V The Effect of Source of Potassium and Basic Oxide Promoter

The objective of this task is to determine effects of two different sources of potassium and addition of another promoter on performance of catalysts B and C. In our standard catalyst preparation procedure silicon oxide is introduced by addition of a dilute potassium silicate (K_2SiO_3) solution to the iron/copper precipitate. This procedure introduces potassium in the excess of the desired amount. Potassium is completely removed by washing of the precipitate. Addition of the desired amount of potassium promoter is accomplished via "incipient wetness" method, using $KHCO_3$ dissolved in water. An obvious alternative to the above procedure is to utilize potassium from K_2SiO_3 as the source of potassium, i.e. discontinue with washing when the residual amount of potassium equals the desired amount of promoter. Catalysts B and C were synthesized using potassium silicate as the source of the potassium promoter, and performance of these catalysts was compared with those synthesized using our usual procedure (Section IV-2).

In many of the older German preparation procedures basic oxides such as: MnO, MgO and CaO were used as promoters (Anderson, 1956). In particular, calcium oxide was used as a standard promoter in Ruhrchemie catalysts, and Kölbel stated that CaO increases catalyst activity and possibly causes the increase in molecular weight of the product (Anderson, 1956; p.133). The effect of CaO promotion on the performance of catalysts B and C (two levels of promotion per catalyst) was investigated in this task. Synthesized catalysts were characterized (Section IV-1) and tested first in a fixed bed reactor, and the two most promising catalyst formulations were tested in the STSR (Section IV-2).

V-1 Catalyst Characterization Studies

Six new catalysts (four containing CaO as a promoter, and two using potassium silicate solution as the source of potassium promoter) were synthesized. The synthesized catalyst were characterized by atomic absorption spectroscopy (AAS), BET surface area

(SA) and pore size distribution (PSD) measurements, and reduction behavior under temperature programmed and isothermal conditions.

Elemental Analysis

The CaO containing catalysts were prepared by impregnation of Fe-Cu-SiO_2 precursor from batch-3. For catalyst C series (100 Fe/3 Cu/4 K/x Ca/16 SiO_2) the copper (2.9-3.2 pbw of Cu per 100 pbw of Fe), and calcium (2.2 and 6.3 pbw of Ca per 100 pbw of Fe) contents are close to the nominal amounts (Table V-1.1). Their potassium (4.6-4.8 pbw of K per 100 pbw of Fe) and silica (17-22 pbw of SiO_2 per 100 pbw of Fe) contents are slightly higher than the nominal compositions. Similarly, for catalyst B series (100 Fe/5 Cu/6 K/x Ca/24 SiO_2) the copper, potassium and calcium contents are close to the nominal values but the silica content is higher than the corresponding nominal amount (24 pbw of SiO_2 per 100 pbw of Fe).

Catalysts C (S3416-4-K) and B (S5624-5-K) were prepared from Fe-Cu-SiO_2 precursors from batch-4 and batch-5, respectively, using potassium silicate as the source of both potassium and silicon oxide promoters. The excess potassium was removed by washing of the Fe-Cu-SiO_2 precursors (Appendix 1). Both potassium and silicon oxide contents of these two catalysts were higher than the corresponding nominal amounts.

BET Surface Area and Pore Volume

Surface areas obtained from single-point method are similar to those obtained from the BET plot (multiple point) method (Table V-1.1). Catalysts containing 6 pbw of Ca per 100 pbw of Fe (S3416-3+6 Ca and S5624-3+6 Ca) have surface areas of 73-105 m^2/g, and those containing 2 pbw of Ca per 100 pbw of Fe (S3416-3+2 Ca and S5624-3+2 Ca) have surface areas between 190 and 221 m^2/g, whereas the surface area of the corresponding catalysts without CaO is about 290 m^2/g. The pore volume of the catalysts with 6 parts of Ca per 100 parts of Fe is 0.26-0.30 cm^3/g, whereas the baseline catalysts B and C have pore volumes between 0.43 and 0.51 cm^3/g. These results show that the addition of calcium

Table V-1.1 Effect of Calcium Addition and Source of Potassium on the Textural Properties of Iron Catalysts

Catalyst Code	Amount Prepared (g)	Composition 100 Fe/w Ca x Cu/y K/z SiO_2	BET Surface Area (m^2/g)		Pore Volume cm^3/g
			Single point	BET plot	
S3416-3	173	/ 2.9 / 3.5 / 18	262	291	0.43
S3416-3+2 Ca	12	2.2 / 3.2 / 4.8 / 17	190	190	0.36
S3416-3+6 Ca	13	6.3 / 3.2 / 4.6 / 22	106	105	0.30
S3416-4	215	/ 3.1/ 3.6 / 19	310	306	0.45
S3416-4-K	20	/ 3.2 / 5.6 / 21	312[a]	277	0.41
S5624-3	240	/ 4.8 / 5.2 / 24	258	284	0.51
S5624-3+2 Ca	13	2.2 / 5.5 / 5.0 / 22	224	221	0.46
S5624-3+6 Ca	14	6.1 / 5.1 / 5.3 / 31	100	73.2	0.26
S5624-5	405	/ 5.2 / 7.8 / 29		287	0.54
S5624-5-K	34	/ 5.2 / 6.6 / 30	300[a]	270	0.59

[a] : Catalyst dried at 120°C, others were calcined at 300°C for 5 h.

Nominal (intended) catalyst compositions:

S3416-3-2Ca	100 Fe/2 Ca/3 Cu/4 K/16 SiO_2
S3416-3-6Ca	100 Fe/6 Ca/3 Cu/4 K/16 SiO_2
S5624-3-2Ca	100 Fe/2 Ca/5 Cu/6 K/24 SiO_2
S5624-3-6Ca	100 Fe/6 Ca/5 Cu/6 K/24 SiO_2

decreases the surface area and pore volume of the baseline catalysts and that this effect is more pronounced at a higher level of CaO promotion.

Catalysts C (S3416-4-K) and B (S5624-5-K) prepared from Fe-Cu-SiO_2 precursors from batch-4 and batch-5, respectively, using potassium silicate as the source of both potassium and silicon oxide promoters, have similar surface areas and pore volumes as the baseline catalysts C and B prepared by impregnation of Fe-Cu-SiO_2 precursors with potassium bicarbonate.

Pore Size Distributions

Figures V-1.1(a) and V-1.1(b) show the effect of potassium source on the pore size distribution (PSD) of catalyst C (batch-4) and catalyst B (batch-5). Pore size distributions of the catalysts originating from the same Fe-Cu-SiO_2 precursor are similar.

Figure V-1.2 shows the effect of calcium addition on the pore size distribution of catalysts C and B. It is found that the addition of calcium oxide promoter results in a shift towards larger pores. These results again suggest that the calcium oxide plays significant role in controlling the catalyst structure and texture.

Reduction Behavior

The effect of calcium addition on the reduction behavior of catalyst C (batch-3) is shown in Figure V-1.3(a). The catalyst has two dominant peaks at about 306 and 530°C corresponding to the reduction of Fe_2O_3 to Fe_3O_4 (first stage) and Fe_3O_4 to Fe (second stage), respectively. With the addition of CaO, both reduction peaks shifted to higher temperatures. The first reduction peak is located at about 321°C and the second peak is located at 609°C for the catalyst with 6 pbw of Ca per 100 pbw of Fe. These results indicate that the addition of calcium retards the onset of iron reduction for both stages of the reduction, and causes the broadening of both reduction peaks.

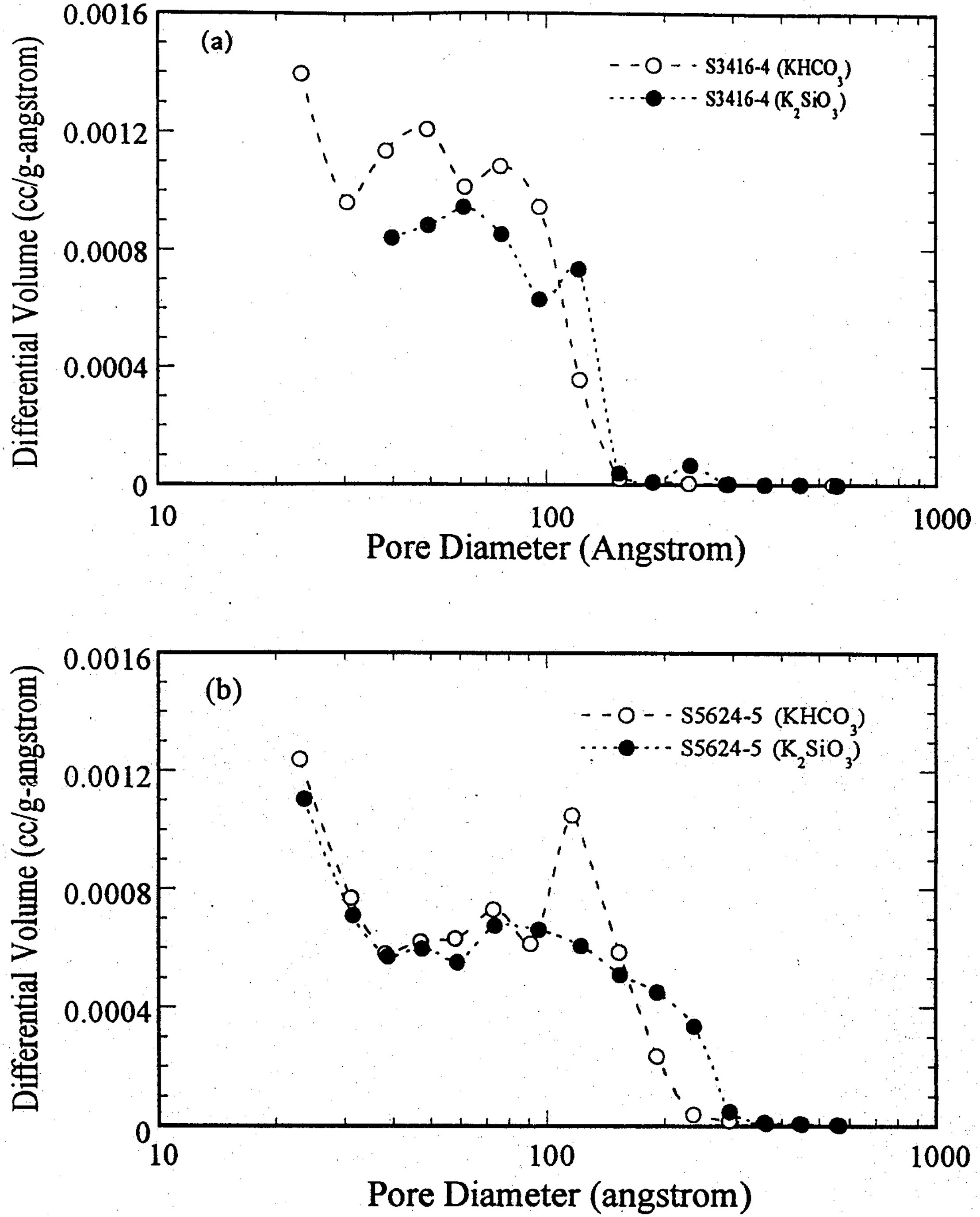
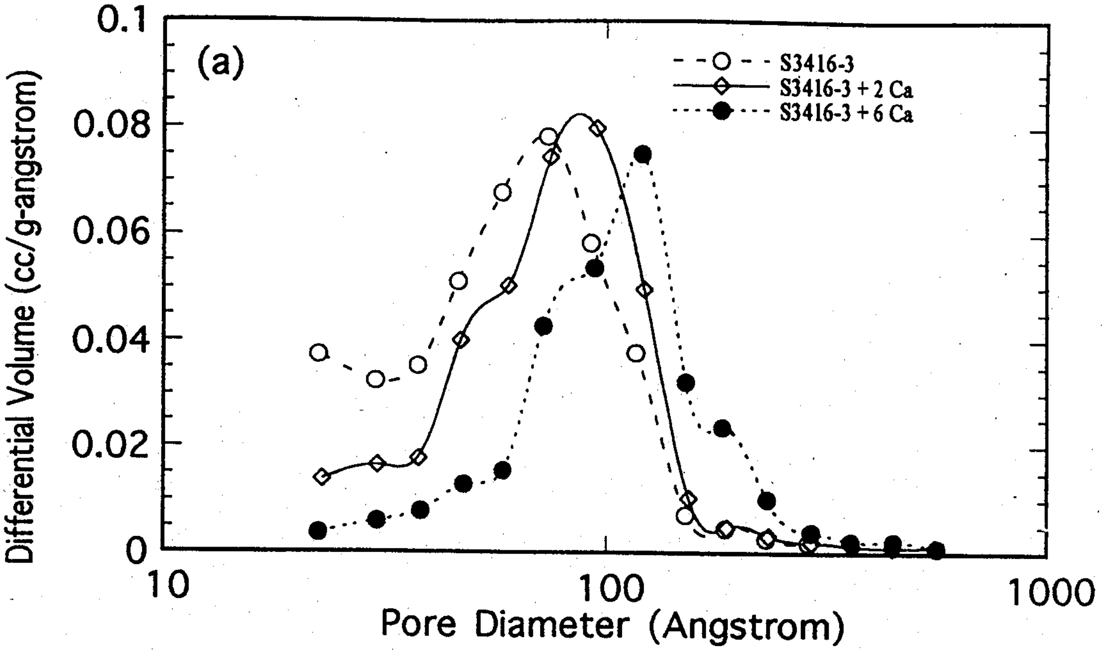


Figure V-1.1 Effect of potassium source on the pore size distributions of (a) Catalyst C (100 Fe/3 Cu/4 K/16 SiO$_2$) and (b) Catalyst B (100 Fe/5 Cu/6 K/24 SiO$_2$).



