IV Reproducibility of Catalyst Preparation

The objective of this task is to verify reproducibility of catalyst synthesis procedure on a laboratory scale. Four new batches of catalyst with nominal composition 100 Fe/5 Cu/6 K/24 SiO_2 (catalyst B; S5624) and three new batches of catalyst with nominal composition 100 Fe/3 Cu/4 K/16 SiO_2 (catalyst C; S3416) were synthesized, characterized by different techniques (Section IV-1), and some of them were tested in slurry reactors (Section IV-2).

IV-1 Catalyst Characterization Studies

Several batches (90 to 405 g) of catalysts B and C were synthesized using the procedure developed in our laboratory (Appendix 1). Different batches of the catalyst with the same nominal composition are designated with the serial number (catalyst code) followed by an Arabic numeral designating the specific batch (e.g., S3416-2 refers to batch-2 of catalyst with nominal composition 100 Fe/3 Cu/4 K/16 SiO_2). Synthesized catalysts were characterized by atomic absorption spectroscopy (AAS), BET surface area (SA), pore volume (PV), pore size distribution (PSD) measurements, temperature-programmed reduction (TPR) and isothermal reduction.

Catalyst Composition and Textural Properties

The catalyst composition was determined by AAS using a Varian Spectra AA-30 spectrophotometer. Detailed description of experimental equipment and procedures is provided in Appendix 2. Results of elemental analysis are shown in Table IV-1.1, and major findings are summarized below:

(1) For catalyst C, both the copper and the silica contents agree well among different batches, however, potassium content of batch-2 (3.6 parts by weight (pbw) of K per 100 pbw of Fe), batch-3 (3.5 pbw of K per 100 pbw of Fe) and batch-4 (3.6 pbw of K per 100 pbw of Fe) catalysts is significantly lower than that of batch-1 (5.8 - 6.7 pbw of K per 100 pbw of Fe). The actual potassium content of the catalysts synthesized during the current contract (batches 2 to 4) is closer to the nominal one, than that of batch-1 (synthesized during the

Table IV-1.1 Elemental Analysis and Textural Properties of Synthesized Catalysts

Nominal Composition Designation	Amount Prepared (g)	Composition 100 Fe x Cu/y K/z SiO_2	BET Surface Area (m^2/g) Single point	BET plot	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)
S3416-2	101	3.1 / 3.6 / 19	316	315	0.43
S3416-2 (c)		3.5 / 6.5 / 18			
S3416-3 (d)	173	2.9 / 3.5 / 16	262	291	0.43
S3416-3 (c)		3.2 / 6.9 / 20			
S3416-4	215	3.1 / 3.6 / 19	310	306	0.45
100 Fe/5 Cu/6 K/24 SiO_2					
S5624-1	67	5.4 / 6.2 / 24 5.1 / 8.1 / 26(a) 5.5 / 6.6 / 24(e)	202	235 222 (a)	0.71 0.68 (a)
S5624-2	90	5.4 / 5.1 / 22	228	238	0.23
S5624-3	240	4.8 / 5.2 / 24	258	284	0.51
S5624-4	200	5.2 / 6.5 / 23	295	299	0.48
S5624-5	405	5.2 / 7.8 / 29		287	0.54

(a): Bukur (1994).
(b): measurements conducted at UOP.
(c): additional amount of K was added to obtain a better agreement with the actual K content of the original catalyst (S3416-1).
(d): contains 0.34 wt% sodium (Na/Fe = 0.006 by mass).
(e): measurements conducted at PETC, DOE.

previous contract). However, in order to obtain the desired catalytic performance, additional potassium was added by impregnation to the catalyst from batches 2 and 3, to obtain about 6.5-6.9 pbw of K per 100 pbw of Fe. Results obtained from measurements conducted at different laboratories with the same catalyst batch (S3416-1) are in good agreement.

(2) For catalyst B the potassium content of batches 2 - 5 varies from 5.1 to 7.8 pbw of K per 100 pbw of Fe, and the copper content varies between 4.8 to 5.5 pbw of Cu per 100 pbw of Fe. The copper content of these catalysts is close to the desired nominal value. The potassium content of batches 4 and 5 is slightly higher than the nominal amount, but is comparable to that of the batch-1 catalyst. The silica contents are similar for batches 2 to 4, and comparable to the value obtained for batch-1 catalyst. The silica content (29 pbw of SiO_2 per 100 pbw of Fe) of batch-5 is slightly higher than the nominal value.

(3) A relatively high sodium content in the catalyst S3416-3 is due to the use of washing water which was not purified properly. Its potential impact on catalytic results is expected to be small, since sodium can also serve as an alkali promoter.

Surface areas and pore volumes were measured by physical adsorption of nitrogen at 77 K using Micromeritics Digisorb 2600 instrument, and values obtained are summarized in Table IV-1.1. Surface areas obtained from the single-point BET method on a Micromeritics Pulse Chemisorb 2705 instrument are also included for comparison purposes. Differential pore volume distributions (PSD) obtained by nitrogen adsorption are shown in Figure IV-1.1. From the surface area and pore volume size distribution results, it can be seen that:

(1) The surface areas obtained from the single-point BET method are close to those obtained from the multi-point BET plot (with relative error less than 10 %).

(2) The BET surface areas of catalyst C (for batches from 1 to 4) vary between 245 to 310 m^2/g, and those of catalyst B (for batches from 1 to 5) are between 222 and 299 m^2/g. The maximum variation in BET areas among different batches is about 20%. Also, multiple measurements with the same catalyst (batch-1) were in good agreement.

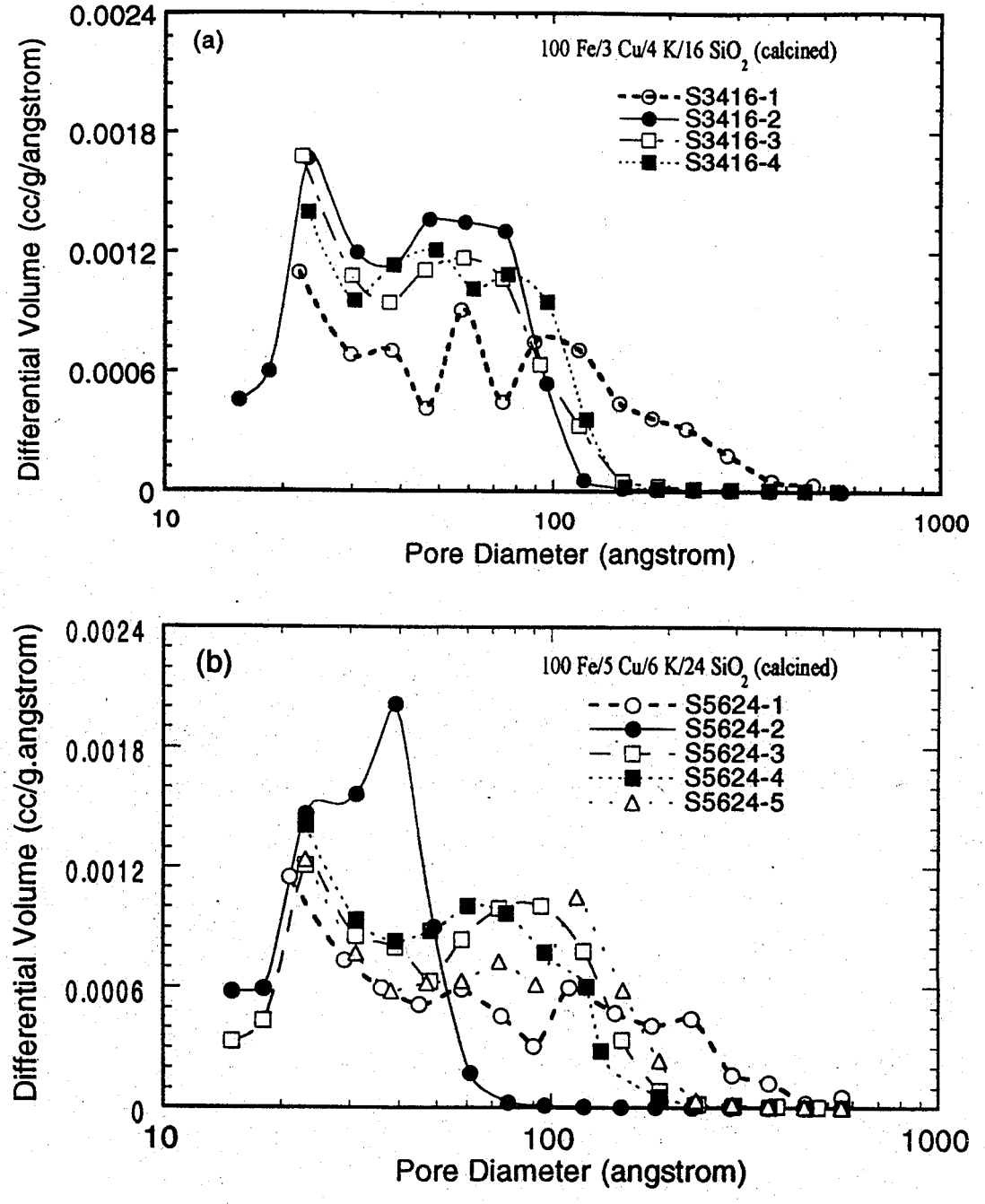


Figure IV-1.1 Pore size distributions of iron catalysts from different batches:(a) Catalyst C (100 Fe/3 Cu/4 K/16 SiO_2) and (b) Catalyst B (100 Fe/5 Cu/6 K/24 SiO_2).

(3) Pore volumes for all new batches (2 - 5) are lower than those of catalysts synthesized during the previous contract (batch-1 in both series), even though the surface areas are similar as indicated.

(4) Pore diameters (Figure IV-1.1) of synthesized catalysts are between 2 and 20 nm. For the catalyst B series, the pore size distributions of catalysts from batches 1 and 5 are similar, and both have two major pore diameters. One is a mesopore with the pore diameter of 2.5 nm, and the other is a macropore with the pore diameter of about 10 nm. However, the pore size distribution of batch-2 catalyst is quite different, and it exhibits a very narrow pore size distribution with dominant pore diameters between 2.5 and 4 nm. For the catalyst C series, all four batches show similar pore size distributions and have two dominant pore diameters. The mesopores are about 2.5 nm in diameter, and the macropores have dominant pore diameters between 4 and 10 nm.

(5) Micropores with pore diameters less than 1.5 nm may exist in the catalysts investigated, but they are beyond the detectable limit of the technique employed.

Reduction Behavior of Catalysts

Reduction behavior of synthesized catalysts was studied in both temperature-programmed mode (TPR method) and isothermal mode of operation. In the latter mode of operation, the temperature was ramped from a room temperature to a desired reduction temperature at a rate of 5°C/min either in helium (TGA unit) or in a mixture of hydrogen and nitrogen (TPR unit), and then held constant.

Temperature Programmed Reduction (TPR)

Temperature-programmed reduction (TPR) studies were performed using a 5% H_2 / 95% N_2 mixture as a reductant. In a typical TPR experiment about 20 mg of catalyst was packed in a quartz reactor and purged with helium to remove the moisture from the catalyst sample. Then the catalyst sample was heated in a flow of 5%H_2/95%N_2 (flow rate = 40 ml/min) from room temperature to 800-900°C at a rate of 20°C/min. The degree of reduction

values are calculated from measured hydrogen consumption, and calibration data with standard CuO sample.

Peak positions (temperature values corresponding to maxima in hydrogen consumption) and degree of reduction values from TPR experiments with catalysts C and B from different batches are summarized in Table IV-1.2. Figures IV-1.2(a) and IV-1.2(b) show the TPR profiles of catalyst C (batch-2 to batch-4) and B (batch-2 to batch-5), respectively. From Figure IV-1.2 it is clear that the reduction of iron oxide proceeds in two steps namely, the reduction of Fe_2O_3 to Fe_3O_4 (first step) and Fe_3O_4 to Fe (second step). For catalyst C samples the first stage reduction peaks are located (Figure IV-1.2a) between 302 to 326°C and the second stage reduction peaks are located between 530 and 585°C. The degree of reduction for the first stage is about 23 - 26%, and total degree of reduction is between 79 and 96% (Table IV-1.2).

