 240 mmol/g-Fe/h/MPa). Activity of the CO and syngas catalysts increased with time during the first 100 h on stream, whereas the activity in run SA-0376 remained fairly stable and the activity in run SB-2486 started to decline after passing through a maximum at about 50 h (this follows the same trend as the syngas conversion in Figure VI-2.4a). Catalyst activity in run SA-0946 remained high and stable up to 400 h on stream (at different gas space velocity and/or reaction pressure), whereas the catalysts in the other three tests deactivated with time on stream.

Methane and C_1+C_2 selectivities (Figure VI-2.5) of hydrogen reduced and unpretreated catalyst increased during the first 100 h of synthesis and then became stable, whereas methane selectivities of the syngas and CO activated catalysts exhibited the opposite trend, i.e. they decreased with time. Initially (during the first 20 h on stream) methane selectivities increased
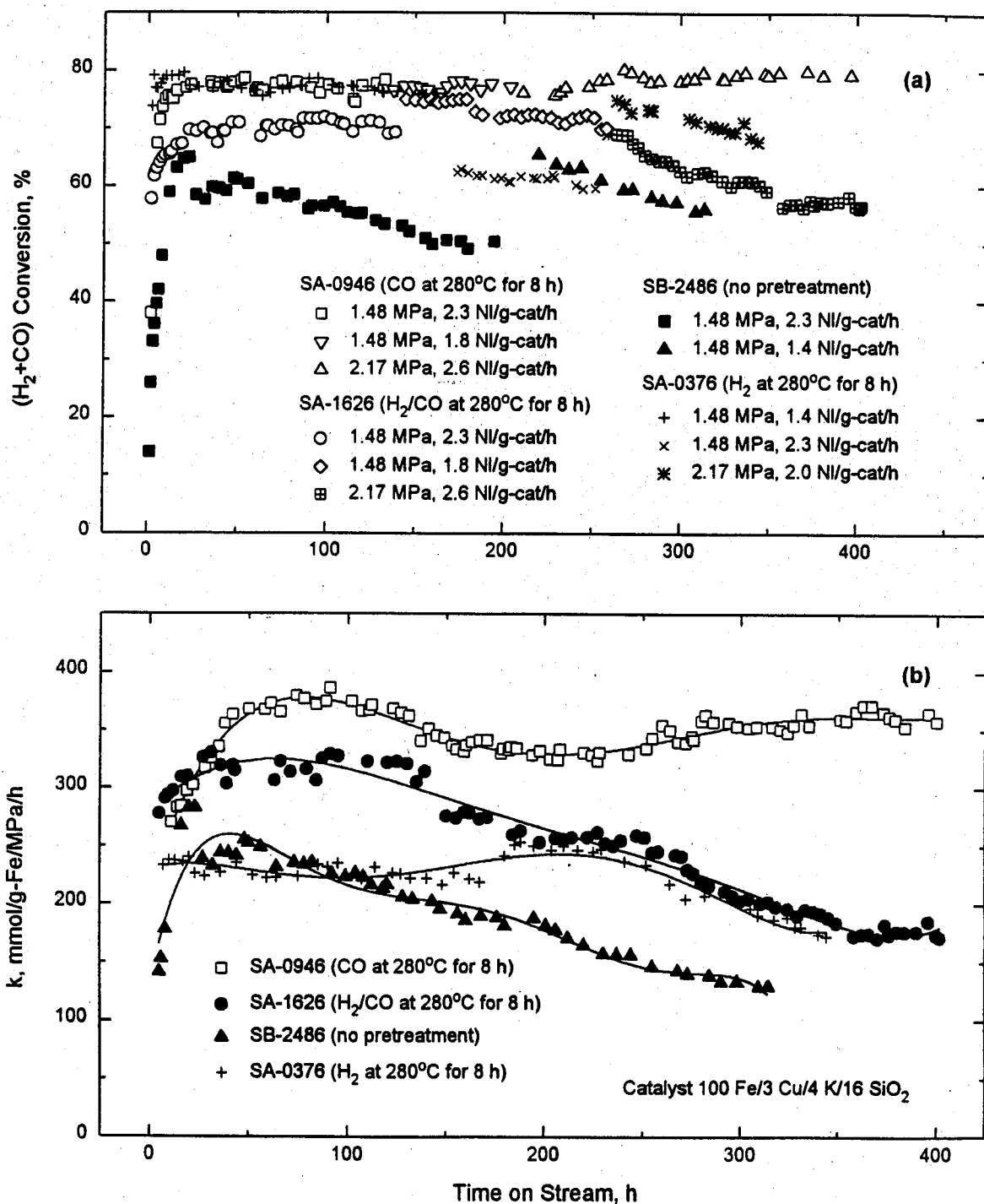
Figure VI-2.4   Effect of reductant type on (a) synthesis gas conversion and (b) apparent reaction rate constant in STSR tests with catalyst C.
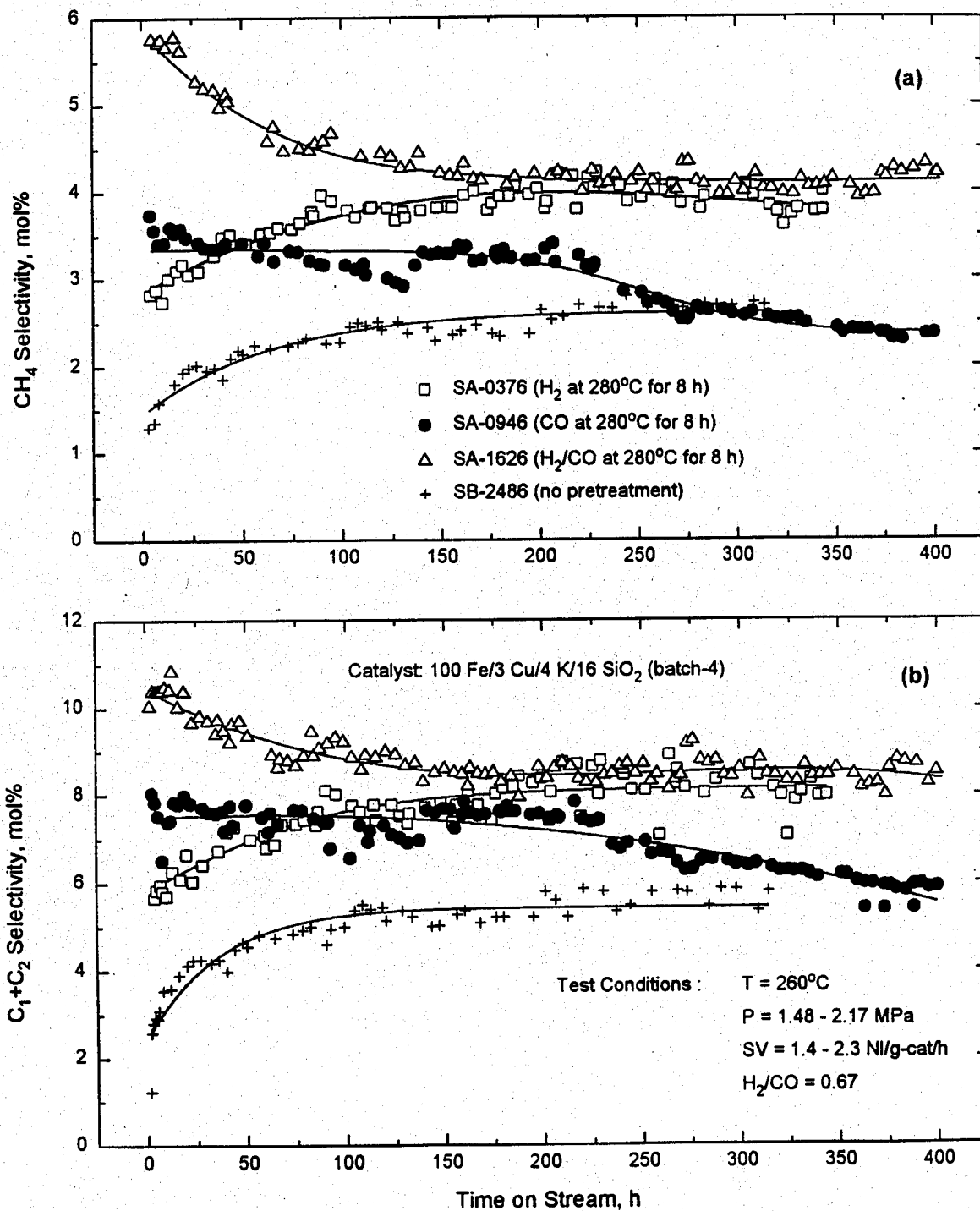
Figure VI-2.5   Effect of reductant type on (a) methane selectivity and (b) (C$_1$+C$_2$) hydrocarbon selectivity in STSR tests with catalyst C.

