VII Calcination Effect Research

Calcination involves heating the dried powder in the temperature range 300-600°C in various atmospheres, usually air. Several processes occur: sintering, solid state reaction, loss of porosity. In most catalyst systems calcination is beneficial since it establishes the correct "state" of the catalyst that is most responsive to activation.

Very little systematic study of the effect of calcination on precipitated F-T catalysts has appeared (Anderson, 1956, 1984), yet this is a promising area for controlling essential properties. It is known that heat treatment of co-precipitated Fe_2O_3-CuO samples gives mixed phases, e.g. $CuFe_2O_4$, that may result in superior dispersions with reductive activation. Calcination results in sintering and loss of surface area. Calcined catalysts have better attrition properties, which is important for the slurry F-T process. Changes in the pore volume and pore size distribution may have significant effect on intraparticle diffusion and consequently on hydrocarbon product distribution. However, there have been no studies to investigate these effects.

In a related study (Hadjigeorghiou and Richardson, 1986) it was reported that Ni/ThO_2 catalysts, used in the F-T synthesis of light hydrocarbons, showed an activity enhancement of up to a factor of ten when the hydrogel was calcined rapidly on a hot-plate (flash calcined) compared with conventional oven heating. This was attributed to rapid reactions in the gel that led to "decoration" of reduced nickel particles by ThO_2 (Richardson et al., 1989). It is possible that this effect may enhance activity of precipitated 100 Fe/x Cu/y K/z SiO_2 catalysts during calcination. The large-scale analogy to the hot-plate is a "spray-roasting" which may be employed in the catalyst scale-up, if this procedure proves to be effective.

The effect of calcination temperature (300-500°C) and flash calcination on physical properties of catalysts B and C is described in section VII-1, whereas results from F-T synthesis tests in fixed bed and stirred tank slurry reactors are described in section VII-2.

VII-1 Catalyst Characterization Studies

Calcinations at temperatures 300-500°C were done in a downflow fixed bed reactor unit. The air flow rate during calcination was set at approximately 50 cm^3/g-cat/min and the catalyst bed temperature was increased to a desired calcination temperature at a rate of 2°C/min. After reaching the final temperature these conditions were maintained for 5 hours. After that the system was allowed to cool down to room temperature with air flowing through the catalyst bed. Calcination at 700°C was done in a high temperature furnace. The furnace was preheated to 700°C first, and the catalyst was spread over a preheated crucible to form a thin layer. During one hour calcination the air flow was fed into the furnace, passing over a thin layer of catalyst. This procedure is referred to as flash calcination.

Calcined catalysts were characterized by BET surface area, pore volume and pore size distributions. The pretreated and used catalysts from slurry and/or fixed bed runs were characterized by XRD and MES.

BET Surface Area and Pore Volume Results

BET surface area and pore volume results of catalysts B (100 Fe/5 Cu/6 K/24 SiO_2, batch-3) and C (100 Fe/3 Cu/4 K/16 SiO_2, batch-4) calcined at different temperatures are summarized in Table VII-1.1. The surface areas of catalyst C and B calcined at 300°C for 5 h (baseline conditions) were about 290 m^2/g, and decreased gradually to about 100 m^2/g with the increase in calcination temperature from 300 to 700°C. The BET surface areas of both catalysts are similar after calcinations at the same conditions (temperature and duration). The surface area of catalysts B and C, is also affected by the duration of calcination , and it decreases with increase in calcination time (results at 500°C at different durations of calcination).

Table VII-1.1 Effect of Calcination Conditions on the Textural Properties of Catalysts B and C

Catalyst	Calcination Temperature, °C / Duration, h	BET Surface Area, m^2/g		Pore Volume, cm^3/g
		Single Point	BET Plot	
100 Fe/3 Cu/4 K/16 SiO_2 S3416-4	300 / 5	310	306	0.45
	400 /5	263	268	0.42
	500 / 0.5	233	-	-
	500 /1	231	216	0.4
	500 / 5	183	188	0.36
	700 / 0.5	118	-	-
	700 / 1	108	106	0.30
100 Fe/5 Cu/6 K/24 SiO_2 S5624-3	300 / 5	258	284	0.51
	400 / 5	271	253	0.48
	500 /1	227	212	0.46
	500 / 5	219	193	0.43
	700 / 0.5	115	108	0.33
	700 / 1	100	96	0.33

Pore volumes of catalysts C and B (calcined at 300°C) were 0.45 and 0.50 cm^3/g, respectively, and the corresponding values after calcination at 700°C were 0.30 and 0.33 cm^3/g, respectively. Total pore volume of catalyst B is slightly larger than that of catalyst C at all calcination temperatures. The pore volumes of these two catalysts are also affected to some extent by the duration of calcination. The decrease in surface area and pore volume with increasing calcination temperature is due to sintering.