Similarly, catalyst B also has two peaks, one at 300 - 315°C and the second one at 570 - 580°C (Figure IV-1.2b). The degree of reduction for the first stage reduction is about 23 - 27% and the total degree of reduction varies between 88 and 98%. It is interesting to note that for both catalysts, B and C, the degree of reduction values for the first stage of reduction (23-27%) are considerably higher than the theoretical value corresponding to the reduction of Fe_2O_3 to Fe_3O_4 (i. e. 12.5%) indicating that part of iron Fe^{2+} is reduced to metallic iron at lower temperatures (300-326°C).

Similarity of peak positions and degree of reduction values of catalysts from different batches is indicative of good reproducibility of catalyst preparation, which was confirmed in stirred tank slurry reactor tests of these catalysts (Section IV-2).

Table IV-1.2 Temperature Programmed and Isothermal Reduction Results with Catalysts B and C from Different Batches

Sample	TPR Peak Position, °C#		Degree of Reduction, (%)		Degree of Reduction, (%) Isothermal Reduction	
	First Stg.	Second Stg.	First stage	Total	TPR unit(*)	TGA unit (**)
100 Fe/3 Cu/4 K/16 SiO_2, S3416-2	320	585	25	87	24	88
100 Fe/3 Cu/4 K/16 SiO_2, S3416-2+K(2)	302	538	23	79	25	70
100 Fe/3 Cu/4 K/16 SiO_2, S3416-3+K(2)	306	530	23	96	25	83
100 Fe/3 Cu/4 K/16 SiO_2, S3416-4	326	576	26	84	23	82
100 Fe/5 Cu/6 K/24 SiO_2, S5624-2	310	578	23	98	22	89
100 Fe/5 Cu/6 K/24 SiO_2, S5624-3	300	580	24	88	24	79
100 Fe/5 Cu/6 K/24 SiO_2, S5624-4	302	570	23	96	21	78
100 Fe/5 Cu/6 K/24 SiO_2, S5624-5	313	570	27	89	24	79

Sample wt = 10 to 20 mg, reducing gas = 5%H_2/95%N_2, flow rate = 40 cc/.min, ramp = 20°C/min, temperature range = room temp to 800°C.

* Sample wt = 400 to 500 mg, reducing gas = 5%H_2/95% N_2, flow rate = 40 cc/min, ramp = 5°C/min, temperature range = room temperature to 280°C and then, maintained at 280°C for 8 h.

** Sample wt = 20 mg, reductant hydrogen, flow rate 40 cc/min, heated in helium flow to 280°C, heating rate = 5°C/min and reduced in hydrogen at 280°C for 8 h.

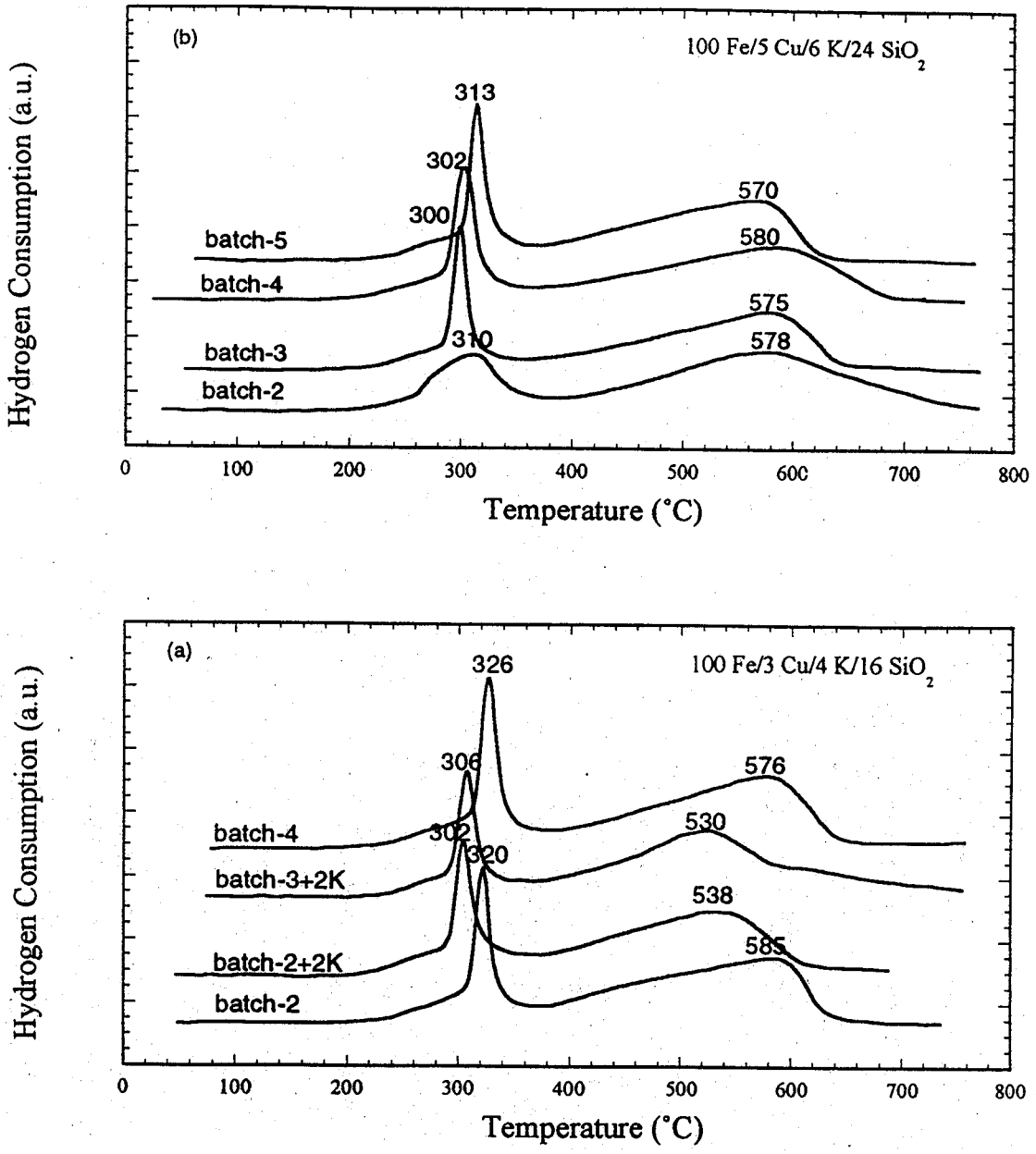


Figure IV-1.2 TPR profiles of iron catalysts from different batches: (a) Catalyst C (100 Fe/3 Cu/4 K/16 SiO_2) and (b) Catalyst B (100 Fe/5 Cu/6 K/24 SiO_2).

Isothermal Reduction Behavior

In isothermal reductions conducted in the TPR unit, the temperature was ramped at a constant rate of 5°C/min to a final temperature of 280°C in a flow of 5%H_2/95%N_2 mixture. Then the catalyst sample was maintained at this temperature for 8 h in a flow of 5% H_2/95% N_2 (40 ml/min). The degree of reduction as a function of time was calculated from measured hydrogen consumption, and calibration with standard CuO sample.

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 280°C. Then the helium flow was switched to hydrogen (99.995% purity) and the temperature was maintained at 280°C for a total period of 8 h. The degree 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.

Figures IV-1.3a and IV-1.3b show the isothermal reduction behavior (in TPR unit) of catalyst C and catalyst B in diluted hydrogen as a function of reduction time. The final degree of reduction values (i.e. at the end of eight hour reduction period) are between 21 and 25% for all catalysts. These values are similar to those obtained for the first stage of reduction in the TPR mode of reduction.

Final degrees of reduction in pure hydrogen (TGA unit) for catalysts B and C were significantly higher than those obtained in 5% hydrogen stream. For example, for catalyst C the final degree of reduction in pure hydrogen varied between 70% (S3416-2+K(2) batch) and 82-85% for all other batches (Figure IV-1.4a), whereas for catalyst B the final degree of reduction in pure hydrogen was 89% (S5624-2 batch), and about 80% for the other three batches (Figure IV-1.4b).

The above results are consistent with the ones obtained during the temperature programmed reduction (Table IV-1.2), and they indicate that there are no significant differences in the reduction behavior among catalysts from different batches.

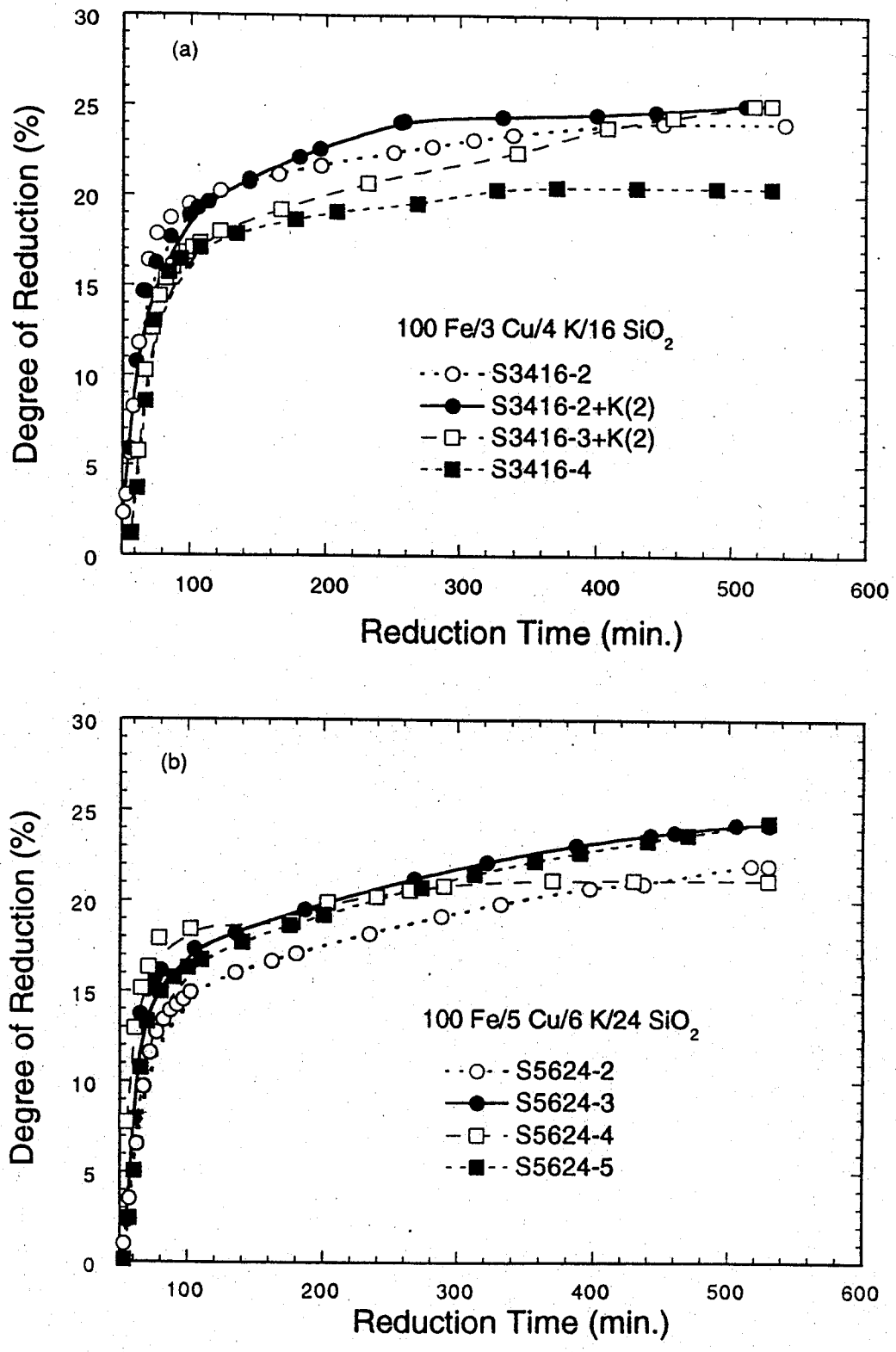
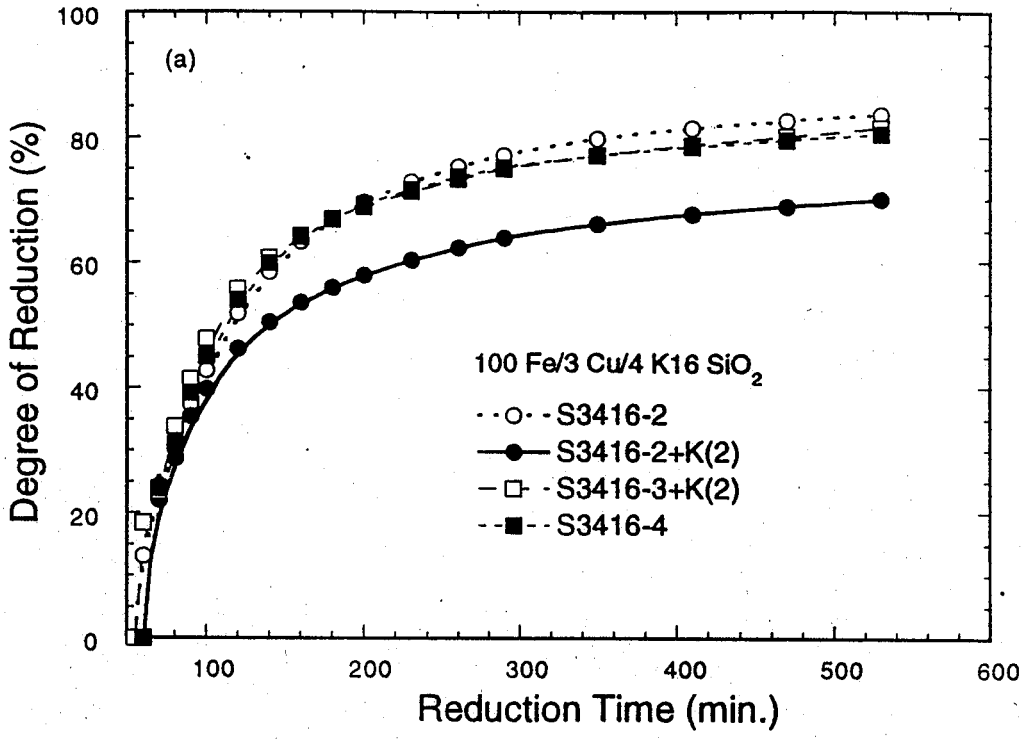