in the following order: No pretreatment (2 mol%) < hydrogen reduced catalysts (~3 mol%) < CO activated catalyst (3.6-4%) < syngas activated catalyst (5.8 - 6%). After 300 h on stream methane selectivity increased in the following order: CO activated catalyst $\approx$ no pretreatment (~2.5 mol%) < hydrogen reduced catalysts (3.6-3.8 mol%) < syngas activated catalyst (4 mol%). During testing at 2.17 MPa methane selectivity of the CO activated catalyst (SA-0946) was low (2.2 - 2.8 mol%). This is similar to values obtained in run SA-1665 (standard hydrogen reduction at 240°C for 2 hours). However, the activity of the catalyst in run SA-1665 at 400 h on stream was significantly lower than that of the CO pretreated catalyst (k = 220 mmol/g-Fe/h/MPa in run SA-1665 vs. k = 360 mmol/g-Fe/h/MPa in run SA-0946).

Total olefin and 2-olefin contents obtained during early periods (84-146 hours) in tests after different pretreatments are shown in Figure VI-2.6. Total olefin content was the highest in run SA-0946 (CO pretreatment at 280°C) and the lowest in run SA-0376 (hydrogen reduction at 280°C). Total olefin content in all tests decreased with increase in carbon number (for C_3+ hydrocarbons) and in run SA-0946 the propene content was about 88%, and that of C_{15} hydrocarbons was 70%, whereas in run SA-0376 the total olefin content decreased from 86% to 55% over the same carbon number range (Figure VI-6.6a). Very high olefin content (including 76% ethylene selectivity) was also obtained in run SB-2486 (no pretreatment). The 2-olefin content increased with increase in carbon number in all four tests. The lowest 2-olefin selectivity was obtained in a test with the catalyst which was not pretreated, and the highest 2-olefin selectivity was obtained with the syngas pretreated catalyst (Figure VI-2.6b).