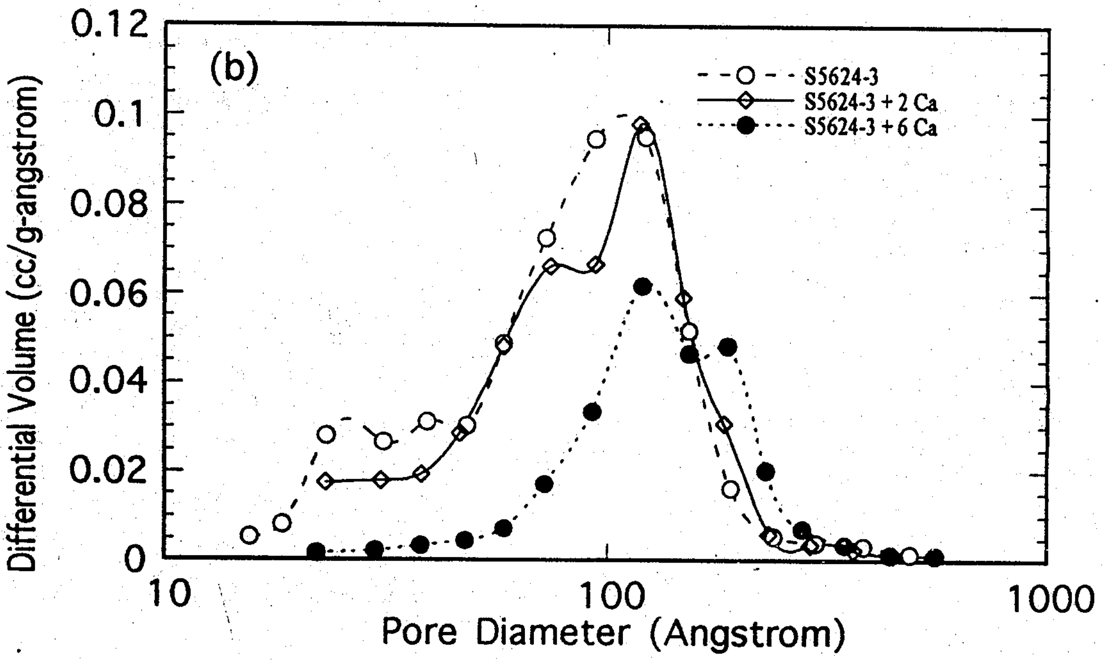


Figure V-1.2 Effect of calcium addition on the pore size distributions of (a) Catalyst C (100 Fe/3 Cu/4 K/16 SiO_2, batch-3) and (b) Catalyst B (100 Fe/5 Cu/6 K/24 SiO_2, batch-3).

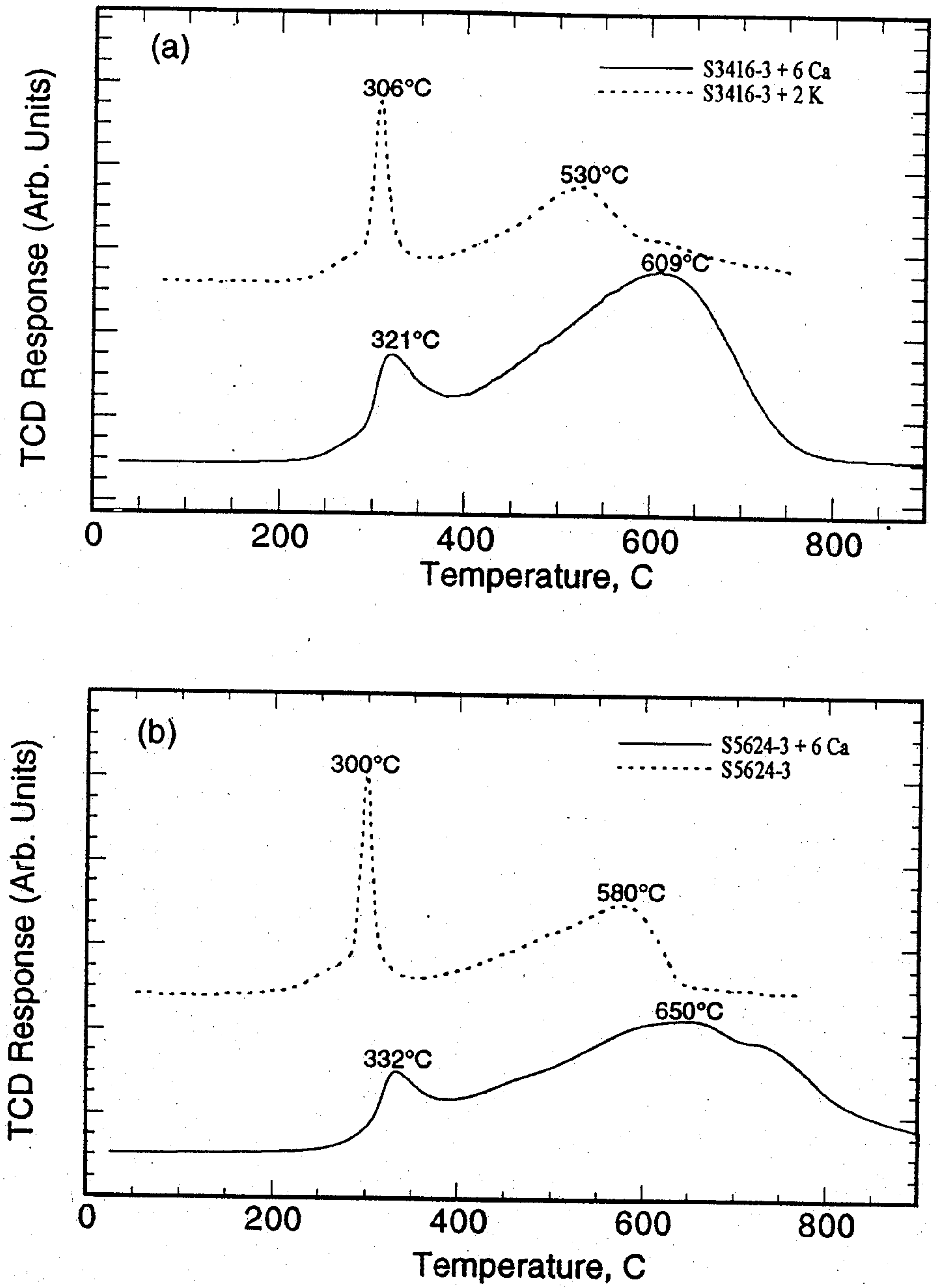


Figure V-1.3 Effect of calcium addition on TPR profiles of catalysts B and C.

Similarly, with catalyst B (batch-3) the reduction peaks are located at about 300°C and 580°C (Figure V-1.3b) corresponding to the first and the second stage of reduction, respectively. In the case of the CaO containing catalyst (S5624-3+6 Ca) the peak positions are shifted to higher temperatures (at 332°C and 650°C). These results suggest that the addition of calcium retards the reduction of iron oxide.

Isothermal reduction experiments were conducted in thermal gravimetric (TGA) unit with pure hydrogen as reductant at 280°C for 8 hours. The final degree of reduction values of catalysts C and B, without CaO promoter, were significantly higher (83 and 79%) than the corresponding values obtained with catalysts containing 6 pbw of Ca per 100 pbw of Fe (68 and 49%). These results confirm that the addition of CaO inhibits reduction of iron in baseline catalysts C and B. In the temperature programmed mode of reduction, the final degree of reduction (at 800°C) values were between 88 and 96% for all four catalysts (Table V-1.2).

Iron Phases in Used Catalysts

Used catalyst samples from studies on the effect of source of potassium promoter and addition of CaO promoter in fixed bed and slurry reactors were analyzed by XRD and MES and results are summarized in Table V-1.3.

Used catalysts B and C, without CaO promoter, from fixed bed reactor tests contained only ε'-$Fe_{2.2}C$ (samples from both top and bottom portions of the reactor). In two tests with catalysts containing 6 pbw of Ca per 100 pbw of Fe (FA-1705 and FB-1515) magnetite and ε'-carbide were identified by both XRD and MES analysis. Activity of the catalysts containing 6 pbw of Ca per 100 pbw of Fe was markedly lower than that of the baseline catalysts B and C (Section V-2.1).

In slurry reactor tests SB-3155 (100 Fe/3 Cu/4 K/2 Ca/16 SiO_2 catalyst) and SA-2405 (100 Fe/5 Cu/6 K/2 Ca/24 SiO_2 catalyst) both magnetite and ε'-carbide were identified by

Table V-1.2 Effect of Calcium Addition on the Reduction Behavior of Catalysts B and C

Catalyst	Reduction Temperature Range, °C	Peak Position, °C##		Degree of Reduction, (%)		Degree of Reduction, (%)
		1st Stage	2nd Stg.	1st stage	Total	Isothermal TGA unit
100 Fe/3 Cu/6 K/16 SiO_2 S3416-3+2 K	RT to 800	306	530	23	96	83
100 Fe/3 Cu/4 K/6 Ca/16 SiO_2 S3416-3+6 Ca	RT to 1000	321	609	16	96 (92)#	68
100 Fe/5 Cu/6 K/24 SiO_2 S5624-3	RT to 800	300	580	24	88	79
100 Fe/5 Cu/6 K/6 Ca/24 SiO_2 S5624-3+6 Ca	RT to 1000	316	645	12	100 (90)#	49

\# The value in the parenthesis represent the %DR value calculated for the reduction temperature range of RT to 800°C.

\## 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.