Figure IV-1.3 Isothermal reduction behavior of iron catalysts from different batches (TPR unit): (a) Catalyst C (100 Fe/3 Cu/4 K/16 SiO_2) and (b) Catalyst B (100 Fe/5 Cu/6 K/24 SiO_2).



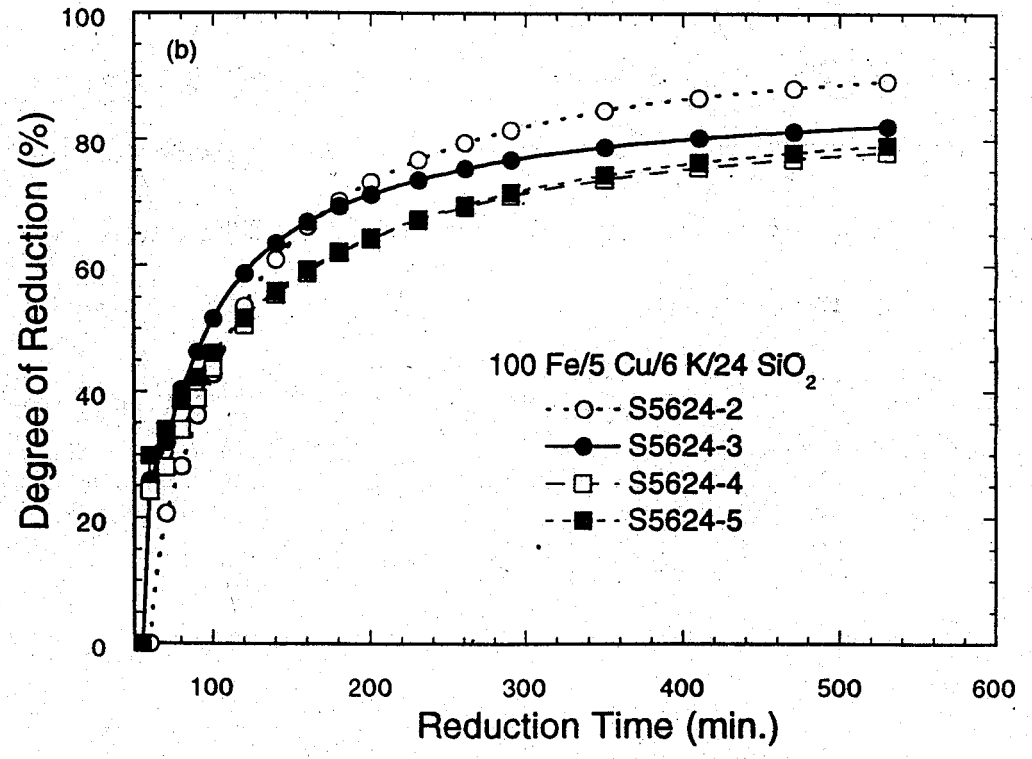


Figure IV-1.4 Isothermal reduction behavior of iron catalysts from different batches (TGA unit): (a) Catalyst C (100 Fe/3 Cu/4 K/16 SiO_2) and (b) Catalyst B (100 Fe/5 Cu/6 K/24 SiO_2).

Iron Phases in Reduced and Used Catalysts

XRD and MES results of pretreated and used catalyst samples are summarized in Tables IV-1.3 and IV-1.4. In general there is a good agreement between XRD and MES results with regard to identity of iron phases in a given sample. Occasional discrepancies in the phase identification are due to the following factors. A significant fraction of iron has not been positively identified by Mössbauer spectroscopy, i. e. it is in the form of small crystallites (less than about 13 nm) which exhibit superparamagnetic behavior at room temperature (Spm phase in Tables IV-1.3 and IV-1.4). On the other hand, XRD can identify phases with crystallites larger than about 4 nm and thus some phases are identified by XRD (e.g. magnetite or metallic iron), but not by MES analysis. Another source of discrepancy, is the difficulty in discriminating between ε'- and χ- carbide with XRD analysis, so that occasionally an iron carbide may be identified as ε'-carbide ($Fe_{22}C$) by XRD analysis, whereas MES analysis identifies this phase as a χ-carbide (Fe_5C_2).

Figure IV- 1.5(a) shows XRD patterns of reduced (in H_2 at 240°C for 2 h and TOS = 0 h) catalyst C from batches 2 to 4. Both magnetite (Fe_3O_4) and α-Fe were identified by XRD in reduced catalysts from preparation batches 2 and 3. The MES results (Table IV-1.3) for these two samples indicate the presence of α-Fe(5-12%), as well as magnetite (7%) for batch-3 catalyst only (SA-2175), and 81% to 95% superparamagnetic (Spm) phase. The catalyst from batch-4 was primarily in the form of magnetite (Figure IV-1-5a and Table IV-1.3). From these results it appears that the catalyst C is not reduced completely and that only a small fraction of iron is in the form of either magnetite or metallic iron.

Figure IV-1.5(b) shows XRD patterns of reduced (in H_2 at 250°C for 4 h and TOS = 0 h) catalyst B from batches 4 and 5. The results indicate that the samples contain poorly crystalline magnetite (Fe_3O_4) and α-Fe suggesting that the particles are too small or less crystalline. However, MES results of these samples show that the reduced

Table IV-1.3 Summary of X-ray Diffraction and MES Analysis of Used Samples (Catalyst C:100 Fe/3 Cu/4 K/16 SiO_2)

Run Number	Catalyst	Time on Stream (TOS), h	Phases Identified by Mössbauer	Phases Identified by XRD
SB-0045	100 Fe/3 Cu/4 K/16 SiO_2 batch-1	400 (EOR)	70% (Spm) and 30% (χ-Fe_5C_2)	Fe_3O_4, ε'-$Fe_{22}C$ and $FeCO_3$
SA-0705	100 Fe/3 Cu/4 K/16 SiO_2 batch-1	526 (EOR)	38% (Spm), 10% ($FeCO_3$) and 52% (χ-Fe_5C_2)	Fe_3O_4, ε'-$Fe_{22}C$ and $FeCO_3$
SB-2695	100 Fe/3 Cu/4 K/16 SiO_2 batch-2	0 142 142 (EOR)	95% (Spm), and 5% (α-Fe) 47% (Spm), 24% (Fe_3O_4), and 29% (ε'-$Fe_{22}C$) 49% (Spm), 23% (Fe_3O_4), and 28% (Fe_5C_2)	Fe_3O_4, and α-Fe Fe_3O_4, and ε'-$Fe_{22}C$ Fe_3O_4, and ε'-$Fe_{22}C$
SA-2715	100 Fe/3 Cu/4 K/16 SiO_2 batch-3	0 138	81% (Spm), 7% (Fe_3O_4), and 12% (α-Fe) 43% (Spm), 13% (Fe_3O_4), and 44% (Fe_5C_2)	Fe_3O_4, and α-Fe Fe_3O_4, ε'-$Fe_{22}C$ and $FeCO_3$
SA-1665	100 Fe/3 Cu/4 K/16 SiO_2 batch-4	500	61% (Spm), 7% (Fe_3O_4), 27% (ε'-$Fe_{22}C$) and 5% (Fe_5C_2)	Fe_3O_4 and ε'-$Fe_{22}C$
SB-2145	100 Fe/3 Cu/4 K/16 SiO_2 batch-4	0 67 145 213 401 402 (EOR)	69 (Spm), and 31% (Fe_3O_4) 48 (Spm), 24% (Fe_3O_4), 14% (ε'-$Fe_{22}C$) and 14% (Fe_5C_2) 63 (Spm) and 37% (ε'-$Fe_{22}C$) 65 (Spm) and 35% (ε'-$Fe_{22}C$) 55 (Spm) and 45% (ε'-$Fe_{22}C$) 54 (Spm), 3% (Fe_3O_4), 39% (ε'-$Fe_{22}C$) and 4% (Fe_5C_2)	Fe_3O_4 Fe_3O_4, and ε'-$Fe_{22}C$ Fe_3O_4, and ε'-$Fe_{22}C$ Fe_3O_4, and ε'-$Fe_{22}C$ Fe_3O_4, and ε'-$Fe_{22}C$ 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 slurry tests with catalyst C (100 Fe/3 Cu/4 K/16 SiO_2) were: T = 260°C, P = 1.48 - 2.17 MPa , H_2/CO = 0.67, SV = 1.4 - 2.1 Nl/g-cat/h.