Lumped hydrocarbon product distributions and product yields obtained in tests SA-0946 (CO pretreatment), SA-1626 (syngas pretreatment), SB-2486 (no pretreatment) and SA-2186 (TAMU pretreatment, see section VI-2.3) are summarized in Table VI-2.3, together with results from Mobil's and Rheinpreussen's bubble column slurry reactor tests of precipitated Fe-Cu-K catalysts. Low methane and gaseous hydrocarbon selectivities (C_1+C_2 and C_2-C_4 hydrocarbons) were obtained in runs SA-0946, SA-2186 and SB-2486 at reaction pressures of 1.48 and 2.17 MPa. Catalyst productivity (expressed as gHC/g-Fe/h) at reaction pressure of
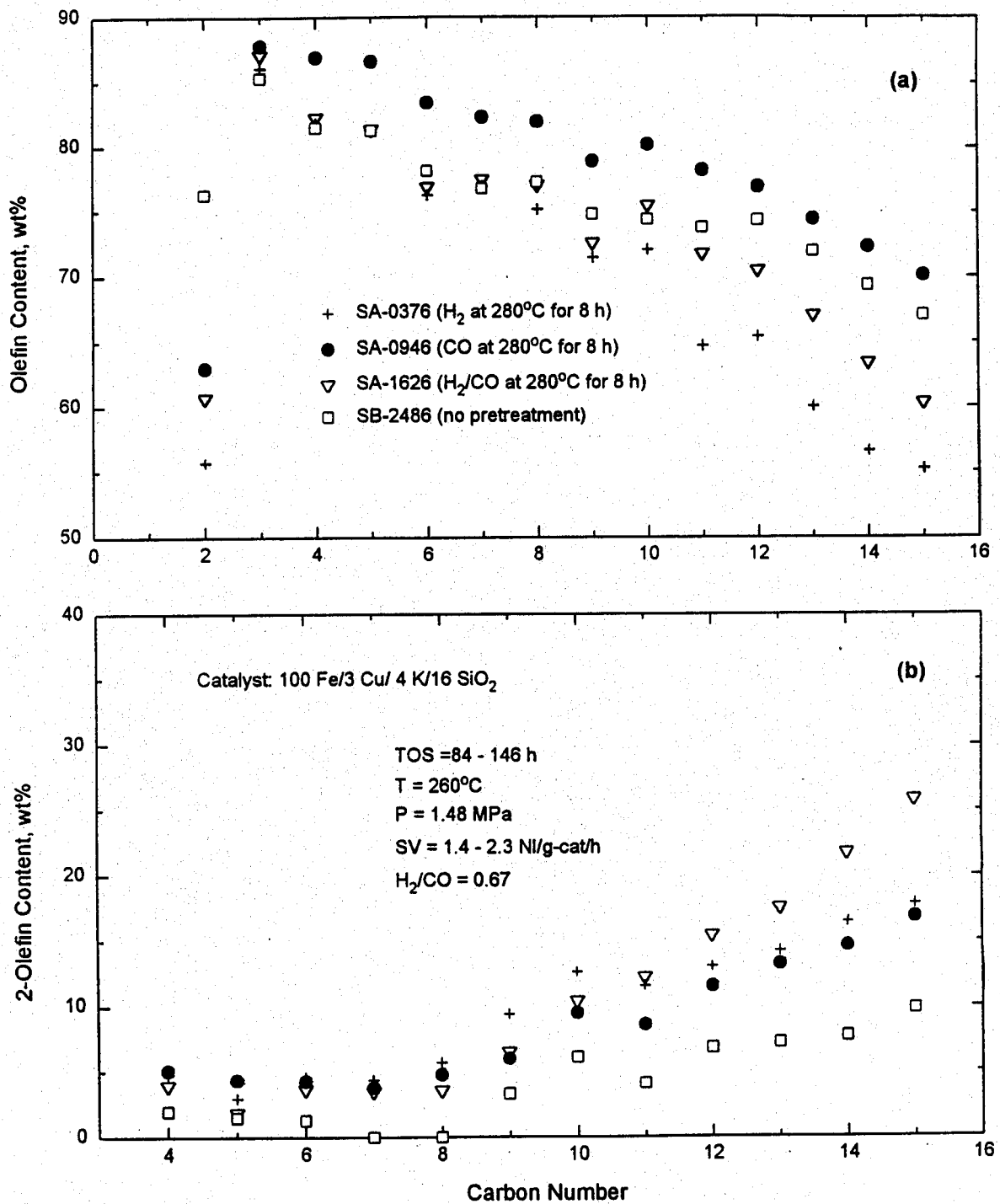
Figure VI-2.6   Effect of reductant type on (a) olefin content and (b) 2-olefin content in STSR tests with catalyst C.

Table VI-2.3 Effect of Pretreatment Procedure on Catalyst Performance in Slurry Reactor Tests

Run ID Pretreatment	SA-0946 CO, 280°C	SA-1676 H₂/CO, 280°C	SB-2486 no pretr.	SA-2186 TAMU pretr.	Mobil[a] CT-256-13 Kuo (1985)	Rheinpreussen[a] Kölbel et al. (1955)
Test conditions						
Temperature, °C	260	260	260	260	257	268
Pressure, MPa	1.48	2.17	1.48	2.17	1.48	1.20
Space velocity, Nl/g-Fe/h	3.0	4.4	2.4	5.8	2.3	3.1
Feed H₂/CO ratio	0.67	0.67	0.67	0.67	0.73	0.67
Time on stream, h	216	396	245	314	475	
CO conversion, %	85.0	59.4	66.9	83.6	90	91
(H₂+CO) conversion, %	79.9	56.3	62.4	79.0	82	89
(H₂/CO) usage ratio	0.57	0.58	0.55	0.57	0.59	0.63
Hydrocarbon selectivites, wt%						
CH₄	3.6	5.1	3.2	3.0	2.7	3.2[b]
C₂-C₄	15.5	17.5	11.7	14.1	11.1	31.3
C₅-C₁₁	18.9	24.2	19.3	16.2	18.1	53.6
C₁₂⁺	62.0	53.2	65.8	66.6	68.1	11.9
C₁+C₂	8.1	9.9	6.2	7.0	5.6	6.8
Yields						
Nm³/kg-Fe/h	2.4	2.5	1.5	4.5	1.9	2.8
g HC/Nm³(H₂+CO)	202	191	197	190	206	178
g C₃⁺/Nm³(H₂+CO)	186	172	185	177	195	166
g Oxy/Nm³(H₂+CO)	7.7	13.3	11.8	7.9		
g HC/g-Fe/h	0.49	0.47	0.29	0.86	0.39	0.49

[a] Slurry bubble column reactor test.