Table V-1.3 Iron Phases in Used Catalysts from Fixed Bed and Slurry Reactor Tests

Run Number	Catalyst	Time on Stream (TOS), h	Phases Identified by Mössbauer	Phases Identified by XRD
FA-1605	100 Fe/3 Cu/4 K/16 SiO_2 S3416-4, $KHCO_3$ source	120 (top)	49% (Spm) and 51% (ε'-$Fe_{2.2}C$)	ε'-$Fe_{2.2}C$
		120 (bot)	50% (Spm) and 50% (ε'-$Fe_{2.2}C$)	ε'-$Fe_{2.2}C$
FB-1985	100 Fe/3 Cu/4 K/16 SiO_2 S3416-4, K_2SiO_3 source	120 (top)	53% (Spm) and 47% (ε'-$Fe_{2.2}C$)	ε'-$Fe_{2.2}C$
		120 (bot)	49% (Spm) and 51% (ε'-$Fe_{2.2}C$)	ε'-$Fe_{2.2}C$
SB-3115	100 Fe/3 Cu/4 K/2 Ca/ 16 SiO_2 S3416-3+2 Ca	354	49% (Spm), 8% (Fe_3O_4) and 42% (ε'-$Fe_{2.2}C$)	Fe_3O_4 and ε'-$Fe_{2.2}C$
FA-1525	100 Fe/3 Cu/4 K/2 Ca/ 16 SiO_2 S3416-3+2 Ca	120 (EOR)	-	ε'-$Fe_{2.2}C$
FB-1515	100 Fe/3 Cu/4 K/6 Ca/ 16 SiO_2 S3416-3+6 Ca	140 (top)	44 (Spm), 9% (Fe_3O_4) and 47% (ε'-$Fe_{2.2}C$)	Fe_3O_4, and ε'-$Fe_{2.2}C$
		140 (bot)	40 (Spm), 16% (Fe_3O_4) and 44% (ε'-$Fe_{2.2}C$)	Fe_3O_4, and ε'-$Fe_{2.2}C$
FB-1715	100 Fe/5 Cu/6 K/24 SiO_2 S5624-3, $KHCO_3$ source	119 (top)	40% (Spm) and 60% (ε'-$Fe_{2.2}C$)	ε'-$Fe_{2.2}C$
		119 (bot)	42% (Spm) and 58% (ε'-$Fe_{2.2}C$)	ε'-$Fe_{2.2}C$
FA-1795	100 Fe/5 Cu/6 K/24 SiO_2 S5624-5, K_2SiO_3 source	120 (top)	34% (Spm) and 66% (ε'-$Fe_{2.2}C$)	ε'-$Fe_{2.2}C$
		120 (bot)	34% (Spm) and 66% (ε'-$Fe_{2.2}C$)	ε'-$Fe_{2.2}C$
SA-3155	100 Fe/5 Cu/6 K/24 SiO_2 S5624-5, K_2SiO_3 source	0	79% (Spm) and 21% (α-Fe)	Fe_3O_4, and α-Fe
		400	62% (Spm) and 34% (ε'-$Fe_{2.2}C$)	ε'-$Fe_{2.2}C$
SA-2405	100 Fe/5 Cu/6 K/2 Ca/24 SiO_2 S5624-3+2 Ca	0	81% (Spm) and 19% (α-Fe)	Fe_3O_4, and α-Fe
		550	44% (Spm), 6% (Fe_3O_4), 40% (ε'-$Fe_{2.2}C$) and 10%(χ-Fe_5C_2)	Fe_3O_4, and ε'-$Fe_{2.2}C$
		693	58% (Spm), 39% (ε'-$Fe_{2.2}C$) and 3% (χ-Fe_5C_2)	Fe_3O_4, and ε'-$Fe_{2.2}C$
		693 EOR	50% (Spm), 45% (ε'-$Fe_{2.2}C$) and 5% (χ-Fe_5C_2)	Fe_3O_4, and ε'-$Fe_{2.2}C$
FA-1705	100 Fe/5 Cu/6 K/6 Ca/24 SiO_2 S5624-3+6 Ca	120 (top)	43% (Spm), 22% (Fe_3O_4) and 35% (ε'-$Fe_{2.2}C$)	Fe_3O_4, and ε'-$Fe_{2.2}C$
		120 (bot)	26% (Spm), 33% (Fe_3O_4) and 41% (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 were: T = 260°C, P = 1.48 - 2.17 MPa , H_2/CO = 0.67, SV = 1.4 - 2.2 Nl/g-cat/h.
FTS process conditions for fixed bed tests were: T = 250°C, P = 1.48 MPa , H_2/CO = 0.67, SV = 2.0 Nl/g-cat/h.

XRD, whereas MES analysis of samples from run SA-2405 at 693 h reveals the presence of ε'-carbide (39%), small amount of χ-Fe_5C_2 (3%), and significant amount of an iron phase exhibiting superparamagnetic behavior (58% Spm). At least a portion of the latter phase is magnetite (small crystallites less than about 10 nm in diameter). Bulk iron composition of the sample which was exposed to air (EOR) in run SA-2405 is very similar to that of the sample withdrawn from the reactor at 693 hours without exposure to air.

V-2 Reaction Studies

Eight fixed bed reactor tests were conducted; two with baseline catalysts B and C; two with catalysts B and C prepared using potassium silicate as the source of potassium promoter, and four with catalysts containing CaO promoter. On the basis of results from fixed bed reactor tests, three catalysts were selected for testing in slurry reactors. Two of these tests were made with catalysts containing CaO promoter (runs SA-2405 and SB-3115) and one with the catalyst B prepared using potassium silicate as the source of potassium promoter (SA-3155). Nominal catalyst compositions, test and catalyst codes, as well as the general purpose of each of these tests are given in Table V-2.1.

V-2. 1 Fixed Bed Reactor Tests of Modified Catalysts B and C

Four of the synthesized catalysts containing CaO promoter, and two catalysts prepared using potassium silicate as the source of potassium promoter were tested in a fixed bed reactor to determine their activity and selectivity during Fischer-Tropsch synthesis. About 3 g of the catalyst (30 to 60 mesh particle size) diluted 1:7 (reactor B) or 1:9 (reactor A) by volume with glass beads (the same size as the catalyst) was used in fixed bed reactor tests. Prior to F-T synthesis the catalysts were reduced in-situ with hydrogen at atmospheric pressure, 7500 cm^3/min and either 240°C for 2 h (catalysts containing 16 parts of SiO_2 per 100 parts of Fe on a mass basis), or 250°C for 4 h (catalysts containing 24 parts of SiO_2 per 100 parts of Fe on a mass basis). After the conditioning period of about 24 h, during which the reaction temperature was gradually increased from 210 to 250°C, all catalysts were tested at : 250°C, 1.48 MPa (200 psig), 2 Nl/g-cat/h using syngas with H_2 to CO molar feed ratio of about 0.67. Test duration was 120 - 140 h including the conditioning period.

Performance of catalysts having 16 parts by weight (pbw) of SiO_2 per 100 pbw of Fe and containing either CaO promoter (runs FA-1525 and FB-1515), or being prepared using K_2SiO_3 as the source of potassium (FB-1895) is compared with that of the baseline catalyst (catalyst C from batch 4; run FA-1605) in Figures V-2.1 and V-2.2. The syngas conversions

Table V-2.1 Fixed Bed and Stirred Tank Slurry Reactor Tests of Catalysts under Task 5

Test Code	Catalyst Composition / Catalyst Code	Test purpose
FA-1605	100 Fe/3 Cu/4 K/16 SiO_2 S3416-4	Baseline catalyst
FB-1895	100 Fe/3 Cu/4 K/16 SiO_2 S3416-4-K	Effect of potassium source Fixed bed test
FA-1525	100 Fe/3 Cu/4 K/2 Ca/16 SiO_2 S3416-3-2Ca	Effect of CaO promoter Fixed bed test
FB-1515	100 Fe/3 Cu/4 K/6 Ca/16 SiO_2 S3416-3-6Ca	Effect of CaO promoter Fixed bed test
FB-1715	100 Fe/5 Cu/6 K/24 SiO_2 S5624-3	Baseline catalyst Fixed bed test
FB-1795	100 Fe/5 Cu/6 K/24 SiO_2 S5624-5-K	Effect of potassium source Fixed bed test
FB-1425	100 Fe/5 Cu/6 K/2 Ca/24 SiO_2 S5624-3-2Ca	Effect of CaO promoter Fixed bed test
FA-1705	100 Fe/5 Cu/6 K/6 Ca/24 SiO_2 S5624-3-6Ca	Effect of CaO promoter Fixed bed test
SB-3115	100 Fe/3 Cu/4 K/2 Ca/16 SiO_2 S3416-3-2Ca	Effect of CaO promoter Slurry reactor test
SA-2405	100 Fe/5 Cu/6 K/2 Ca/24 SiO_2 S5624-3-2Ca	Effect of CaO promoter Slurry reactor test
SA-3115	100 Fe/5 Cu/6 K/24 SiO_2 S5624-5-K	Effect of CaO promoter Slurry reactor test

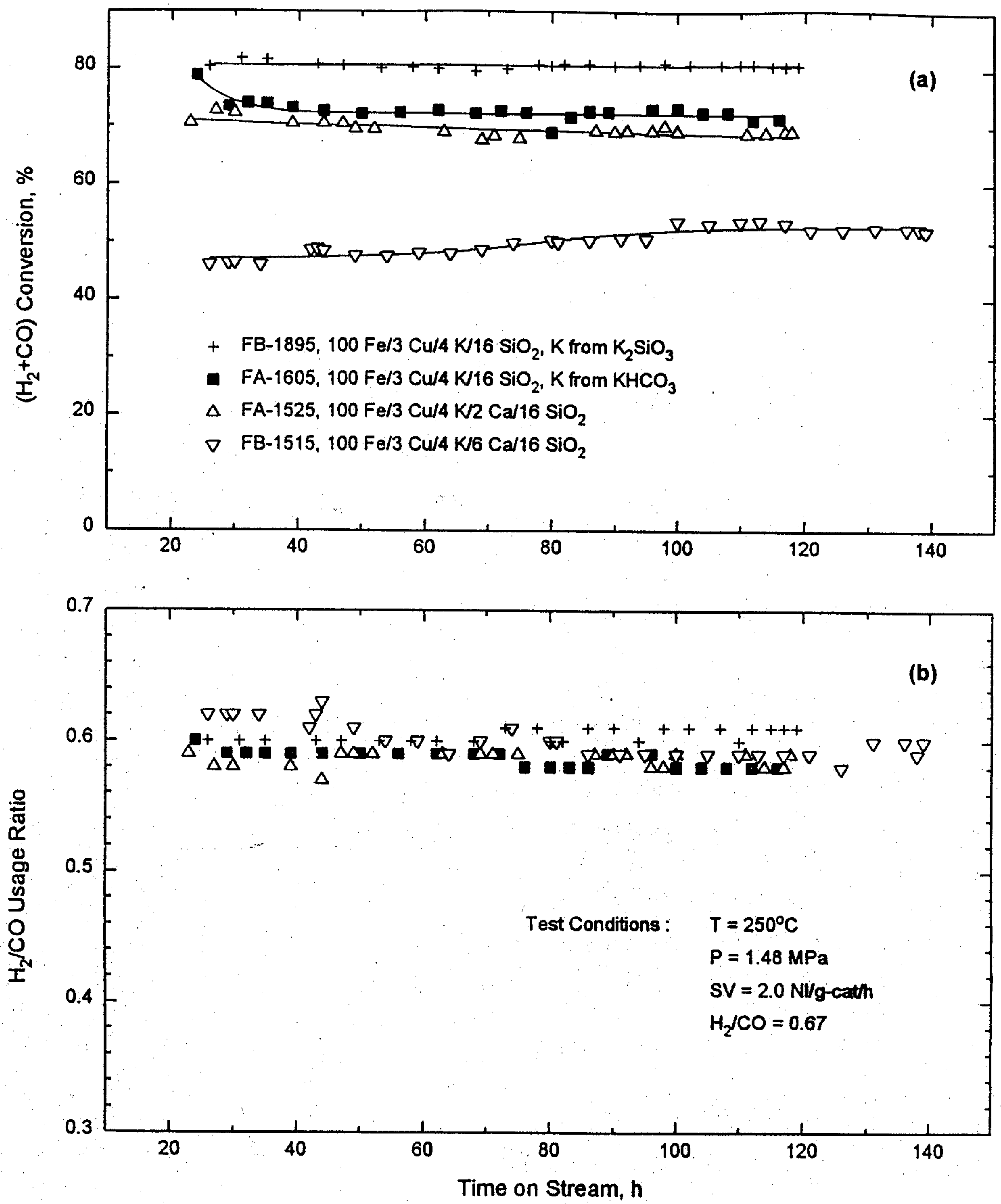


Figure V-2.1 Effect of source of potassium and CaO promoter on (a) synthesis gas conversion and (b) H_2/CO usage ratio in fixed bed reactor tests with catalysts containing 16 parts of SiO_2 per 100 parts of Fe.

decreased with increase in CaO promotion. The activity of the catalyst with lower amount of CaO promoter (run FA-1525 with the 100 Fe/3 Cu/4 K/2 Ca/16 SiO_2 catalyst) was similar to that of the baseline catalyst (run FA-1605), whereas the activity (syngas conversion) of the catalyst containing 6 pbw of Ca per 100 pbw of Fe (FB-1515) was markedly lower (Figure V-2.1a). This may be due to significantly lower surface area of the latter catalyst in comparison to the other catalysts (Table V-1.1). The syngas conversion in run FB-1895 (Catalyst C prepared using K_2SiO_3 as the source of potassium) was about 80 %. By comparison, the baseline catalyst C synthesized using $KHCO_3$ as the source of potassium (FA-1605) was less active (syngas conversion of about 72 %). Usage ratios in all four tests were similar (about 0.6), indicating similar water-gas-shift activities (Figure V-2.1b).