Table IV-1.4 Summary of X-ray Diffraction and MES Analysis of Used Samples (Catalyst B:100 Fe/5 Cu/6 K/24 SiO_2)

Run Number	Catalyst	Time on Stream (TOS), h	Phases Identified by Mössbauer	Phases Identified by XRD
SB-3064	100 Fe/5 Cu/6 K/24 SiO_2 batch-1	54 (EOR)	73% (Spm) and 27% (Fe_3O_4)	-
SB-0665	100 Fe/5 Cu/6 K/24 SiO_2 batch-1	377 (EOR)	52% (Spm) 46% (ε'-$Fe_{2.2}C$) and 2% (χ-Fe_5C_2)	-
SB-1295	100 Fe/5 Cu/6 K/24 SiO_2 batch-3	353 (EOR)	30% (Spm), 68% (ε'-$Fe_{2.2}C$) and 2% (χ-Fe_5C_2)	Fe_3O_4 and ε'-$Fe_{2.2}C$
SA-2615	100 Fe/5 Cu/6 K/24 SiO_2 batch-4	0 119 119 (EOR)	92 (Spm) and 8% (α-Fe) 83 (Spm) and 17% (ε'-$Fe_{2.2}C$) 74 (Spm) and 26% (ε'-$Fe_{2.2}C$)	Fe_3O_4, and α-Fe Fe_3O_4, and ε'-$Fe_{2.2}C$ Fe_3O_4, and ε'-$Fe_{2.2}C$
SB-2585	100 Fe/5 Cu/6 K/24 SiO_2 batch-5	0 120 120 (EOR)	95% (Spm) and 5% (α-Fe) 75% (Spm), 20% (ε'-$Fe_{2.2}C$) and 5% (χ-Fe_5C_2) 68% (Spm), 27% (ε'-$Fe_{2.2}C$) and 5% (χ-Fe_5C_2)	Fe_3O_4, and α-Fe Fe_3O_4, and ε'-$Fe_{2.2}C$ Fe_3O_4, and ε'-$Fe_{2.2}C$

EOR stands for end of the run sample which was exposed to air; TOS = 0 h means reduced sample.
FTS process conditions for slurry tests with catalyst B (100 Fe/5 Cu/6 K/24 SiO_2) were: T = 260°C, P = 1.48 - 2.17 MPa , H_2/CO = 0.67, SV = 1.4 - 2.1 Nl/g-cat/h.

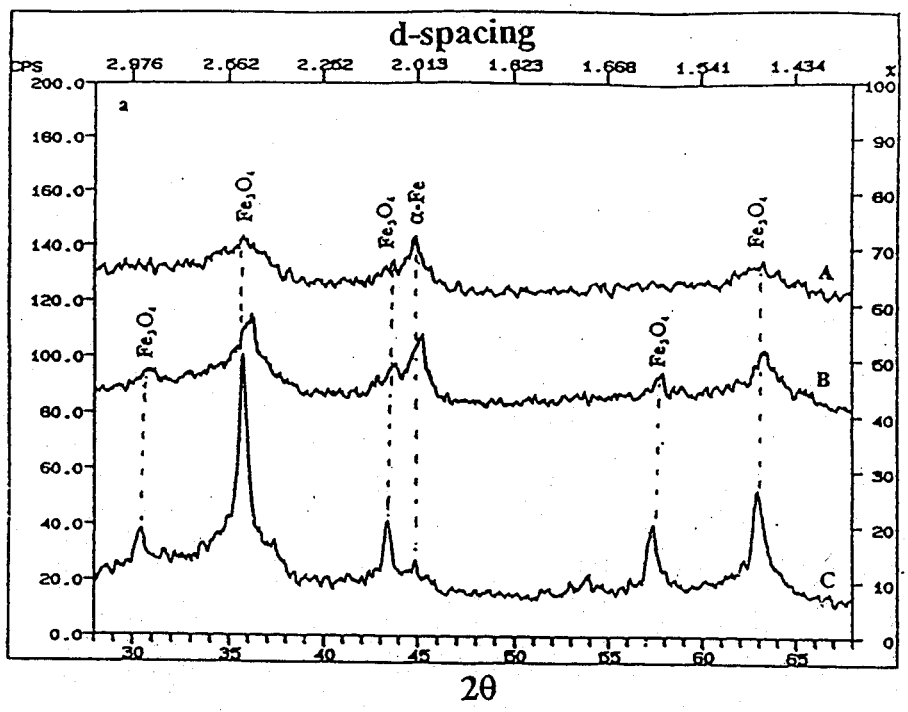


Figure IV-1.5a XRD patterns of reduced (TOS = 0 h) catalysts from slurry tests with catalyst C (100 Fe/3 Cu/4 K/16 SiO_2) from different batches: (A) SB-2695, batch-2; (B) SA-2715, batch-3; and (C) SB-2145, batch-4.

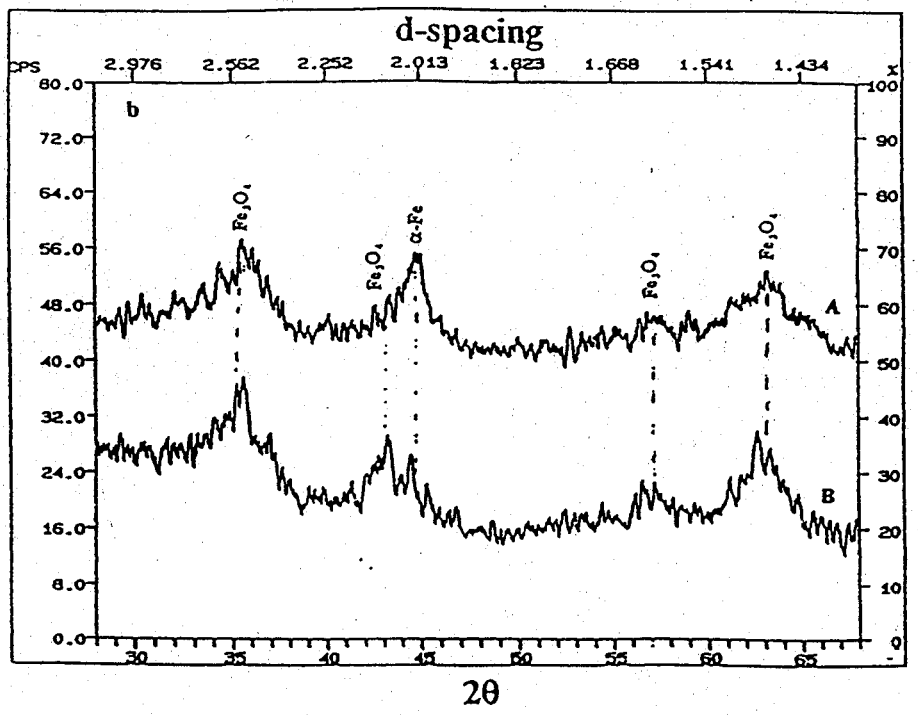


Figure IV-1.5b XRD patterns of reduced (TOS = 0 h) catalysts from slurry tests with catalyst B (100 Fe/5 Cu/6 K/24 SiO_2) from different batches: (A) SB-2615, batch-4; (B) SB-2585, batch-5.

samples contain superparamagnetic (Spm) and α-Fe phases only and no magnetite was detected in the reduced samples by MES.

Figure IV-1.6 illustrates changes in bulk iron phases with time on stream during run SB-2145 with catalyst C from batch-4. Only magnetite was found (Figure IV-1.6a) in the sample withdrawn immediately after the reduction (TOS = 0 h). During the F-T synthesis (Figure IV-1.6b to IV-1.6e) magnetite and ε'-$Fe_{2.2}C$ (pseudo-hexagonal iron carbide) were identified in used catalyst samples. The fraction of magnetite decreased with time (as evidenced by a decrease in size of a peak at about $2\theta = 35$), while the fraction of ε'-carbide phase increased with time on stream (increase in size of a peak at about $2\theta = 43$). During the same period of time, the catalyst activity continued to decline with time on stream (see Section IV-2.2).

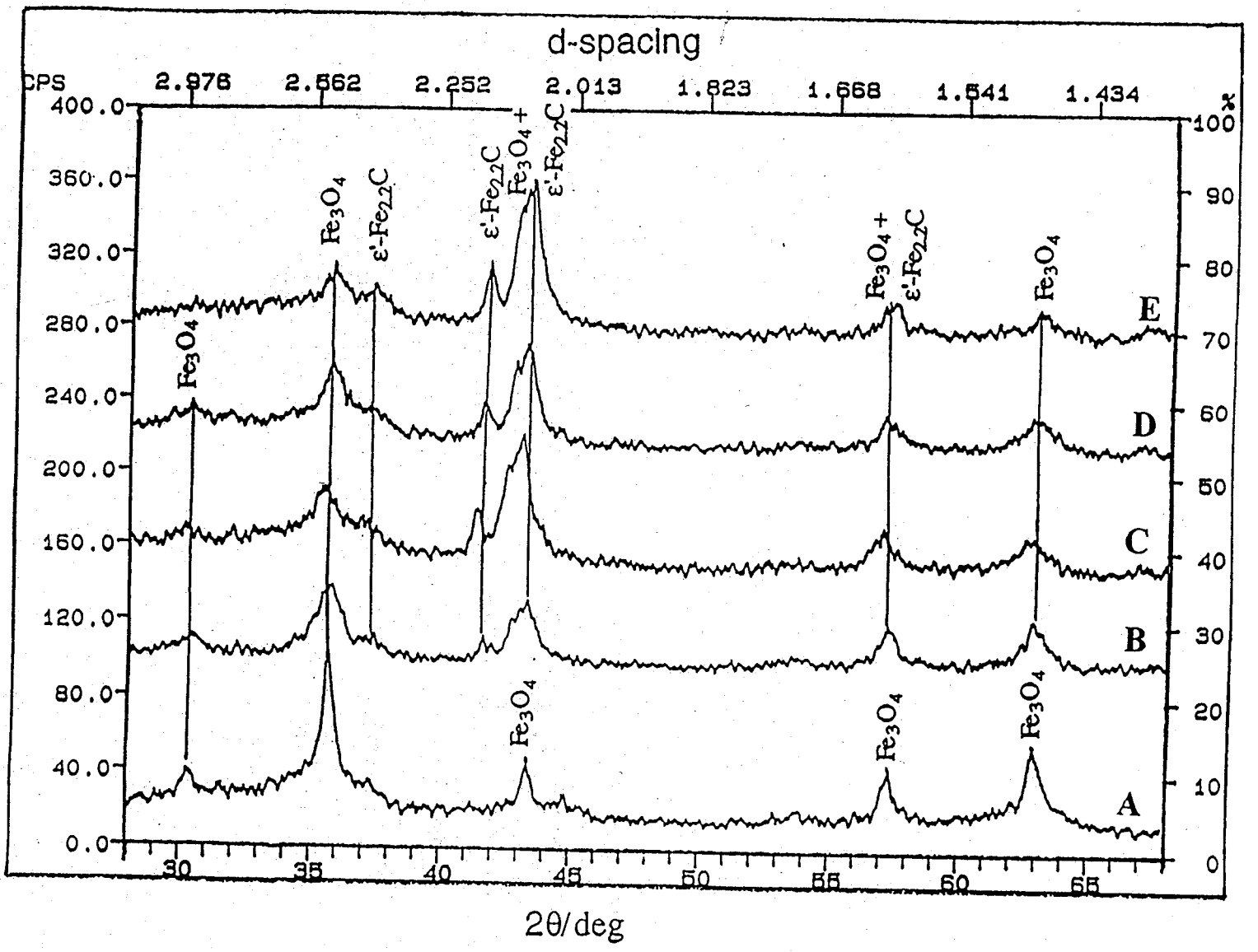


Figure IV-1.6 Changes in bulk iron phases with time on stream during run SB-2145 with catalyst C (100 Fe/3 Cu/4 K/16 SiO_2, batch-4): (A) TOS = 0 h; (B) TOS = 67 h; (C) TOS = 145 h; (D) TOS = 213 h and (E) TOS = 401 h.

IV-2 Reaction Studies

Repeatability of performance of catalysts B and C was demonstrated in multiple tests with catalysts from different preparation batches. Three STSR tests were conducted with catalyst B, and four tests with catalyst C. Results from these tests and comparisons of catalyst performance are described below.