[b] CH₄ + C₂H₆

1.48 MPa in runs SA-0946 and SA-2186 was equal to or higher than that obtained in Mobil's and Rheinpreussen's bubble column reactor tests, and was markedly higher in both runs during testing at 2.17 MPa. The highest catalyst productivity, 0.86 g hydrocarbons produced/g-Fe/h, was achieved using the TAMU pretreatment procedure, while maintaining the desired selectivity. This is the best performance to date, in our laboratory or anywhere else, for catalysts developed for high wax production ("high alpha" catalysts). The performance of the CO activated catalyst was also superior relative to other catalysts developed for high wax production : catalyst productivity of 0.71 gHC/g-Fe/h, and hydrocarbon selectivity within the DOE's performance targets (low methane and C_1+C_2 selectivities).

VI-2.3   Run SA-2186 with 100 Fe/3 Cu/4 K/16 SiO$_2$ Catalyst (Batch-4)

Twelve grams of the catalyst (< 270 mesh in size) was loaded for the test, together with 313 g Durasyn 164 oil as the initial slurry medium. A new pretreatment procedure (referred to as TAMU pretreatment) was employed. Pretreatment conditions were provided in Table VI-2.1.

Following the reduction, the catalyst was tested at 260°C, 1.48 MPa, syngas molar feed ratio of 0.67 ($H_2/CO = 0.67$) and gas space velocity of 2.3 Nl/g-cat/h. Catalyst activity, measured by (H_2+CO) conversion and the apparent reaction rate constant is shown in Figures VI-2.7a and VI-2.7b, respectively. The syngas conversion increased rapidly with time during the first 20 hours of testing and then stabilized at about 76-78%. The usage ratio (not shown) decreased from 0.62 to 0.58 at 20 h and then remained stable at these conditions. The apparent reaction rate constant followed the same trend as the syngas conversion, and