Methane (Figure V-2.2a) and gaseous (C_2 - C_4) hydrocarbon selectivities (Figure V-2.2b) were slightly higher on the CaO promoted catalysts, than on the baseline catalyst. Methane selectivity in run FB-1895 was between 6 and 7 mol%, and gaseous (C_2 - C_4) hydrocarbon selectivity was between 20 and 22 mol%. The baseline catalyst C had lower methane selectivity (5.1 - 5.9 mol%), and its (C_2 - C_4) hydrocarbon selectivity (21 - 24 mol%) was slightly higher than that obtained in run FB-1895.

Performance of catalysts having 24 pbw of SiO_2 per 100 pbw of Fe and containing either CaO promoter (runs FB-1425 and FA-1705), or being prepared using K_2SiO_3 as the source of potassium (FA-1795) is compared with that of the baseline catalyst (catalyst B from batch 3; run FB-1715) in Figures V-2.3 and V-2.4. As in the case of tests with catalysts containing 16 parts by weight (pbw) of SiO_2 per 100 pbw of Fe, the syngas conversions decreased with increase in CaO promotion. The activity of the catalyst with lower amount of CaO promoter (run FB-1425 with the 100 Fe/5 Cu/5 K/2 Ca/24 SiO_2 catalyst), and of the catalyst B prepared using K_2SiO_3 as the source of potassium (FA-1795) was similar to that of the baseline catalyst B from batch 3 (FB-1715), whereas the activity (syngas conversion) of the 100 Fe/5 Cu/6 K/6 Ca/24 SiO_2 catalyst (run FA-1705) was markedly lower (Fig. V-2.3a). This may be due to significantly lower surface area of the latter catalyst in comparison to the

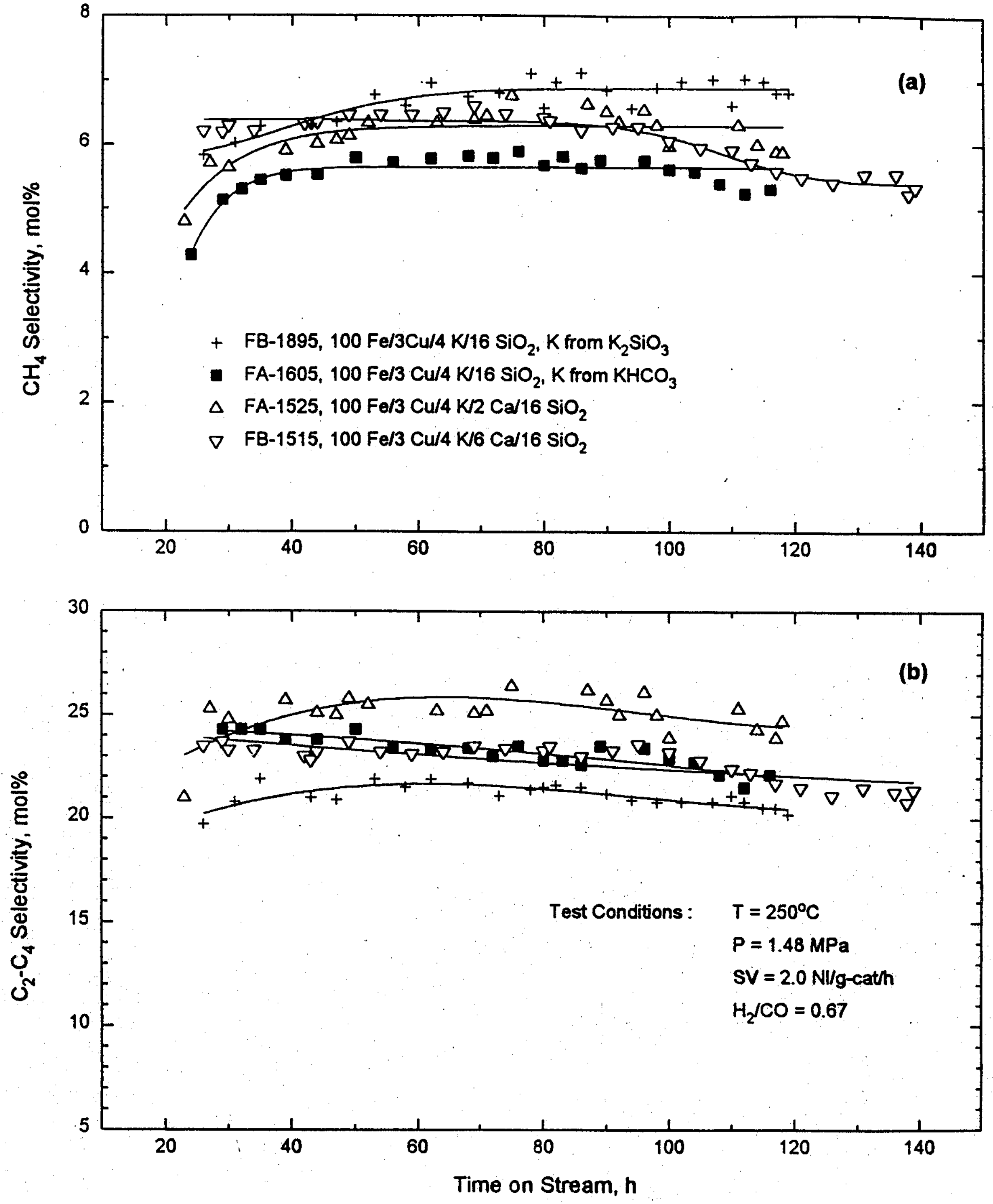


Figure V-2.2 Effect of source of potassium and CaO promoter on (a) methane selectivity and (b) (C_2 - C_4) hydrocarbon selectivity in fixed bed reactor tests with catalysts containing 16 parts of SiO_2 per 100 parts of Fe.

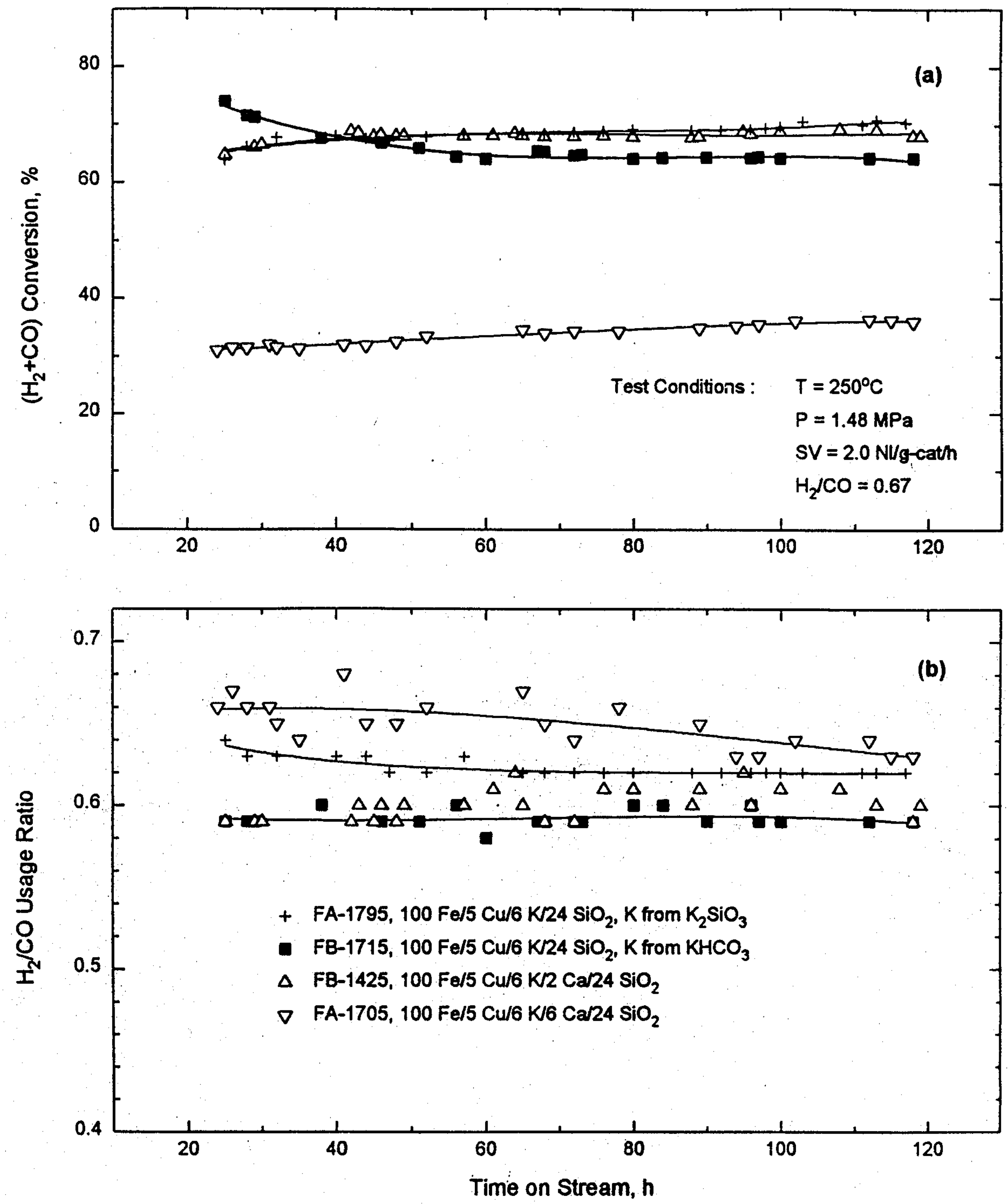


Figure V-2.3 Effect of source of potassium and CaO promoter on (a) synthesis gas conversion and (b) H_2/CO usage ratio in fixed bed reactor tests with catalysts containing 24 parts of SiO_2 per 100 parts of Fe.