IV-2. 1 Stirred Tank Slurry Reactor Tests of Catalyst B

Three new tests with the catalyst B from batch-3 (run SB-1295), batch-4 (run SA-2615) and batch-5 (run SB-2585) were conducted in slurry reactors. In each of the tests, about 10 g of catalyst with particle size less than 53 μm (270 mesh) was suspended in Durasyn 164 oil (a new trade name for hydrogenated 1-decene homopolymer liquid - C_{30}, obtained from Albemarle Co.) to form a 3.4 wt% slurry. Similar slurry concentrations were used in three tests with the catalyst B from batch-1 (runs SB-1931, SB-3354 and SB-0665). In all six tests, the catalyst was reduced with H_2 at 250°C, 0.8 MPa (100 psig), 4000-7500 cm^3/min for 4 hours. Tests SB-2855 and SA-2615 lasted about 120 h, whereas the remaining tests were of longer durations. Initial catalyst behavior during the first 120 h of testing at 260°C, 1.48 MPa, space velocity of 1.8 Nl/g-cat/h using synthesis gas with molar feed ratio $H_2/CO = 0.67$ will be discussed first, followed by discussion of results obtained in some of the tests which lasted longer than 120 hours.

Comparison of catalyst activity in terms of (H_2+CO) conversion and the apparent first order rate constant, k, obtained in six STSR tests with the 100 Fe/5 Cu/6 K/24 SiO_2 catalyst is given in Figure IV-2.1. Syngas conversions in all six tests are within 10% of the mean value of conversion, i. e. 71 ± 6 %. Catalyst from batch-5 (run SB-2585) was the least active (66-71 % conversion), whereas the catalyst from batch-4 (SA-2615) was the most active (74-77 % conversion). Comparison of catalyst activity in terms of the apparent first order

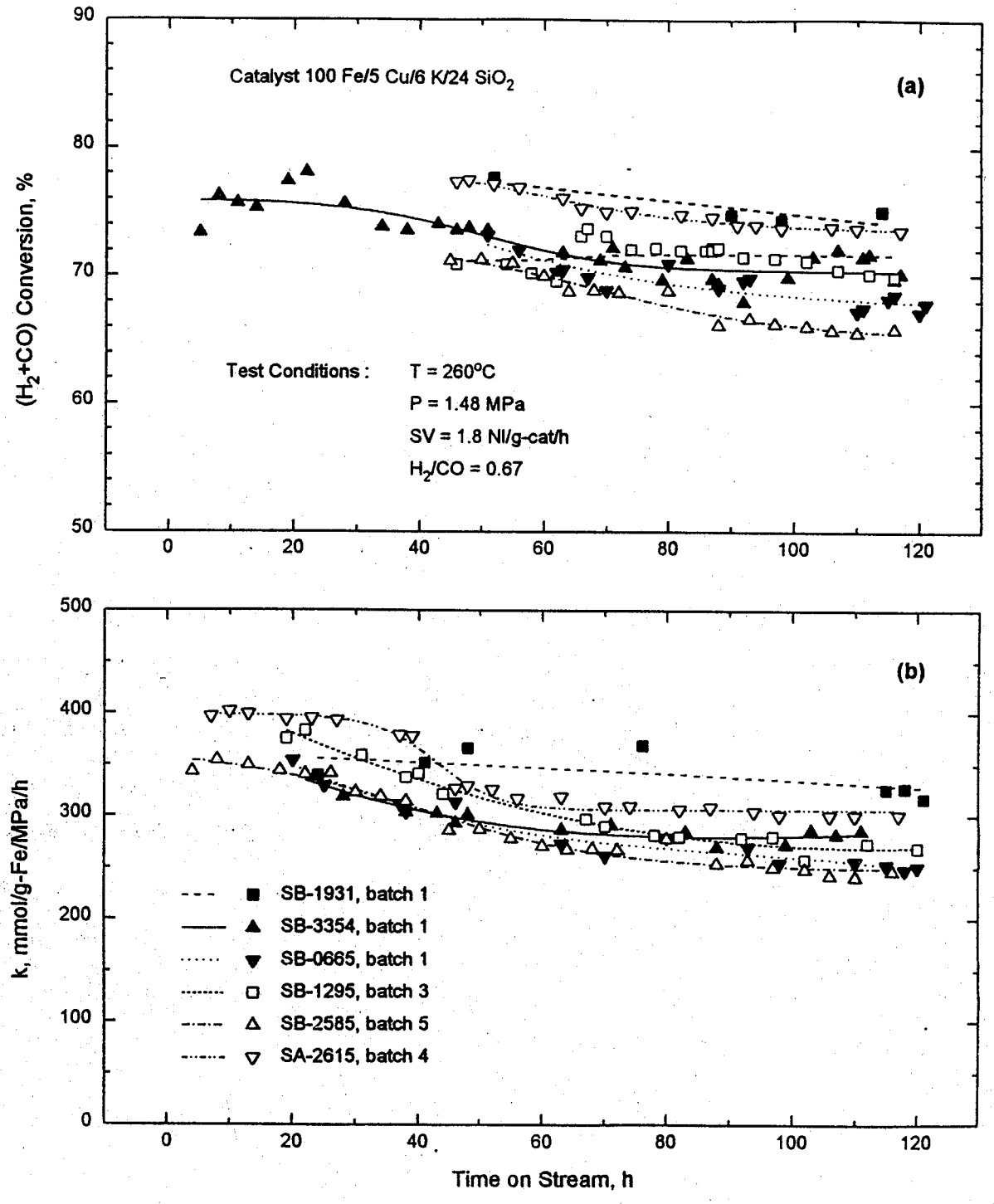


Figure IV-2.1 Synthesis gas conversion (a) and apparent reaction rate constant (b) as a function of time for STSR tests of catalyst B.

reaction rate constant, k, is shown in Figure IV-2.1b. Catalyst deactivation was observed in all six tests. The lowest deactivation rate was obtained in run SB-1931 with batch-1 catalyst, however, this low deactivation rate was not observed in two other tests of the same catalyst (runs SB-3354 and SB-0665). At about 100 h on stream numerical values of the apparent rate constant were between 248 mmol/g-Fe/h/MPa (SB-2585) and 301 mmol/g-Fe/h/MPa (run SA-2615).

Methane and C_1+C_2 selectivities are shown in Figure IV-2.2a and Figure IV-2.2b, respectively. Similar values of selectivities were obtained in all three tests of the catalyst from batch-1 (runs SB-1931, SB-3354, and SB-0665), and in run SB-2585 with batch-5 catalyst, whereas higher values were obtained in tests with batch-3 (SB-1295) and batch-4 (SA-2615) catalysts. A possible reason for higher methane and C_1+C_2 selectivities obtained in run SB-1295 is that potassium content of batch-3 catalyst is lower than that of the other batches (5.2 K per 100 Fe (batch-3) vs. 6.2 - 7.8 K per 100 Fe in other batches). However, the catalyst from batch-4 (SA-2615) had higher potassium loading (6.5 K per 100 Fe) than the catalyst from batch-3, and yet its methane and C_1+C_2 selectivities were higher.

Results from testing at a lower gas space velocity of 1.6 Nl/g-cat/h (the other process conditions being the same as during the first 120 h on stream) are shown in Figures IV-2.3 and IV-2.4. Synthesis gas conversion (i.e. catalyst activity) was fairly stable in all three tests (two with batch-1, and one with batch-3 catalyst) and was between 65 and 75% (Figure IV-2.3). Methane and C_1+C_2 selectivities were also stable with time and varied between 3-4 mol% and 6-8 mol%, respectively (Figure IV-2.4). Catalyst from batch-3 (SB-1295) produced more gaseous hydrocarbons than batch-1 catalyst, which was also observed during the first 120 h of testing (Figures IV-2.2).

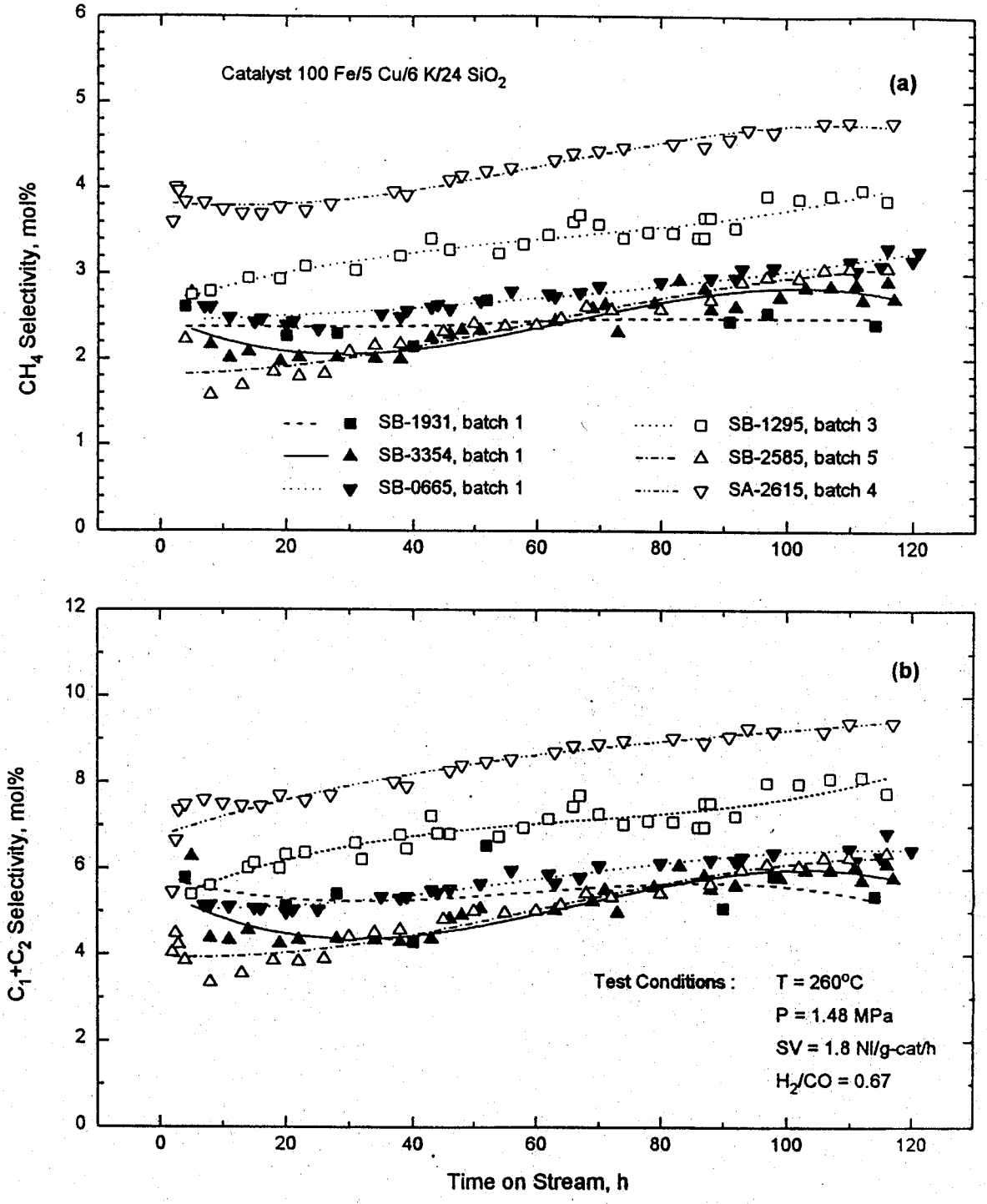


Figure IV-2.2 Methane selectivity (a) and (C_1+C_2) hydrocarbon selectivity (b) as a function of time for STSR tests of catalyst B.