was fairly constant between 20 and 200 hours on stream (about 400 mmol/g-Fe/h/MPa). At 209 h on stream, the reaction pressure and gas space velocity were increased to 2.17 MPa and 3.4 Nl/g-cat/h (5.8 Nl/g-Fe/h). After 20 hours at these conditions, the syngas conversion was about 76%, and then increased with time reaching 83% at about 500 h on stream. The apparent reaction constant also increased with time during testing at 2.17 MPa, and reached 450 mmol/g-Fe/h/MPa at 500 hours.
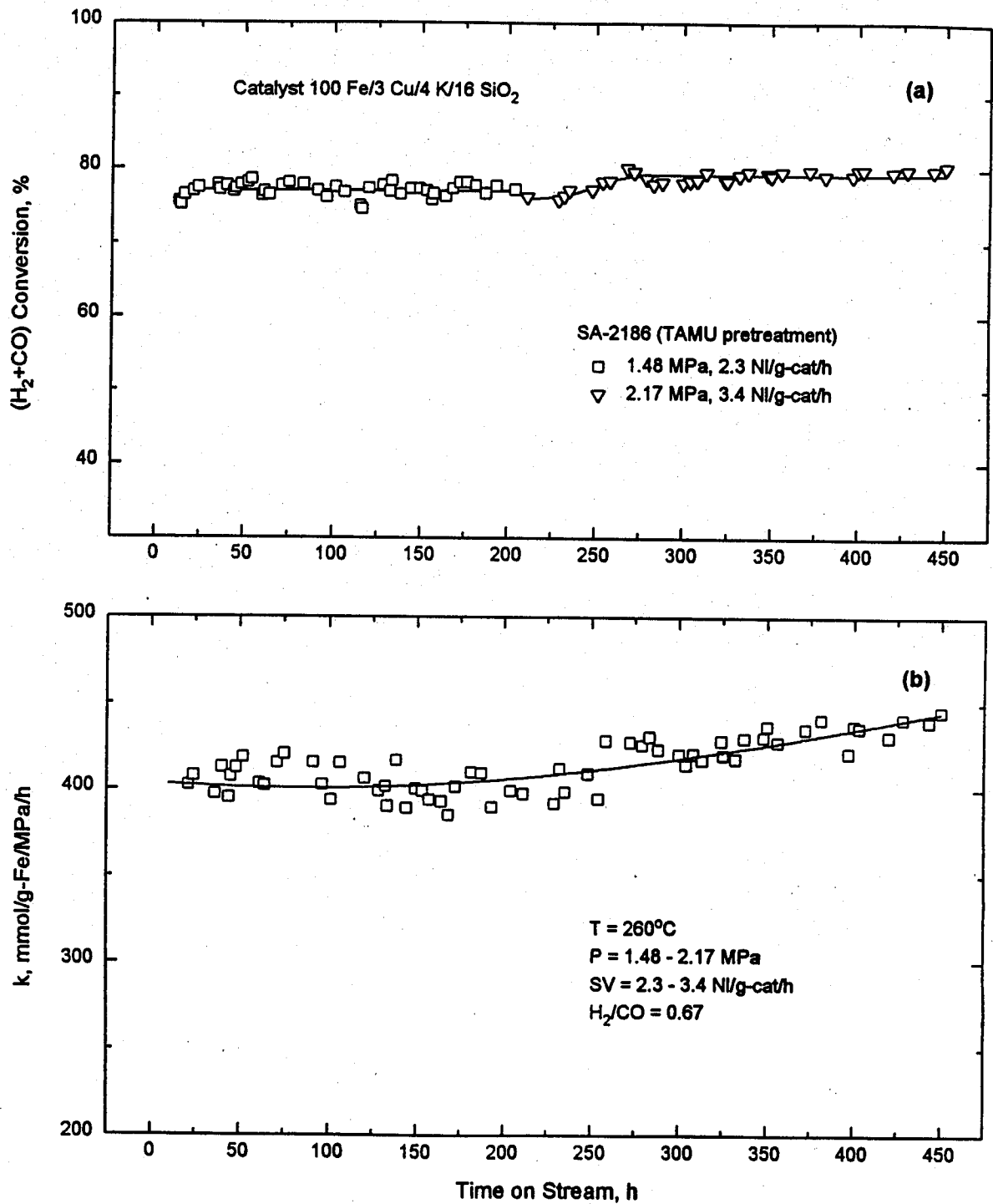
Figure VI-2.7   Synthesis gas conversion (a) and apparent reaction rate constant (b) as a
function of time for STSR test of catalyst C after TAMU pretreatment
procedure.

After 20 h on stream, methane selectivity (Figure VI-2.8a) varied between 2.9 and 3.3 mol%, and C_1+C_2 hydrocarbon selectivity was between 6.6 and 7.8 mol% (Figure VI-2.8b). Gaseous hydrocarbon selectivities were gradually decreasing during testing at 2.17 MPa. At 500 h on stream, the methane and C_1+C_2 selectivities were 2.5 and 6.4 mol%, respectively.

The catalyst productivity at 260°C, 2.17 MPa, syngas molar feed ratio of 0.67 (H_2/CO = 0.67) and gas space velocity of 3.4 Nl/g-cat/h was 0.86 (g hydrocarbons produced/g-Fe/h). As noted above, this is the highest catalyst productivity obtained in our laboratory, and is significantly higher than that obtained in the two most successful bubble column slurry reactor operations at comparable conversions and low methane selectivities (Mobil's work, and Kölbel's Rheinpreussen demonstration plant unit). Two main reasons for higher catalyst space-time-yield (productivity) obtained in the present study relative to the previous ones are: (1) the use of higher reaction pressure, and (2) higher intrinsic activity of our catalyst.