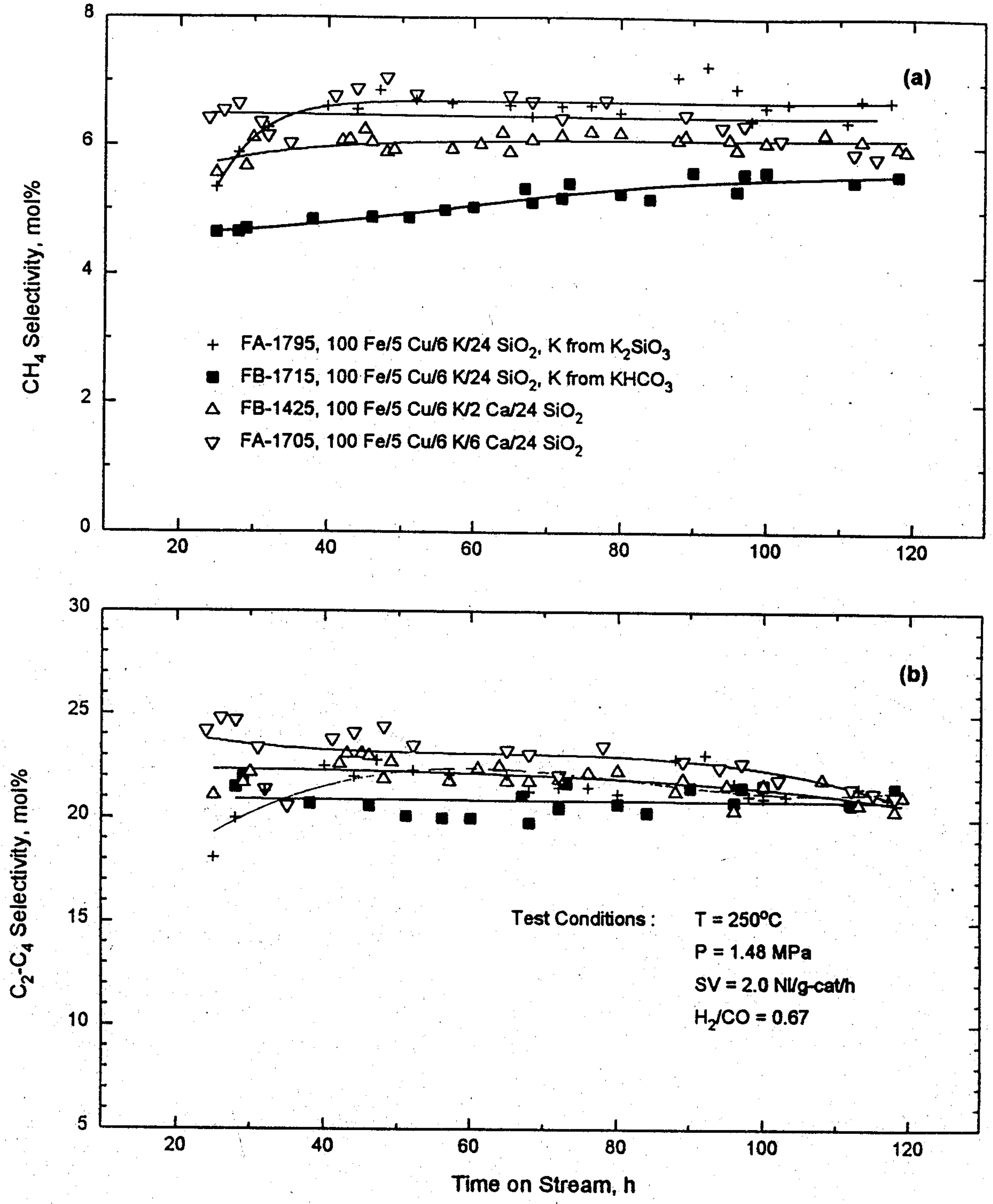


Figure V-2.4 Effect of source of potassium and CaO promoter on (a) methane selectivity and (b) (C_2 - C_4) hydrocarbon selectivity in fixed bed reactor tests with catalysts containing 24 parts of SiO_2 per 100 parts of Fe.

other catalysts (Table V-1.1). Usage ratios (Figure V-2.3b) in run FA-1705 were higher than in the other three tests, indicating lower WGS activity.

Methane (Figure V-2.4a) and gaseous (C_2 - C_4) hydrocarbon selectivities (Figure V-2.4b) on the CaO promoted catalysts and on the catalyst B prepared using K_2SiO_3 as the source of potassium, were slightly higher than those obtained with the baseline catalyst B.

V-2. 2 Continuous Stirred Tank Reactor Tests of Modified Catalysts B and C

Two catalysts containing 2 pbw of Ca per 100 pbw of Fe (100 Fe/3 Cu/2 Ca/4 K/16 SiO_2 and 100 Fe/5 Cu/5 K/2 Ca/24 SiO_2) were evaluated in a STSR, to determine the impact of CaO promotion on the long term catalyst stability (deactivation). The effect of potassium source on the catalyst performance was also studied in slurry phase reactor test, run SB-3155 with 100 Fe/5 Cu/ 6 K/24 SiO_2 catalyst. For these three tests about 9.5 g of the catalyst was loaded into a slurry reactor with Durasyn 164 oil as a start-up liquid to form 3.3 wt% slurry. Catalysts were reduced with hydrogen, at 0.8 MPa, 7500 cm^3/min, and 250°C for 4 h (catalysts containing 24 parts of SiO_2 per 100 parts of Fe on a mass basis) or 240°C for 2 h (catalysts containing 16 parts of SiO_2 per 100 parts of Fe).

V-2. 2. 1 Effect of CaO Promotion on Performance of Catalyst C

Changes in synthesis gas conversion and apparent reaction rate constant with time on stream in tests of the 100 Fe/3 Cu/2 Ca/4 K/16 SiO_2 catalyst (run SB-3115) and the baseline catalyst C from preparation batch-4 (run SA-1665) are shown in Figure V-2.5. The Fe-Cu-SiO_2 precursors for these two catalysts were from two different batches. The CaO containing catalyst was prepared by impregnation of Fe-Cu-SiO_2 precursor from batch-3 first with calcium acetate followed by impregnation with potassium bicarbonate. However, since the test results from different batches of baseline catalyst C were reproducible (Section IV-2), data from run SA-1665 can be used to evaluate the effect of CaO promotion. Run SA-1665 lasted about 500 h, but only the data from first 400 h are shown here.

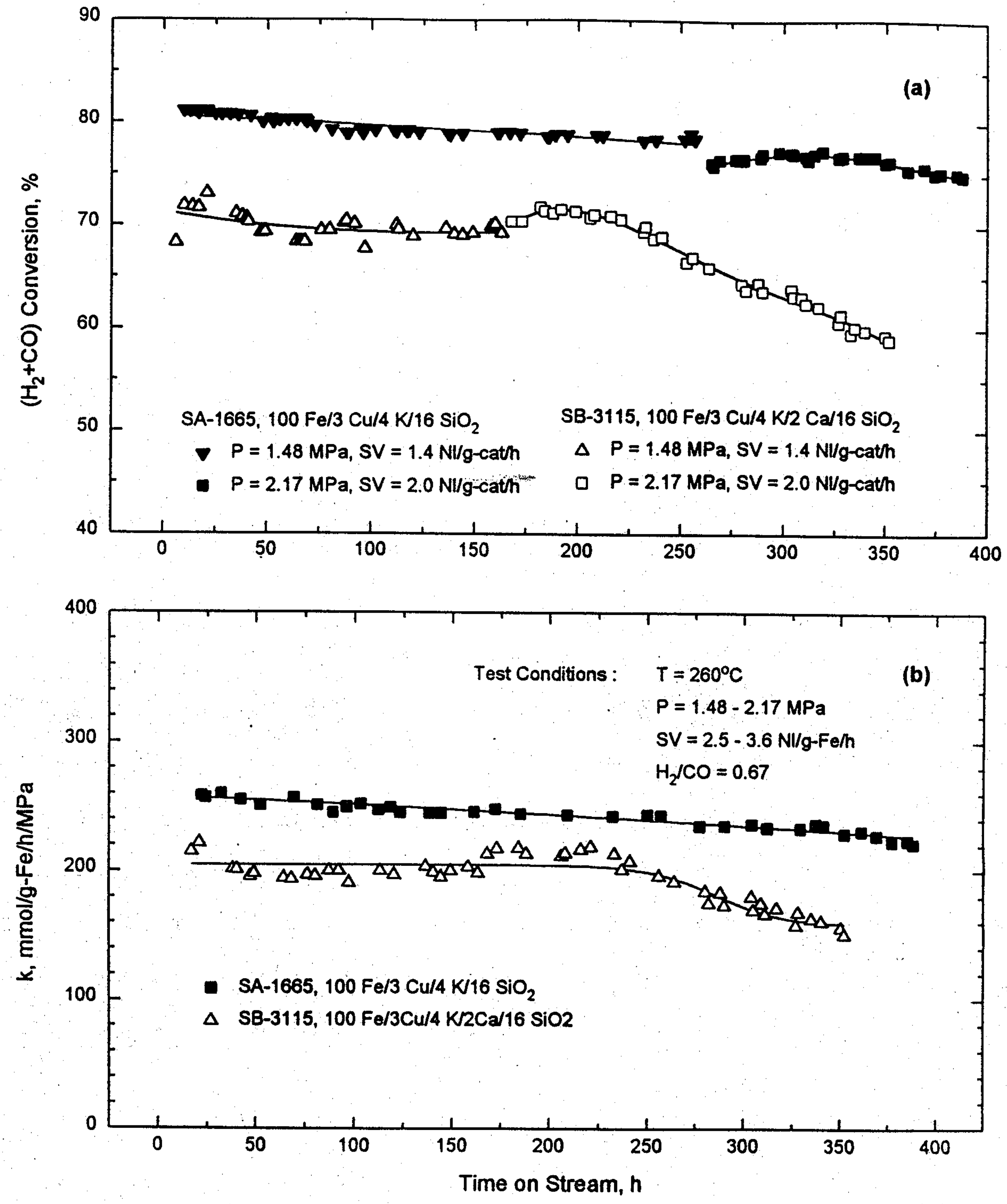


Figure V-2.5 Effect of CaO promoter on (a) synthesis gas conversion and (b) apparent reaction rate constant in STSR tests with catalysts containing 16 parts of SiO_2 per 100 parts of Fe.

Figure V-2.5 shows that the CaO containing catalyst tested in run SB-3115 had lower activity, i.e. lower syngas conversion and the apparent reaction rate constant, than the catalyst C in run SA-1665. The CaO containing catalyst started to deactivate around 220 h on stream, whereas the catalyst C in run SA-1665 was fairly stable during 400 h of testing.

Also, the CaO containing catalyst had higher methane (Figure V-2.6a) and C_2-C_4 (Figure V-2.6b) hydrocarbon selectivities during testing at 1.48 MPa. After the pressure was increased to 2.17 MPa (while proportionally increasing the gas space velocity to 2.0 Nl/g-cat/h) in run SB-3115, the methane and gaseous hydrocarbons selectivities started to decrease (170 - 220 h), and then remained stable (220 - 350 h). The hydrocarbon selectivity of the CaO containing catalyst depends on the reaction pressure (at constant P/SV ratio), whereas gaseous hydrocarbon selectivity was independent of pressure in run SA-1665 with catalyst C.

Olefin and 2-olefin selectivities for runs SA-1665 and SB-3115 are shown in Figure V-2.7. The addition of CaO promoter resulted in a decrease of the total olefin content and in increase of the 2-olefin content, at the reaction pressure of 1.48 MPa. After the pressure was increased from 1.48 MPa to 2.17 MPa in run SB-3115, the total olefin content increased and 2-olefin content decreased, and olefin selectivities became similar to those obtained in run SA-1665 with the baseline catalyst C.

Hydrocarbon and Carbon Number Product Distributions

Lumped hydrocarbon distribution, activity parameters and product yields obtained in runs SA-1665 and SB-3115 are shown in Table V-2.2. The CaO promoted catalyst produced more lower molecular products than the baseline catalyst C. For example at the reaction pressure of 1.48 MPa the gasoline fraction (C_5-C_{11} hydrocarbons) in run SB-3115 was about 38% of total hydrocarbons, whereas in run SA-1665 it was 12% only. Upon increasing the reaction pressure to 2.17 MPa in run SB-3115 the fractions of gaseous hydrocarbons and gasoline fraction (C_5-C_{11} hydrocarbons) decreased, and the fraction of higher molecular weight hydrocarbons (C_{12}+) increased.