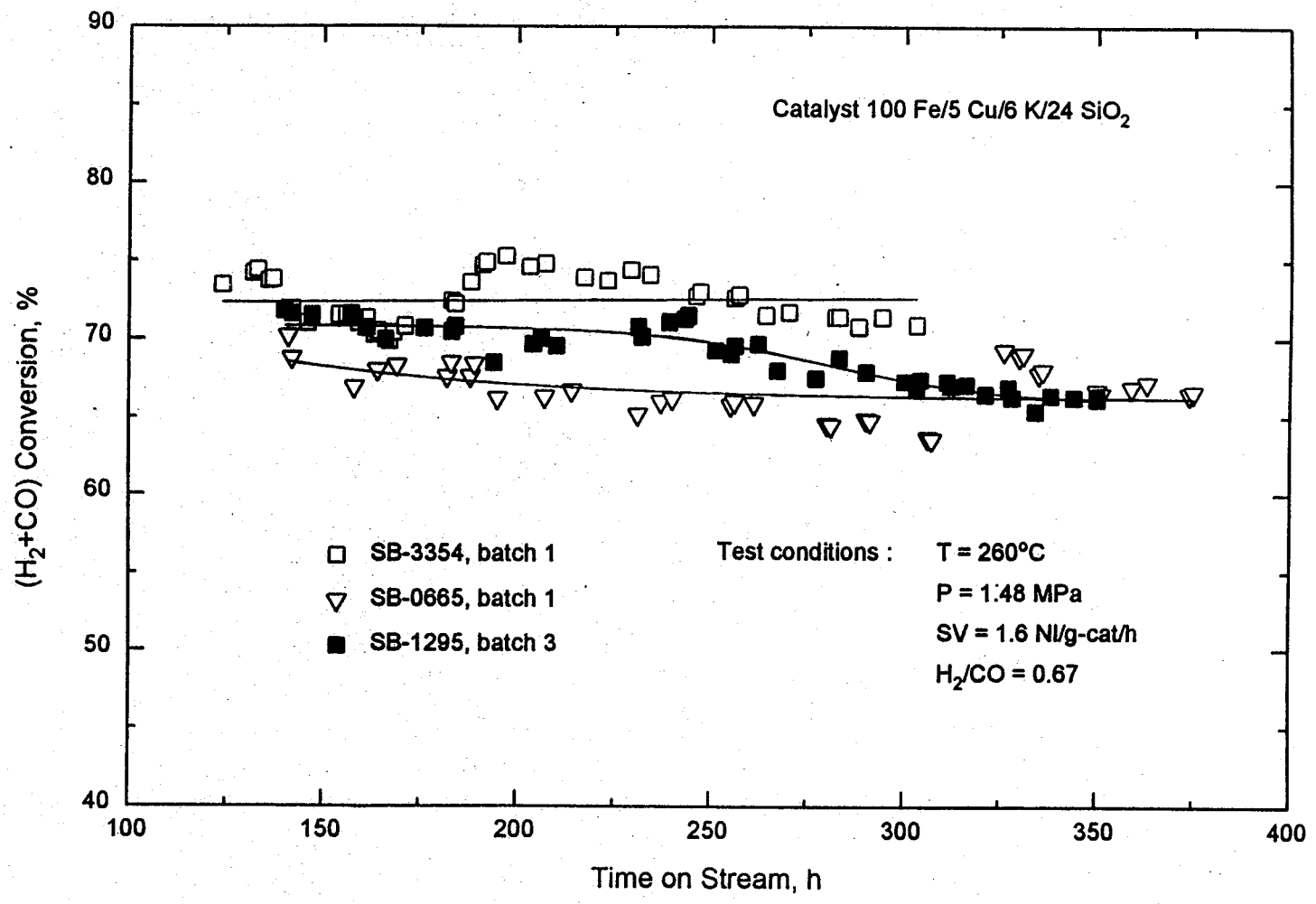


Figure IV-2.3 Synthesis gas conversion as a function of time for STSR tests of catalyst B.

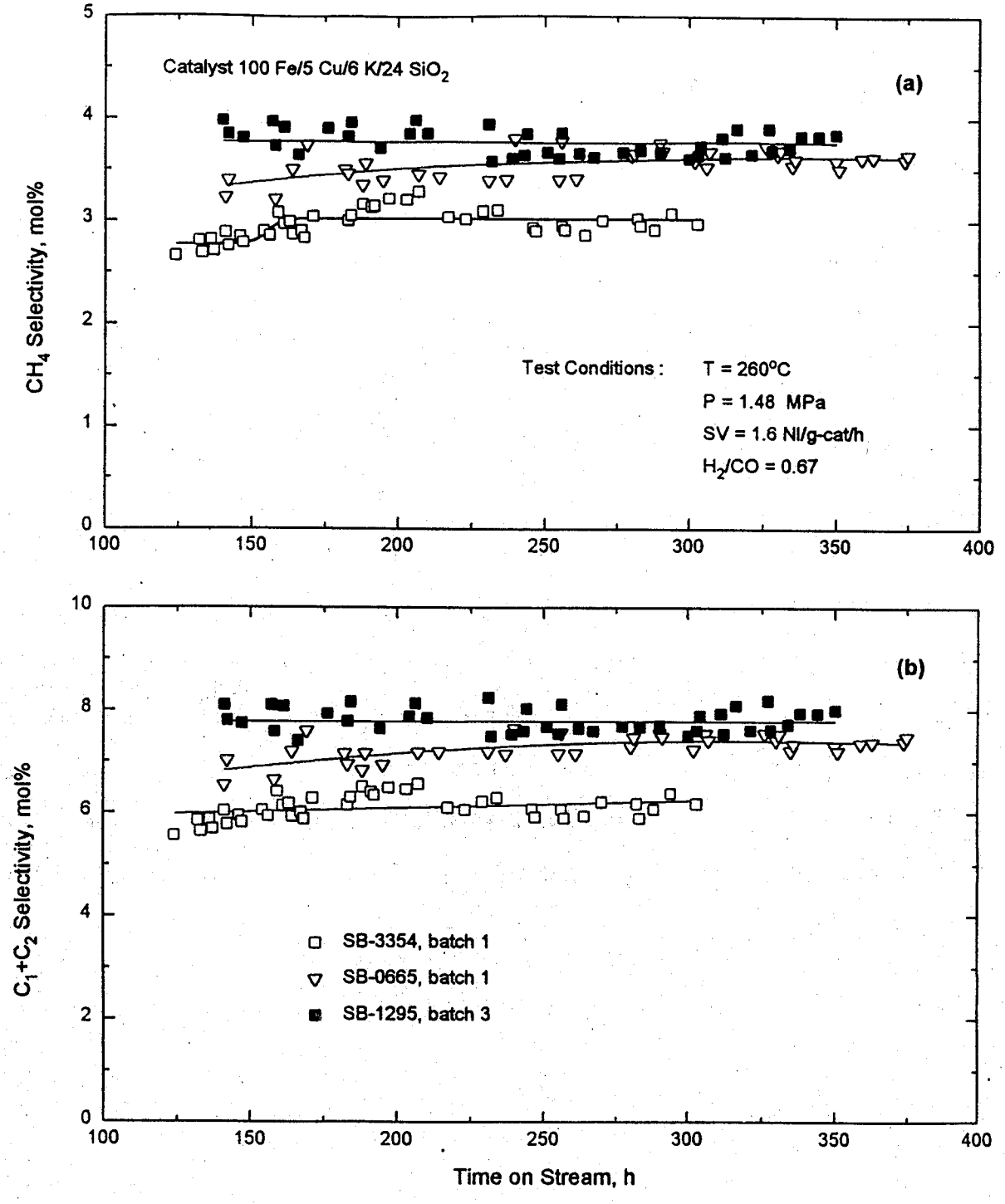


Figure IV-2.4 Methane selectivity (a) and (C_1+C_2) hydrocarbon selectivity (b) as a function of time for STSR tests of catalyst B.

Hydrocarbon Product Distribution

Lumped hydrocarbon distribution, activity parameters and product yields during the first 120 hours of testing of catalyst B from four preparation batches are shown in Table IV-2.1. In runs SB-3354 (batch-1 catalyst) and SB-2585 (batch-5 catalyst) methane and gaseous hydrocarbon (C_2-C_4) selectivities were lower than in other tests. Gasoline fraction (C_5-C_{11} hydrocarbons) was about 22% of total hydrocarbons, and diesel fraction (C_{12}-C_{18} hydrocarbons) varied from 14 to 22%.

Olefin selectivities in tests with catalysts from batches 3-5 were similar to those obtained in tests with batch-1 catalyst (runs SB-1931, SB-3354 and SB-0065). Total olefin content and 2-olefin content dependence on carbon number for three tests with batch-1 catalyst were shown previously in Figure III-2.5.

IV-2. 2 Stirred Tank Slurry Reactor Tests of Catalyst C

About 10 g (runs SB-2695, SA-2715 and SA-1665) or 30 g (in run SB-2145) of catalyst C together with Durasyn 164 oil was loaded to a slurry reactor, so that the slurry concentration was about 3.4 wt% in tests SB-2695 (batch-2 catalyst), SA-2715 (batch-3 catalyst) and SA-1665 (batch-4 catalyst) and about 9.7 wt% in run SB-2145 (batch-4 catalyst). Similar slurry concentrations (2.3-7 wt%) were used in three tests with the catalyst C from batch-1 (runs SB-0261, SB-0045 and SA-0075). Pretreatment conditions (H_2 at 240°C, 0.8 MPa, 7500 cm^3/min for 2 h) were the same in all tests. Results obtained during the first 120 h of testing at 260°C, 1.48 MPa, 1.4 Nl/g-cat/h using synthesis gas with molar feed ratio $H_2/CO = 0.67$ are discussed first, followed by discussion of results obtained in some of the tests which lasted longer than 120 hours.

Catalyst activity was similar in all seven tests. For example, syngas conversions (Figure IV-2.5a) were between 78 and 84 % (i.e., 81 ± 3%), whereas values of the apparent reaction rate constant (Figure IV-2.5b) were between 225 and 290 mmol/g-Fe/h/MPa (mean value of about 250 mmol/g-Fe/h/MPa).

Table IV-2.1 Performance of 100 Fe/5 Cu/6 K/24 SiO_2 Catalyst[a] from Different Batches in Slurry Reactor Tests

Test designation Batch-#	SB-3354 1	SB-0665 1	SB-1295 3	SA-2615 4	SB-2585 5
Test conditions					
Temperature, °C	260	260	260	260	260
Pressure, MPa	1.48	1.48	1.48	1.48	1.48
Space velocity, Nl/g-cat/h [b]	1.8	1.8	1.8	1.8	1.8
Feed H_2/CO ratio	0.67	0.67	0.67	0.67	0.67
Time on stream, h	97	110	122	87	102
CO conversion, %	76.0	71.1	74.3	77.7	69.6
(H_2+CO) conversion, %	71.5	67.0	69.6	73.6	66.0
STY, mmol (H_2+CO)/g-cat/h [b]	57	54	57	59	53
k, mmol/g-Fe/h/MPa [c]	282	284	259	299	248
(H_2/CO) usage ratio	0.57	0.57	0.56	0.58	0.57
$K_p = P_{CO2} \cdot P_{H2}/P_{CO}/P_{H2O}$	27	20	39	22	
% CO converted to CO_2	48.6	47.8	48.9	47.9	48.7
Hydrocarbon selectivity, wt%					
CH_4	3.2	4.1	4.4	5.5	2.9 [d]
C_2-C_4	12.4	15.3	15.6	19.0	12.0 [d]
C_5-C_{11}	18.5	22.9	21.8	23.2	
C_{12}-C_{18}	13.7	22.1	18.4		
C_{12}+	65.9	57.7	58.2	52.3	
C_1+C_2	6.4	8.0	8.3	10.5	6.0 [d]
Yield, g/Nm³(H_2+CO) Converted					
Hydrocarbons	207	193	205	202	
Oxygenates	6.3	9.2	6.9	5.1	
Catalyst productivity, g HC/g-cat/h [b]	0.26	0.23	0.26	0.27	