Concluding Remarks on the Pretreatment Effect Research

A very rapid achievement of steady state activity (Figure VI-2.1) of the hydrogen reduced catalysts (SB-3425, SA-0376 and SB-2145) indicates either that magnetite and α-Fe are active for FTS or that they are rapidly converted to an active carbide phase. However, the conversion of magnetite to zero-valent iron is a slow step in reduction of iron oxide, and it is unlikely that it can occur to an appreciable extent after 2 h of exposure to syngas at 260°C. For example, the unreduced iron requires about 20 h of exposure to reach its steady state activity (SB-2486). Activity of the unreduced catalyst (largely Fe^{3+} iron) is low initially, and it increases during the first 25 h of synthesis, due to formation of magnetite and/or ε'-carbide, indicating that one or both of these phases are active for FTS. Activity of the CO reduced catalyst is rather low initially (χ-carbide), and increases gradually with time. This behavior is not consistent with a hypothesis that iron carbide is the active phase for the FTS. If the latter hypothesis was correct, one would expect the initial activity of the partially carbided catalyst to be markedly greater than that of the catalyst in the form of magnetite (run SB-3425). Also, the
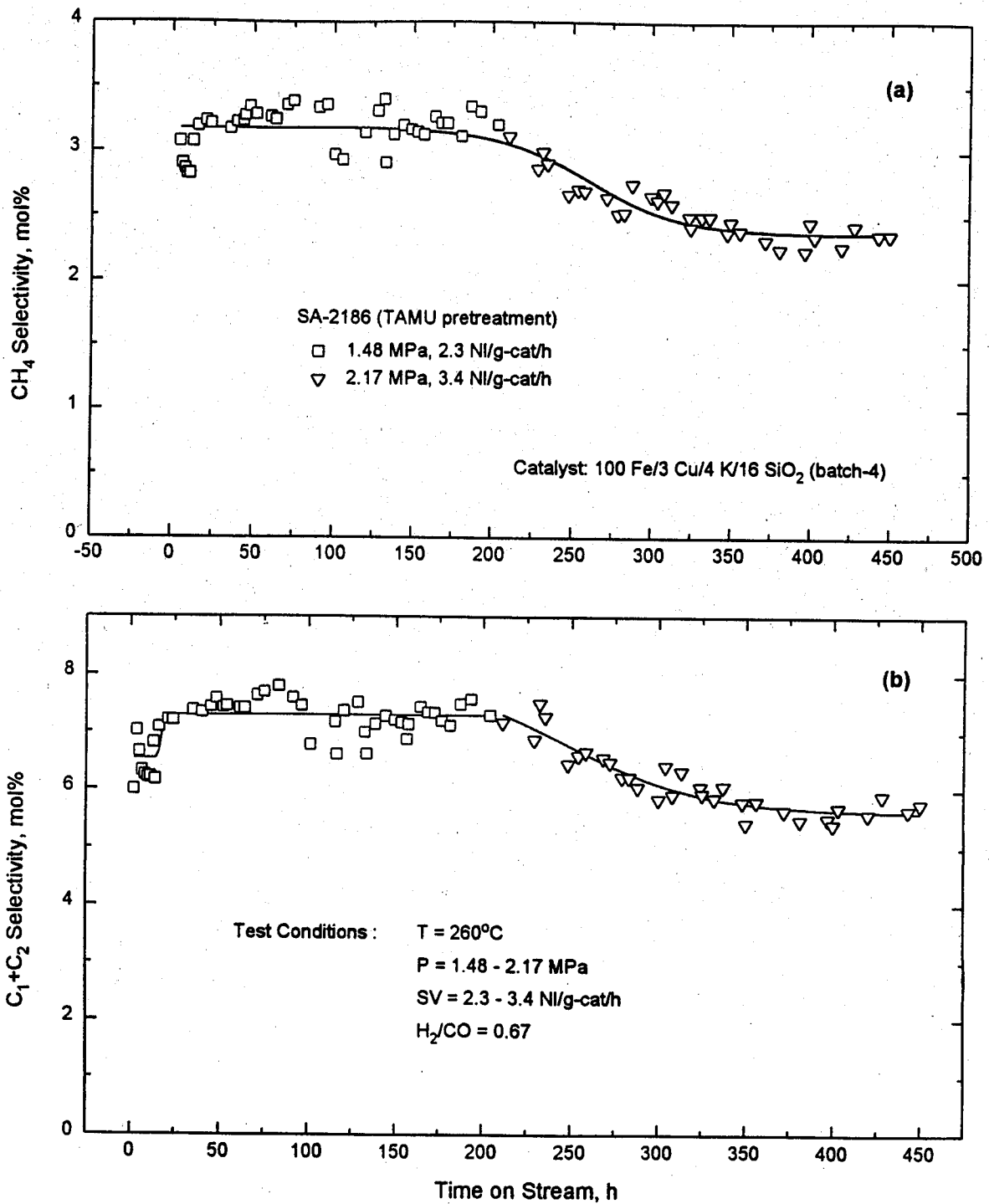
Figure VI-2.8   Methane selectivity (a) and ($C_1 + C_2$) hydrocarbon selectivity (b) as a function of time for time for STSR tests of catalyst C after TAMU pretreatment procedure.