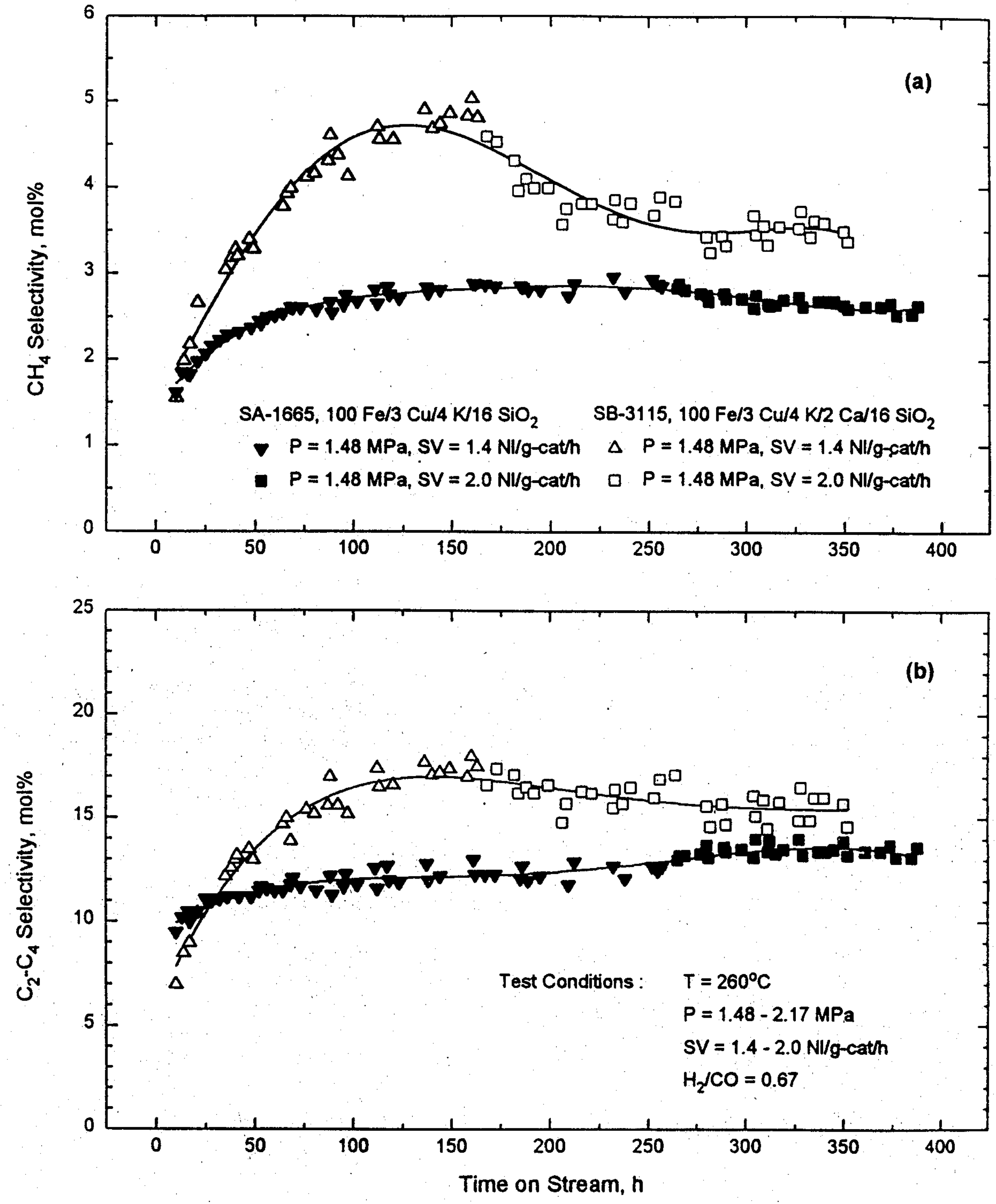


Figure V-2.6 Effect of CaO promoter on (a) methane selectivity and (b) $(C_2 - C_4)$ hydrocarbon selectivity in STSR tests with catalysts containing 16 parts of SiO_2 per 100 parts of Fe.

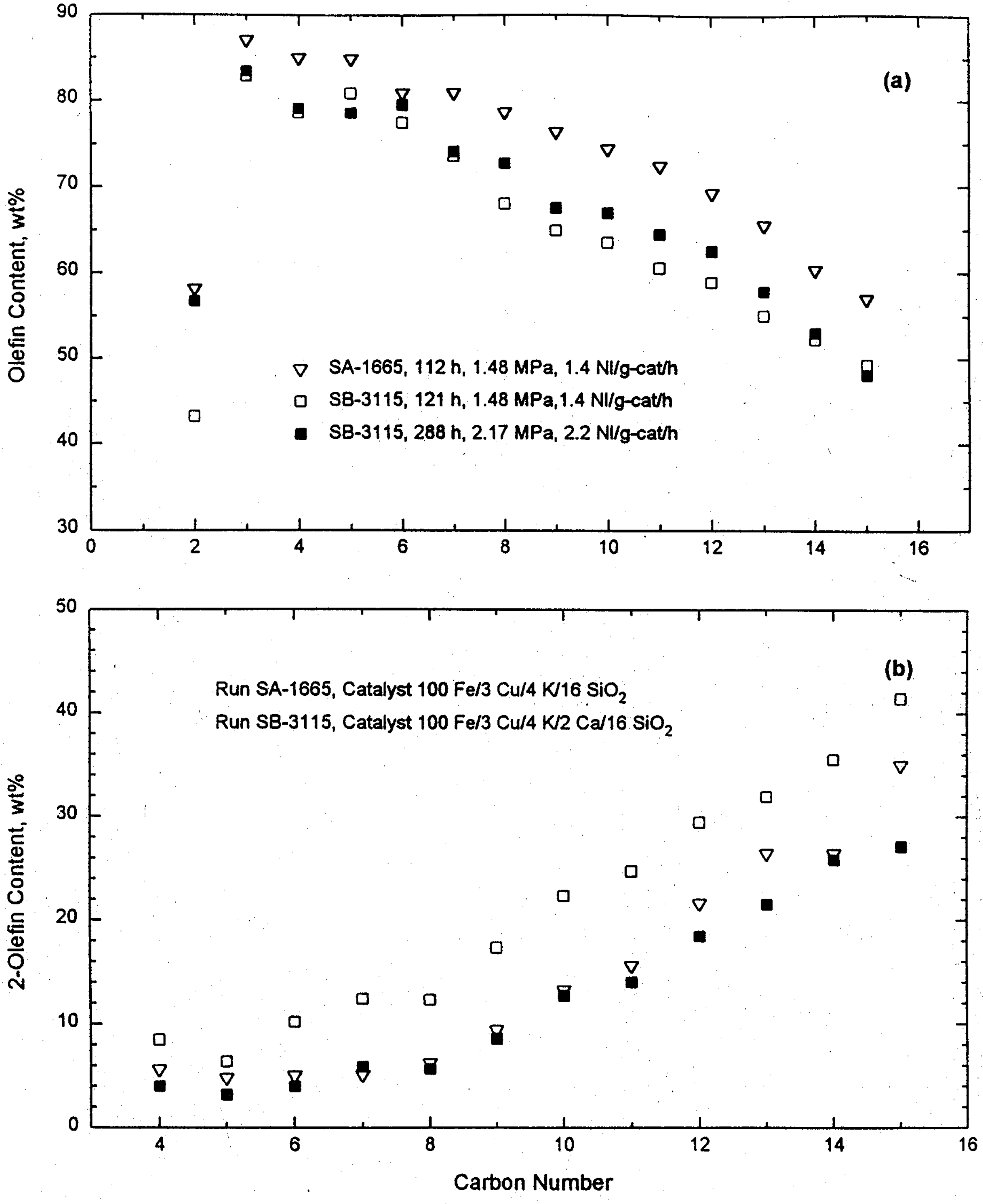


Figure V-2.7 Effect of CaO promoter on (a) olefin content and (b) 2-olefin content as a function of carbon number for catalysts containing 16 parts of SiO_2 per 100 parts of Fe.

Table V-2.2 Performance of the Baseline and CaO Promoted Catalyst C in Slurry Reactor Tests

Test designation	SA-1665		SB-3115	
Catalyst	100 Fe/3 Cu/4 K/16 SiO_2 (K from $KHCO_3$)[a]		100 Fe/3 Cu/4 K/2 Ca/16 SiO_2 (K from $KHCO_3$)[b]	
Test conditions				
Temperature, °C	260	260	260	260
Pressure, MPa	1.48	2.17	1.48	2.17
Space velocity, Nl/g-cat/h	1.4	2.0	1.4	2.0
Feed H_2/CO ratio	0.67	0.67	0.67	0.67
Time on stream, h	112	361	121	288
CO conversion, %	84.1	80.1	72.2	65.7
(H_2+CO) conversion, %	79.0	75.8	68.8	62.9
STY, mmol (H_2+CO)/g-cat/h	49	69	43	58
k, mmol/g-Fe/h/MPa [c]	238	222	194	166
(H_2/CO) usage ratio	0.57	0.58	0.59	0.60
$K_p = P_{CO2} \cdot P_{H2} / P_{CO} / P_{H2O}$	33	26	31	14
% CO converted to CO_2	48.9	48.4	48.4	47.4
Hydrocarbon selectivity, wt%				
CH_4	3.2	3.1	5.4	4.4
C_2-C_4	12.3	13.9	17.5	16.9
C_5-C_{11}	12.0	17.9	37.8	29.3
C_{12}-C_{18}			22.8	18.9
C_{12}+	72.5	65.1	43.3	49.4
C_1+C_2	6.6	5.8	9.7	8.9
Yield, g/Nm^3(H_2+CO) Converted				
Hydrocarbons	204	203	198	190
Oxygenates	2.4	5.9	7.6	17.1
Catalyst productivity, g HC/g-cat/h	0.22	0.32	0.19	0.25

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

[b] Iron content of this catalyst (0.587 g-Fe/g-cat)

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

Carbon number distribution at 121 h on stream in run SB-3115 was fitted with a three parameter model of Huff and Satterfield, and the estimated values of parameters were as follows: $\alpha_1 = 0.71$; $\alpha_2 = 0.90$, and $\beta = 0.90$.

V-2. 2. 2 Effect of CaO Promotion and Potassium Source on Performance of Catalyst B

Activity comparisons between the baseline catalyst B from batch-3 (SB-1295), modified catalyst B containing CaO promoter (precursor from batch-3; run SA-2405) and catalyst B prepared using potassium silicate as the source of potassium promoter (precursor from batch-5; run SA-3155) are made in Figure V-2.8a (in terms of syngas conversions) and Figure V-2.8b (in terms of the apparent reaction rate constant). During the first 120 h on stream, the catalyst B was slightly more active than the CaO containing catalyst (higher apparent rate constant), whereas after that the latter catalyst had higher activity. This is primarily due to the fact that the CaO containing catalyst (SA-2405) maintained its activity better than the catalyst B (SB-1295). The CaO containing catalyst deactivated slowly during testing at 2.17 MPa (240-400 hours on stream). The catalyst B prepared using K_2SiO_3 as potassium source was less active than the baseline catalyst B. The syngas conversions and apparent reaction rate constant in run SA-3155 were lower than those obtained in run SB-1295, whereas the H_2/CO usage ratio was higher indicating lower WGS reaction activity (Table V-2.3).