[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

[d] in mol%

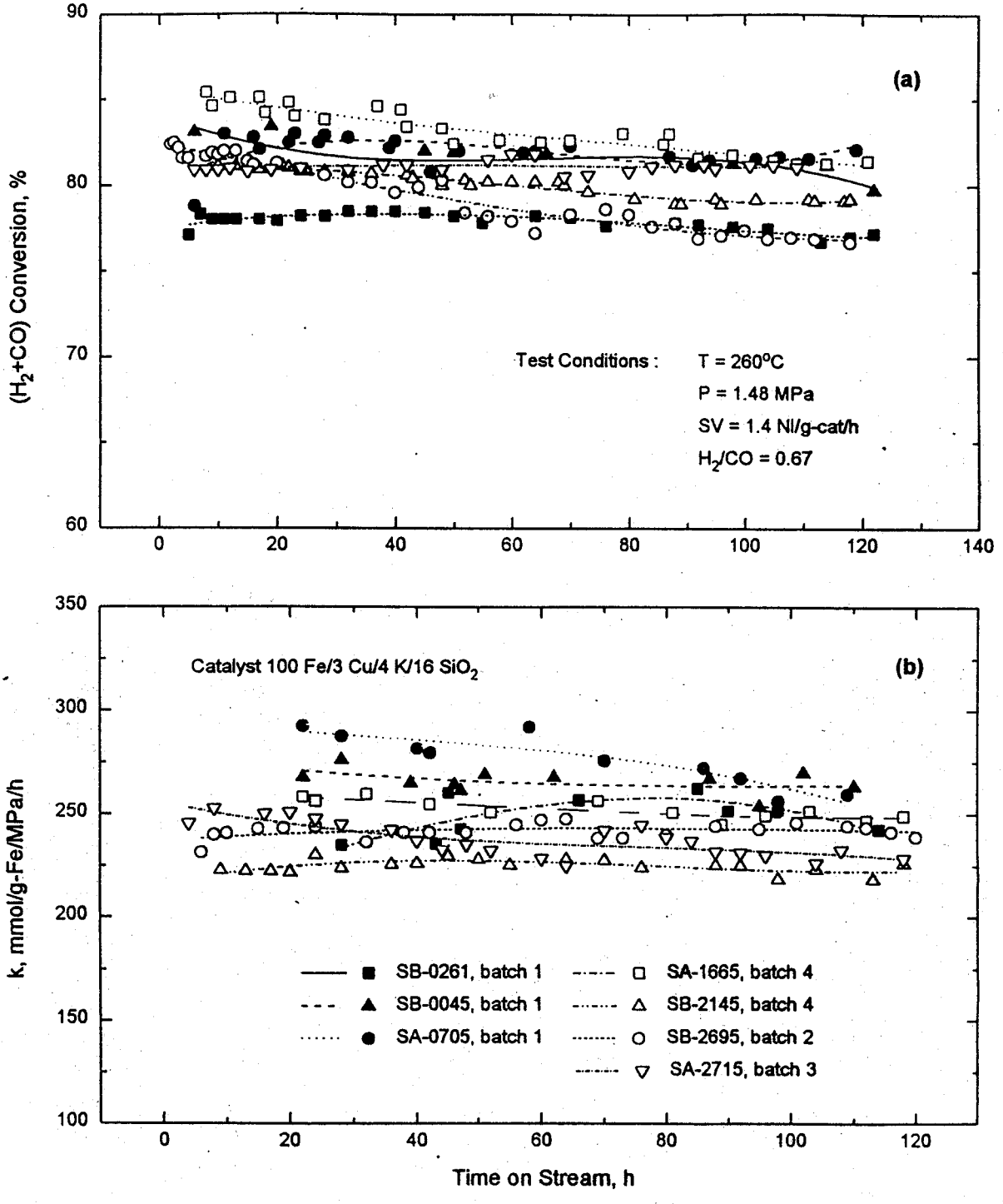


Figure IV-2.5 Synthesis gas conversion (a) and apparent reaction rate constant (b) as a function of time for STSR tests of catalyst C.

Methane (Figure IV-2.6a) and C_1+C_2 selectivities (Figure IV-2.6b) were also similar in all seven tests. At about 100 h on stream, the mean value of methane selectivity from all seven tests is 2.6 %, whereas the minimum value is 2.1 % (SA-2715) and maximum 3.1 % (runs SB-2145 and SA-0705). Also, the mean value of C_1+C_2 selectivity at about 100 h on stream is 5.7 %, whereas the minimum and the maximum are: 4.8 % (SA-2715) and 6.5 % (SA-0705), respectively. Lower methane and gaseous hydrocarbon selectivities obtained in tests with catalysts from batches 1-3, in comparison to the catalyst from batch-4, are consistent with higher potassium loading of these catalysts.

High syngas conversions and low gaseous hydrocarbon selectivities were obtained after 120 h on stream in tests which lasted 400-520 hours (Figures IV-2.7 and IV-2.8). Catalyst from batch-4 (runs SB-2145 and SA-1665) deactivated more rapidly than the catalyst from batch-1 (runs SB-0045 and SA-0075). Methane selectivity was between 2.5 and 3.5 mol% in all four tests, and C_1+C_2 selectivity varied between 5.5 and 7 mol% (Figure IV-2.8).

Hydrocarbon Product Distribution

Lumped hydrocarbon distribution, activity parameters and product yields during the first 120 hours of testing of catalyst C from four preparation batches are shown in Table IV-2.2. Methane and gaseous hydrocarbon (C_2-C_4) selectivities were low in all seven tests, and the fraction of liquid plus wax hydrocarbons (C_5+ hydrocarbons) was greater than 85% of total hydrocarbons produced. Gasoline fraction (C_5-C_{11} hydrocarbons) was about 10-18% of total hydrocarbons, and diesel fraction (C_{12}-C_{18} hydrocarbons) varied from 15 to 18%. The amount of wax produced was significant in all tests, and yields of oxygenates were small.

Olefin selectivities in tests with catalysts from batches 2-4 were similar to those obtained in tests with batch-1 catalyst (runs SB-0261, SB-0045 and SA-0705). Total olefin content and 2-olefin content dependence on carbon number for three tests with batch-1 catalyst were shown previously in Figure III-2.10.

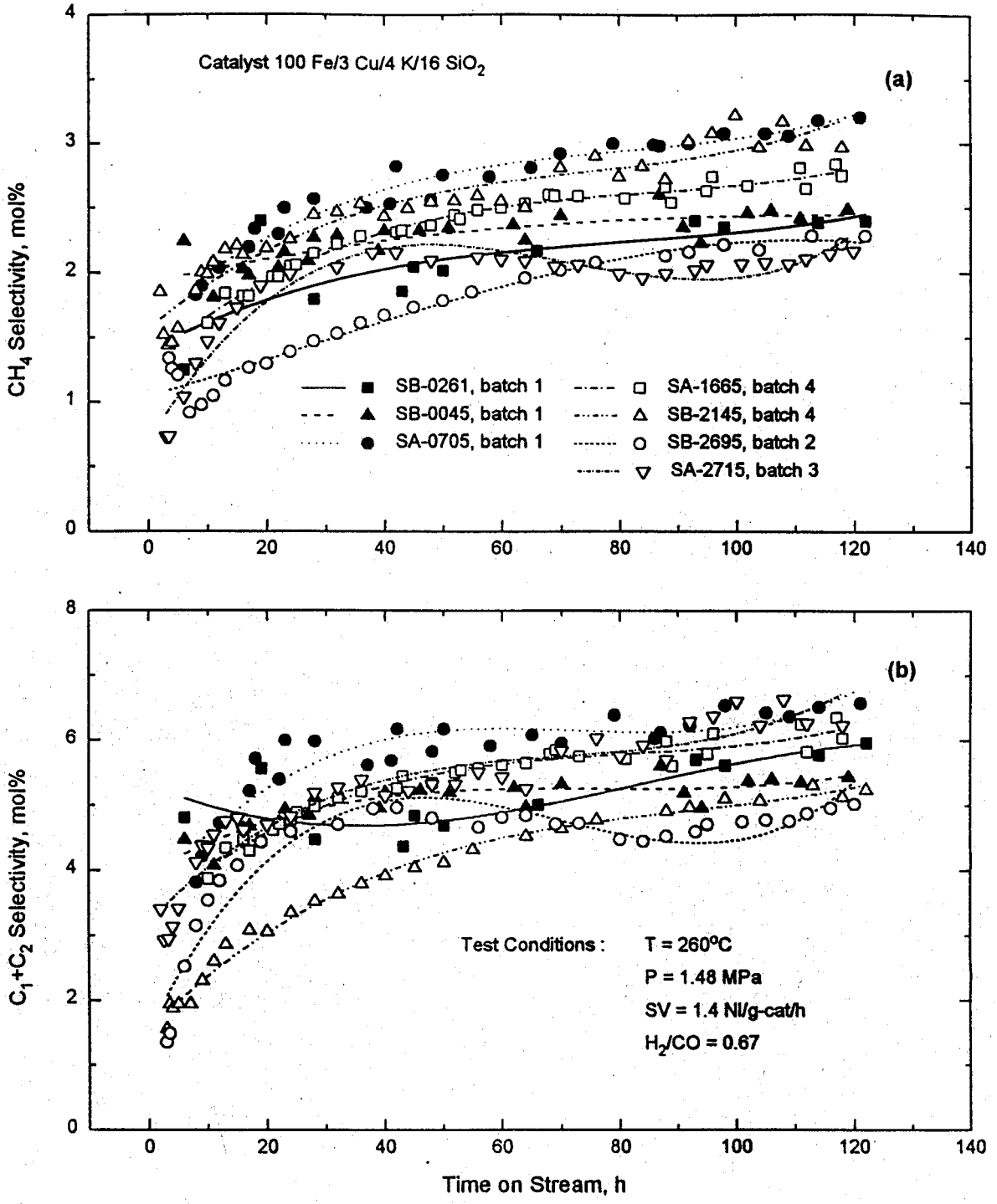


Figure IV-2.6 Methane selectivity (a) and (C_1+C_2) hydrocarbon selectivity (b) as a function of time for STSR tests of catalyst C.