catalyst in test SA-0946 had a long induction period, and its activity at ~20 h on stream was similar to that of the unreduced catalyst. Initial activity of the syngas activated catalyst (mixture of iron carbides and magnetite) was high, but it also went through an induction period lasting approximately 25 h. It is possible that the active surface sites of the CO and syngas pretreated catalysts were partially blocked with excess carbon formed during the pretreatment, and that this had caused lower than expected activity. Steady state activities, of catalysts pretreated by CO and syngas were higher than those of the hydrogen and unreduced catalysts. Magnetite was virtually absent in the CO and syngas pretreated catalysts, whereas both hydrogen and unreduced catalyst contained both magnetite and ε'-carbide (Section VI-1, Table VI-1.2). These observations are consistent with the hypothesis that both magnetite and iron carbides are active for FTS, and that iron carbides have higher FTS activity than magnetite.

Methane selectivities of the CO and syngas pretreated catalysts decreased with time, whereas those of the hydrogen reduced and unreduced catalysts increased with time (Figures VI-2.2a and VI-2.5a). These data suggest that methane selectivity is low on catalysts containing iron oxides, and is higher on carbided catalysts. A possible reason for markedly higher methane selectivity on carbided catalysts during early periods of synthesis, is that part of methane is produced by reaction between hydrogen and surface carbon formed during the pretreatment.

Significant improvements in the catalyst activity were obtained through the use of different pretreatment procedures. Our standard reduction procedure with the catalyst C (hydrogen reduction at 240°C for 2 hours) resulted in the initial activity, expressed in terms of the apparent reaction rate constant, of about 250 mmol/g-Fe/h/MPa. The activity decreased with time and at about 400 h the apparent rate reached the value of 220 mmol/g-Fe/h/MPa (run SA-1665) or 140 mmol/g-Fe/h (run SB-2145). The initial activity of the catalyst reduced with hydrogen at 250°C for 4 hours (run SB-3425) was about 350 mmol/g-Fe/h/MPa, which represents a 40% increase relative to the standard reduction procedure. However, the catalyst

activity decreased with time and at about 300 h the apparent rate constant was 250 mmol/g-Fe/h/MPa (similar to the value obtained in run SA-1665).

The CO pretreatment (SA-0946), syngas pretreatment (SA-1626) and TAMU pretreatment (SA-2186) also resulted in improved catalyst activity, relative to the standard reduction procedure. The initial values of the apparent reaction rate constant, after these pretreatments, were 300-400 mmol/g-Fe/h/MPa, corresponding to 20-60% increase in activity relative to the standard procedure. Activity of the CO and TAMU pretreated catalysts increased with time, and at 400 hours the values of the apparent reaction rate constants were 360 and 430 mmol/g-Fe/h, respectively. As the result of the improvement in the catalyst activity, while maintaining low methane and gaseous hydrocarbon selectivities, the catalyst productivities in these two tests were markedly higher than those obtained in Mobil's and Rheinpreussen's slurry bubble column reactor tests. The catalyst productivity in Rheinpreussen test was 0.49 gHC/g-Fe/h, and those obtained in runs SA-0946 and SA-2186 were 0.71 and 0.86 gHC/g-Fe/h, respectively (Table VI-2.3). This represents 45-75% improvement in catalyst productivity relative to that achieved in Rheinpreussen's demonstration plant unit, and sets new standards of performance for "high alpha" iron catalysts. We believe that the performance of our catalyst B (100 Fe/5 Cu/6 K/24 SiO_2) can be also improved through the use of better pretreatment procedures.

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