During testing at 1.48 MPa (200 psig) the baseline catalyst B had either similar (first 30-40 h on stream) or lower methane (Figure V-2.9a), and C_2-C_4 (Figure V-2.9b) hydrocarbon selectivities than the CaO containing catalyst. However, when the pressure was increased to 2.17 MPa (at 237 h on stream) in run SA-2405, methane and gaseous hydrocarbon selectivities started to decrease and at 300 h were similar to those obtained in test SB-1295 (here the system pressure is still 1.48 MPa). The data show that hydrocarbon selectivities of the CaO containing catalyst are dependent upon the reaction pressure, and this was also observed in run SB-3115 with the 100 Fe/3 Cu/2 Ca/4 K/16 SiO_2 catalyst. During the first 100 h on stream, methane and gaseous hydrocarbon selectivities in run SA-3155 (K

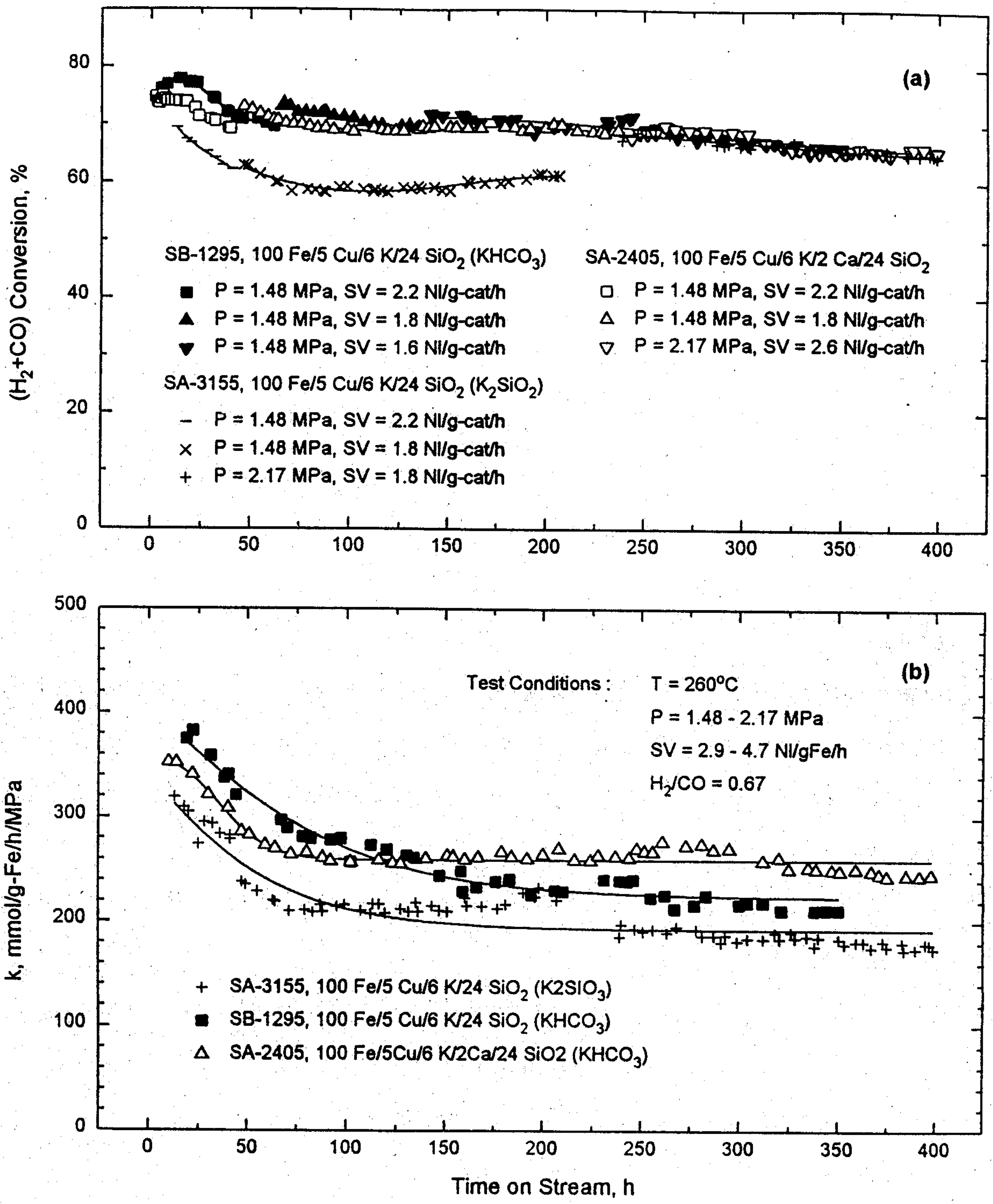


Figure V-2.8 Effect of source of potassium and CaO promoter on (a) synthesis gas conversion and (b) apparent reaction rate constant in STSR tests with catalysts containing 24 parts of SiO_2 per 100 parts of Fe.

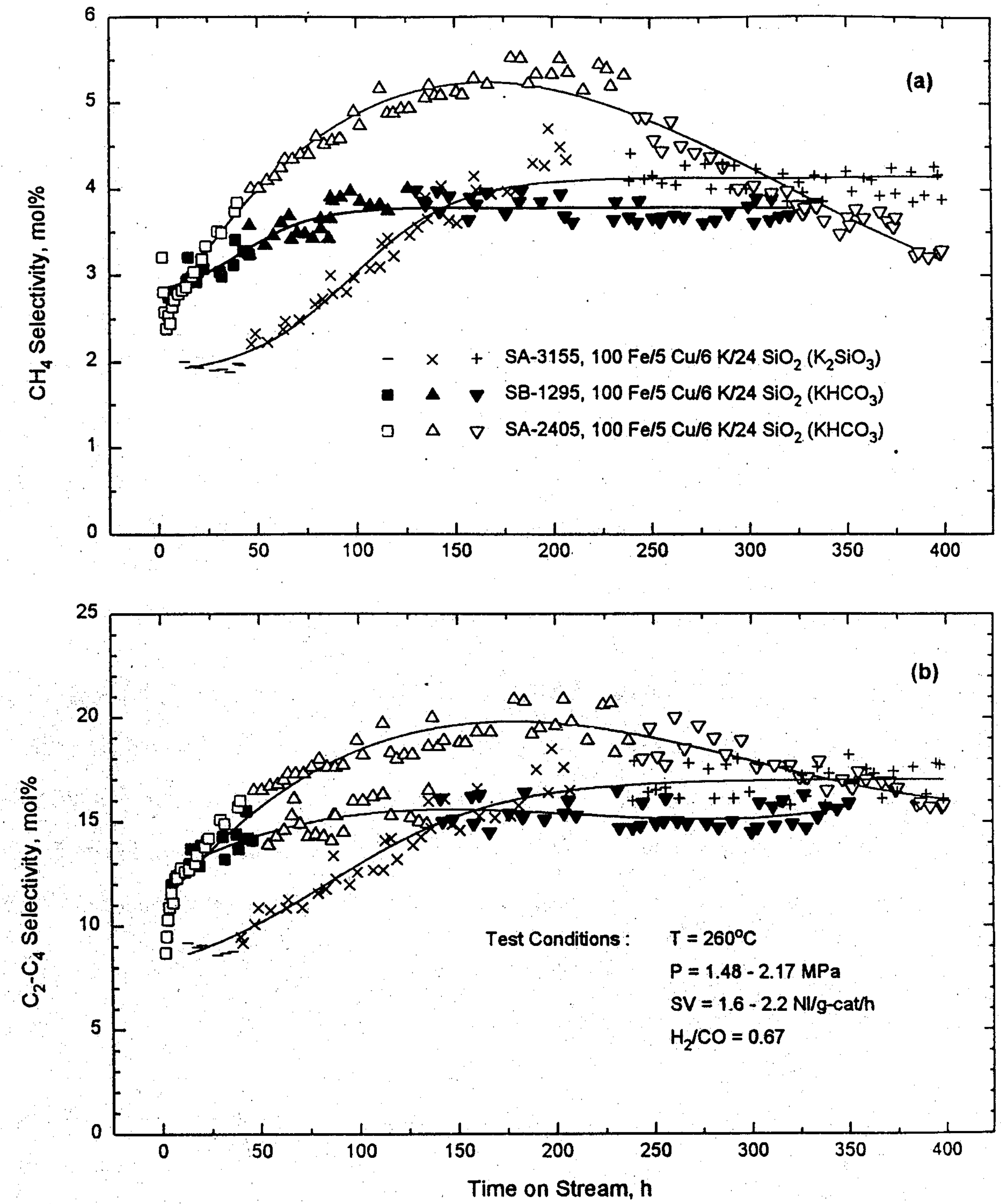


Figure V-2.9 Effect of source of potassium and CaO promoter on (a) methane selectivity and (b) (C_2 - C_4) hydrocarbon selectivity in STSR tests with catalysts containing 24 parts of SiO_2 per 100 parts of Fe (for the description of symbols see Figure V-2.8).

from K_2SiO_3) were significantly lower than in run SB-1295, but these differences in selectivity diminished with time and gaseous hydrocarbon selectivities in the two tests were similar after 140 h (Figure V-2.9). Gaseous hydrocarbon selectivities in run SA-3155 were not affected by reaction pressure (i.e. they were nearly the same during operation at 1.48 MPa and 2.17 MPa).

Olefin and 2-olefin selectivities obtained in runs SB-1295, SA-2405 and SA-3155 are shown in Figure V-2.10. As can be seen from this Figure, the addition of CaO promoter resulted in a decrease of the total olefin content and in an increase of the 2-olefin content during operation at reaction pressure of 1.48 MPa. The total olefin and 2-olefin contents in run SA-2405 during operation at 2.17 MPa were very similar to those in run SB-1295 at 1.48 MPa. The same type of behavior was also observed in run SB-3115 with the 100 Fe/3 Cu/2 Ca/4 K/16 SiO_2 catalyst. Olefin selectivities in run SA-3155 with catalyst B (K from K_2SiO_3) were essentially the same as those obtained in run SB-1295 with the baseline catalyst B (K from $KHCO_3$).

Hydrocarbon and Carbon Number Product Distributions

A typical carbon number distribution obtained in tests SB-1295 and SA-3155 with catalyst B is shown in Figure IV-2.11. Positive deviations from ASF distribution are noted in run SB-1295 for C_{10} - C_{22} carbon number range, but were virtually absent in run SA-3155. Experimental data from both tests were fitted with a three parameter model of Huff and Satterfield, and the estimated values of parameters were as follows: $\alpha_1 = 0.68$; $\alpha_2 = 0.91$; and $\beta = 0.74$.

Lumped hydrocarbon distribution, activity parameters and product yields obtained in runs SB-1295, SA-2405 and SA-3155 are shown in Table V-2.3. The catalyst activity, productivity, and hydrocarbon selectivities in run SA-2405 with the 100 Fe/5 Cu/5 K/2 Ca/24 SiO_2 catalyst at 2.17 MPa (300 psig) were very good. The highest oxygenates yield was obtained in run SA-3155 (8-9 g/Nm^3 (H_2+CO) converted).