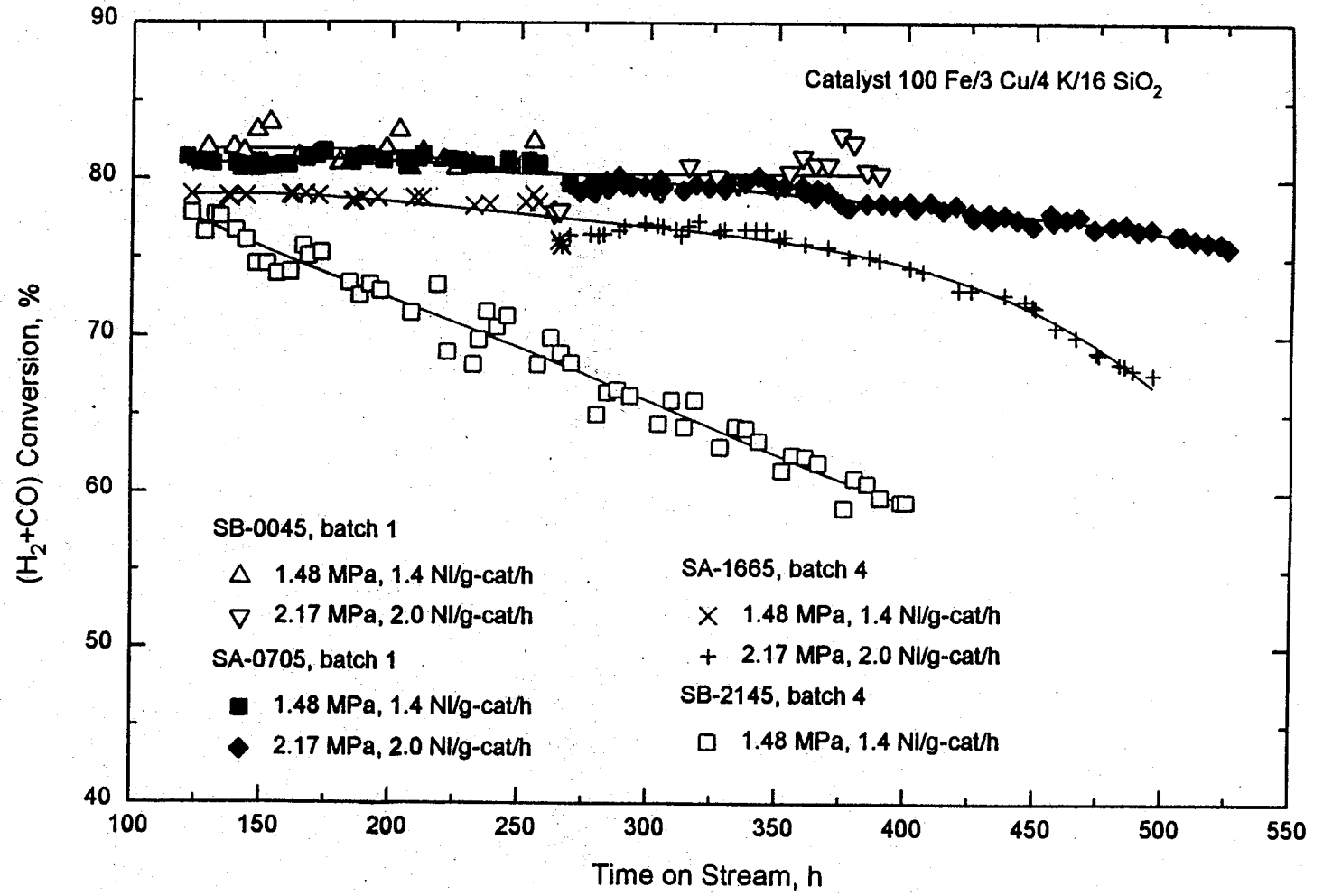


Figure IV-2.7 Synthesis gas conversion as a function of time for STSR tests of catalyst C.

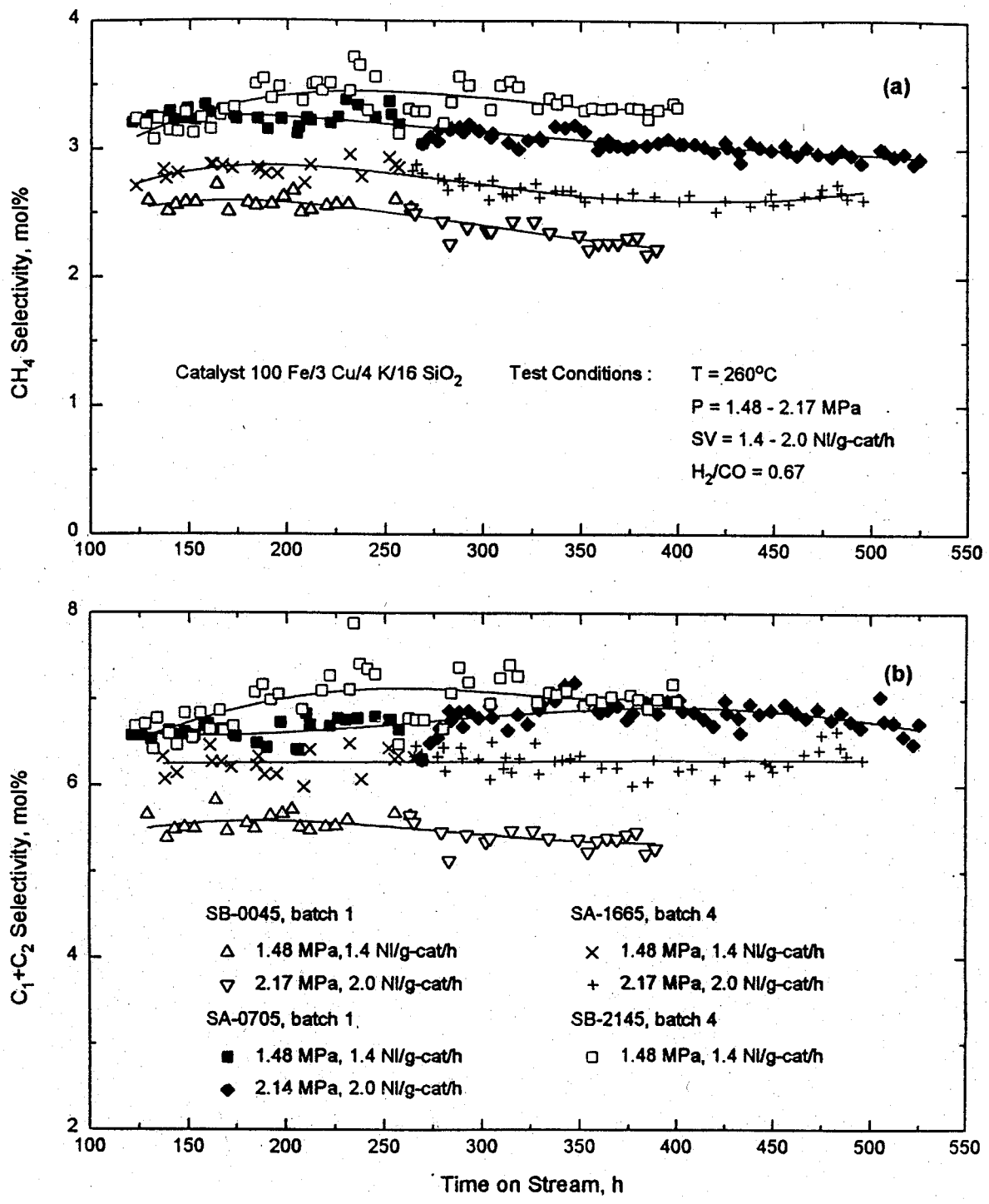


Figure IV-2.8 Methane selectivity (a) and (C_1+C_2) hydrocarbon selectivity (b) as a function of time for STSR tests of catalyst C.

Table IV-2.2 Performance of 100 Fe/3 Cu/4 K/16 SiO_2 Catalyst[a] from Different Batches in Slurry Reactor Tests

Test designation Batch-#	SB-0261 1	SB-0045 1	SA-0705 1	SB-2695 2	SA-2715 3	SA-1665 4	SB-2145 4
Test conditions							
Temperature, °C	260	260	260	260	260	260	260
Pressure, MPa	1.48	1.48	1.48	1.48	1.48	1.48	1.48
Space velocity, Nl/g-cat/h [b]	1.4	1.4	1.4	1.4	1.4	1.4	1.4
Feed H_2/CO ratio	0.67	0.67	0.67	0.67	0.67	0.67	0.67
Time on stream, h	92	95	88	98	88	112	40
CO conversion, %	87.4	87.1	87.5	83.3	87.2	84.1	82.2
(H_2+CO) conversion, %	81.4	81.0	81.4	77.6	81.6	79.0	77.2
STY, mmol (H_2+CO)/g-cat/h [b]	50	51	51	49	50	49	48
k, mmol/g-Fe/h/MPa [c]	251	254	256	218	240	248	222
(H_2/CO) usage ratio	0.57	0.55	0.55	0.55	0.55	0.57	0.56
$K_p = P_{CO2} \cdot P_{H2}/P_{CO}/P_{H2O}$	24	41	36		38	33	37
% CO converted to CO_2	49.2	49.8	48.9	49.1	48.5	48.9	48.4
Hydrocarbon selectivity, wt%							
CH_4	2.7	2.7	3.5	2.2 [d]	2.4	3.2	3.1
C_2-C_4	11.3	10.4	12.5	10.8 [d]	9.3	12.3	11.9
C_5-C_{11}	14.0	13.2	12.3		10.1	12.0	17.7
C_{12}-C_{18}	17.9	14.8					
C_{12}+	70.7	73.5	67.6		78.2	72.6	67.3
C_1+C_2	5.2	5.7	7.1	5.1 [d]	5.2	6.5	6.2
Yield, g/Nm³(H_2+CO) Converted							
Hydrocarbons	197	198	203		201	204	198
Oxygenates	2.2	2.5	2.6		2.5	2.4	3.9
Catalyst productivity, g HC/g-cat/h [b]	0.22	0.23	0.23		0.22	0.22	0.21

[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

[d] in mol%

Concluding Remarks on Tests of Catalysts B and C from Different Batches

In general, catalysts from different preparation batches had similar performance (activity and selectivity) and reproducibility of catalyst preparation procedure is regarded as satisfactory.

Table IV-2.3 summarizes performance of catalysts B and C, and precipitated iron catalysts (Fe-Cu-K) used in Mobil's slurry bubble column reactor and Rheinpreussen's demonstration plant unit. The latter two studies are regarded as the most successful examples of the slurry reactor performance. Process conditions in all tests were similar, with the exception of the use of higher reaction pressure (2.17 MPa) during later periods of two tests with catalyst C.

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 0.39 g HC/g-Fe/h. In Rheinpreussen's demonstration plant unit the C_1+C_2 selectivity was 6.8% at synthesis gas conversion of 89%, and the catalyst productivity was 0.49 g HC/g-Fe/h.

Syngas conversions, methane and C_1+C_2 selectivities obtained in tests with catalysts B and C were similar to those obtained in two tests conducted in slurry bubble column reactors. However, the catalyst productivity in two tests with catalyst C, at 2.17 MPa, was even higher (0.53 or 0.60 g HC/g-Fe/h) than that obtained in Rheinpreussen's test (0.49 g HC/g-Fe/h), whereas at the reaction pressure of 1.48 MPa the catalyst productivity of our catalysts B and C (0.38-0.42 g HC/g-Fe/h) was similar to that obtained in Mobil's study (0.39 g HC/g-Fe/h). Due to complete reactor backmixing in our experiments (stirred tank reactor) it may be expected that the catalyst productivity under the same process conditions would be even higher in a reactor with partial fluid mixing (e.g., bubble column slurry reactor).

Table IV-2.3 Catalyst Performance in Slurry Reactor Tests

Catalyst designation Run ID	B (batch-1) SB-3354	B (batch-3) SB-1295	C (batch-1) SB-0045		C (batch-4) SA-1665		Mobil[a] CT-256-13 Kuo (1985)	Rheinpreussen[a] Kölbel et al. (1955)
Test conditions								
Temperature, °C	260	260	260	260	260	260	257	268
Pressure, MPa	1.48	1.48	1.48	2.17	1.48	2.17	1.48	1.20
Space velocity, Nl/g-Fe/h	3.2	2.9	2.3	3.4	2.3	3.4	2.3	3.1
Feed H_2/CO ratio	0.67	0.67	0.67	0.67	0.67	0.67	0.73	0.67
Time on stream, h	288	243	215	336	220	361	475	
(H_2+CO) conversion, %	74	70.4	80.8	79.9	78.5	75.8	82	89
(H_2/CO) usage ratio	0.57	0.56	0.56	0.57	0.56	0.58	0.59	0.63
Hydrocarbon selectivites, wt%								
CH_4	3.5	4.5	2.9	2.6	3.2	3.0	2.7	3.2[b]
C_2-C_4	12.9	16.3	10.4	10.7	12.2	13.7	11.1	31.3
C_5-C_{11}	19.2	22.9	14.0	14.5	12.8	12.7	18.1	53.6
C_{12}+	64.4	56.2	72.8	72.3	71.9	70.5	68.1	11.9
C_1+C_2	6.9	8.9	5.9	5.7	6.6	6.8	5.6	6.8
Yields								
Nm^3/kg-Fe/h	2.0	2.0	1.9	2.7	1.8	2.6	1.9	2.8
g HC/$Nm^3(H_2+C)$	206	199	207	203	205	205	206	178
g C_3+/$Nm^3(H_2+C)$	192	181	195	191	191	191	195	166
g HC/g-Fe/h	0.42	0.40	0.40	0.60	0.38	0.53	0.39	0.49

[a] Slurry bubble column reactor test.

[b] $CH_4 + C_2H_6$

IV-3 References

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