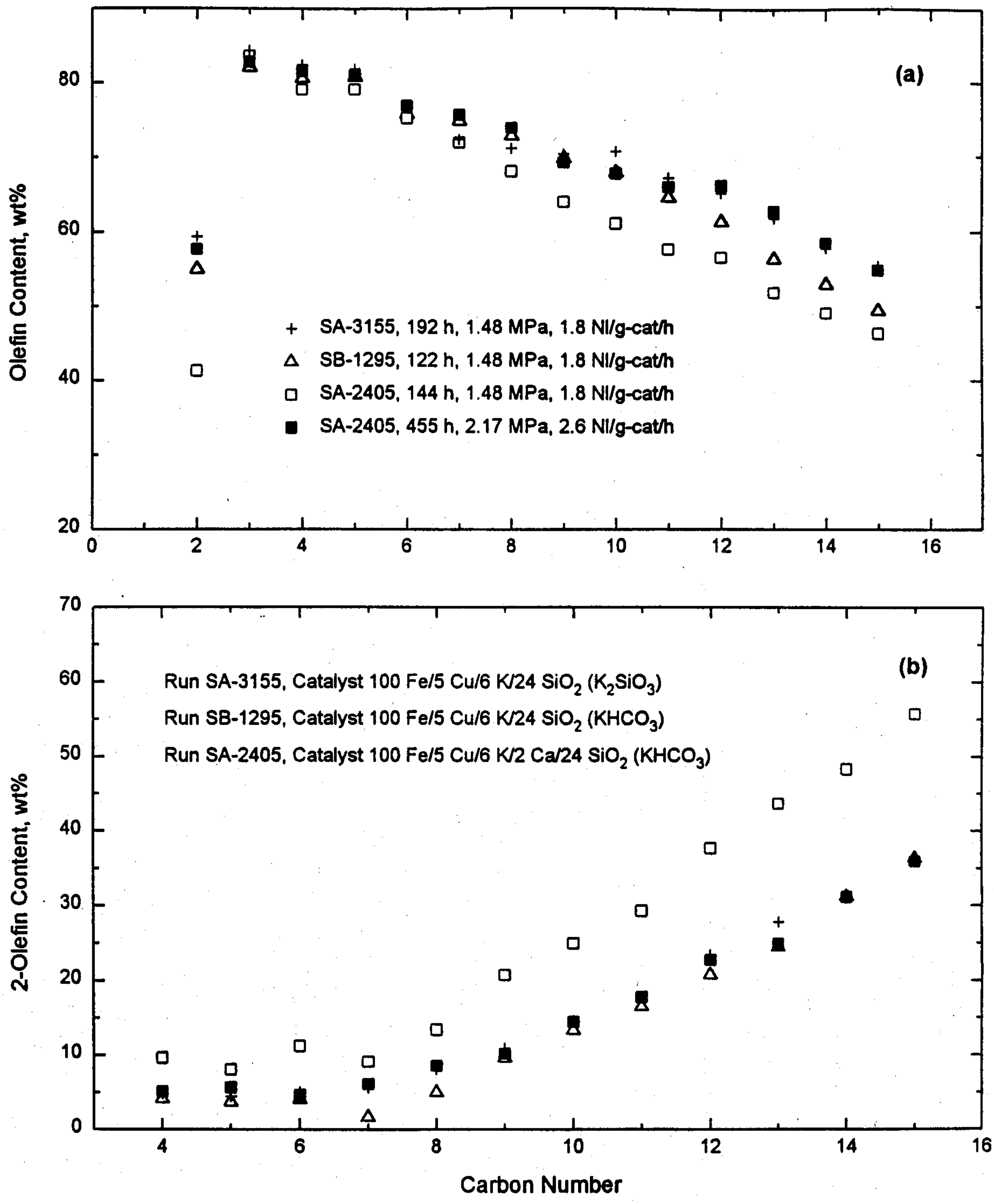


Figure V-2.10 Effect of source of potassium and CaO promoter on (a) olefin content and (b) 2-olefin content as a function of carbon number for catalysts containing 24 parts of SiO_2 per 100 parts of Fe.

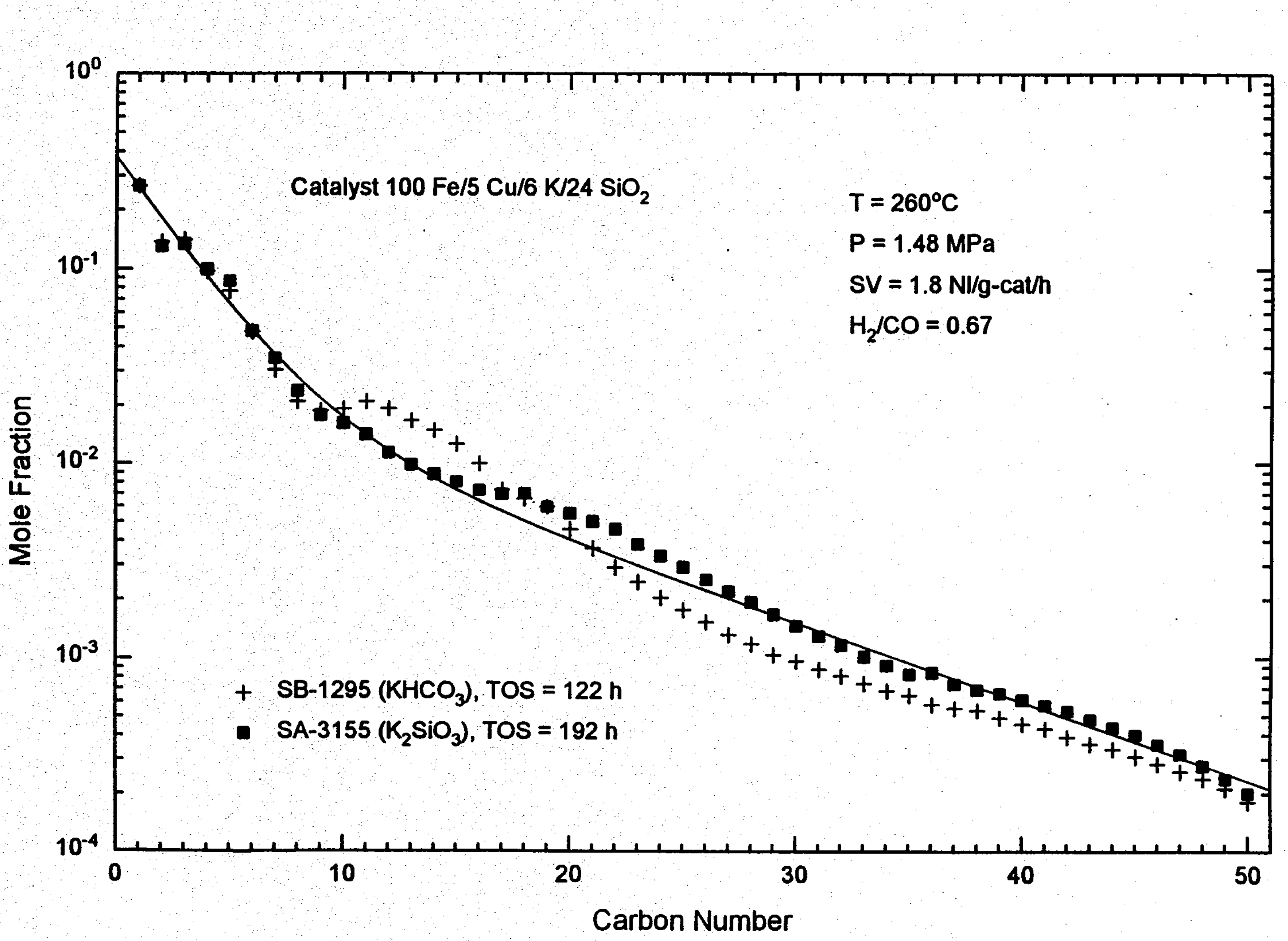


Figure V-2.11 Effect of source of potassium on carbon number product distribution in STSR tests of catalyst B.

Table V-2.3 Performance of the Baseline and Modified Catalyst B in Slurry Reactor Tests

Test designation	SB-1295		SA-2405		SA-3155	
Catalyst	100 Fe/5 Cu/6 K/24 SiO_2 (K from $KHCO_3$)[a]		100 Fe/5 Cu/6 K/2 Ca/24 SiO_2 (K from $KHCO_3$)[b]		100 Fe/5 Cu/6 K/24 SiO_2 (K from K_2SiO_3)[a]	
Test conditions						
Temperature, °C	260	260	260	260	260	260
Pressure, MPa	1.48	1.48	1.48	2.17	1.48	2.17
Space velocity, Nl/g-cat/h	1.8	1.6	1.8	2.6	1.8	1.8
Feed H_2/CO ratio	0.67	0.67	0.67	0.67	0.67	0.67
Time on stream, h	122	338	192	455	192	383
CO conversion, %	74.3	70.3	72.8	66.3	63.1	65.0
(H_2+CO) conversion, %	69.6	66.6	69.1	64.1	61.1	64.1
STY, mmol (H_2+CO)/g-cat/h	57	47	55	75	49	51
k, mmol/g-Fe/h/MPa[c]	259	208	266	240	220	167
(H_2/CO) usage ratio	0.56	0.57	0.58	0.61	0.61	0.64
$K_p = P_{CO2} \cdot P_{H2}/P_{CO}/P_{H2O}$	39	31.5	27	10	6	9
% CO converted to CO_2	48.9	49.1	49.1	48.3	46.6	45.9
Hydrocarbon selectivity, wt%						
CH_4	4.4	4.5	6.5	3.7	5.2	5.0
C_2-C_4	15.6	16.1	21.3	15.8	17.6	18.3
C_5-C_{11}	21.8	18.8	28.6	20.9	27.2	26.8
C_{12}-C_{18}	18.4					14.8
C_{12}+	58.2	60.6	43.6	59.6	50.0	50.0
C_1+C_2	8.3	8.9	11.8	7.8	10.5	9.3
Yield, g/Nm^3(H_2+CO) Converted						
Hydrocarbons	205	199	195	197	199	189
Oxygenates	6.9	6.5	5.1	5.1	8.9	8.1
Catalyst productivity, g HC/g-cat/h	0.26	0.21	0.24	0.33	0.22	0.22

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

[b] Iron content of this catalyst (0.549 g-Fe/g-cat)

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

Concluding Remarks on the Effect of CaO Promotion and Source of Potassium

Four catalysts containing CaO promoter with nominal compositions 100 Fe/3 Cu/4 K/x Ca/16 SiO_2 and 100 Fe/5 Cu/5 K/x Ca/24 SiO_2, where x = 2 or 6, were synthesized and tested in fixed bed reactors. The major findings from these tests are that the addition of small amounts of CaO promoter (x = 2) results in the catalyst performance (activity and gaseous hydrocarbon selectivity) similar to that of the baseline catalysts B and C, whereas the addition of a larger amount of CaO (x = 6) results in markedly lower catalyst activity in comparison to the baseline catalysts. Selectivity of the two catalysts with x = 6, is similar to that of the corresponding baseline catalysts. On the basis of these results it was decided to evaluate two catalysts with x = 2 in stirred tank slurry reactors.

The 100 Fe/5 Cu/5 K/2 Ca/24 SiO_2 catalyst was tested in run SA-2405, and its performance was compared to that of the baseline catalyst B in run SB-1295, whereas results from run SB-3115 with the 100 Fe/3 Cu/4 K/2 Ca/16 SiO_2 catalyst were compared with results obtained with the catalyst C in run SA-1665. General trends in tests with the CaO containing catalysts showed some similarities, as well as differences. For example activity of the 100 Fe/5 Cu/5 K/2 Ca/24 SiO_2 catalyst (run SA-2405) was nearly the same as that of the baseline catalyst B (run SB-1295) but its stability with time (deactivation rate) was better, whereas the 100 Fe/3 Cu/4 K/2 Ca/16 SiO_2 catalyst (run SB-3115) was less active (about 15%) than the baseline catalyst C (run SA-1665) and its deactivation rate was higher. At reaction pressure of 1.48 MPa, selectivity of gaseous hydrocarbons on CaO containing catalysts was higher than that of the corresponding baseline catalysts. However, at reaction pressure of 2.17 MPa the gaseous hydrocarbon selectivity decreased on the CaO containing catalysts, and was nearly the same as that of the baseline catalysts at 1.48 MPa. It appears that the selectivity of the CaO promoted catalysts improves at higher reaction pressures, whereas the selectivity of the catalyst C is essentially independent of reaction pressure (at a constant P/SV ratio to maintain a constant value of the gas residence time at different pressures). The addition of CaO promoter did not result in improved performance of the baseline catalysts, but the CaO promoted catalysts may be suitable for operation at higher reaction pressures. Finally, it is possible that the performance of CaO promoted catalysts may be improved with the use of different pretreatment procedures, but this has not been investigated in the present study.

Some differences in catalyst performance were observed in fixed bed tests of catalysts B (runs FA-1725 and FB-1715) and C (runs FA-1605 and FB-1985) prepared by different methods. In both cases, the activity and methane selectivity of catalysts prepared using potassium silicate as the source of potassium promoter were higher than those of the corresponding baseline catalysts prepared by incipient wetness impregnation using $KHCO_3$ as the source of potassium promoter. On the other hand, in two slurry reactor tests of catalyst B (SB-1295 - K from $KHCO_3$, and SA-3155 - K from K_2SiO_3) it was found that the activity of the catalyst prepared from K_2SiO_3 is about 15 % lower than that of the catalyst prepared by $KHCO_3$ impregnation, whereas gaseous hydrocarbon selectivities were similar after about 140 h on stream.

On the basis of these results we conclude that the baseline procedure utilizing impregnation of Fe-Cu-SiO_2 precursor with the aqueous solution of $KHCO_3$ is the preferred method of catalyst preparation. The second procedure, which avoids the impregnation step, provides satisfactory results, and may be used as an alternative.

V-3 References

Anderson, R. B., 1956, Catalysts for the Fischer-Tropsch Syntheis In *Catalysis*; Emmett, P. H. Ed.; Van Nostrand-Reinhold: New York., Vol. IV, pp. 29-255.