Pore Size Distributions

Figure VII-1.1 illustrates the pore size distribution of catalysts C and B after calcination at different temperatures ranging from 300 to 700°C. The catalysts exhibit bi-modal pore size distributions at all calcination temperatures. The pore size (diameter) varied from about 2 to 20 nm for both catalysts, but the pore size shifted to larger values with increase in calcination temperature. Catalysts calcined at 700°C for 1 hour, had a more narrow pore size distribution, with a large fraction of pores being about 10 nm in diameter.

Iron Phases in Reduced and Used Catalysts

Catalysts B and C calcined at temperatures 300-500°C did not exhibit crystallinity, i.e. they are either amorphous or the crystallites are too small to be detected by XRD. Catalysts B and C calcined at 700°C for 1 h were crystalline, and exhibit the XRD pattern of hematite (α-Fe_2O_3). Results of XRD and MES analysis of reduced and used catalysts from fixed bed and stirred tank slurry reactor tests are summarized in Table VII-1.2.

Used catalysts B and C, calcined at 300-500°C, 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 calcined at 700°C (FA-3495 and FB-0236) magnetite and ε'-carbide were identified in samples from the bottom portion of the reactor (oxidizing atmosphere) by both XRD and MES analysis, whereas only ε'-carbide was identified in samples from the top portion of the reactor (reducing atmosphere).

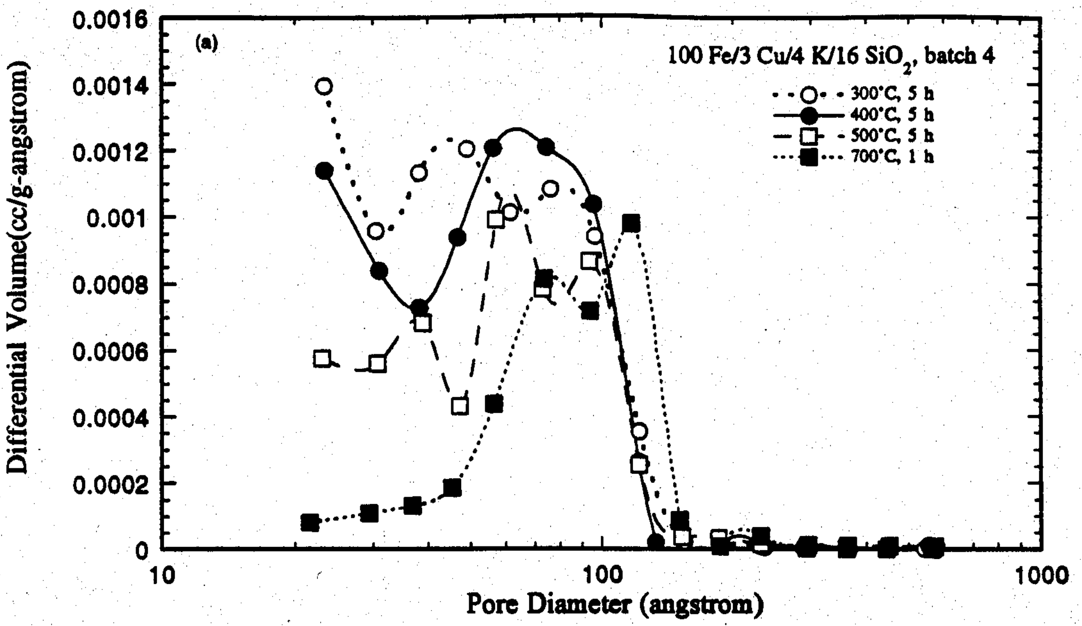

Figure VII-1.1a Effect of calcination temperature on the pore size distribution of catalyst C (100 Fe/3 Cu/4 K/16 SiO_2, batch-4).

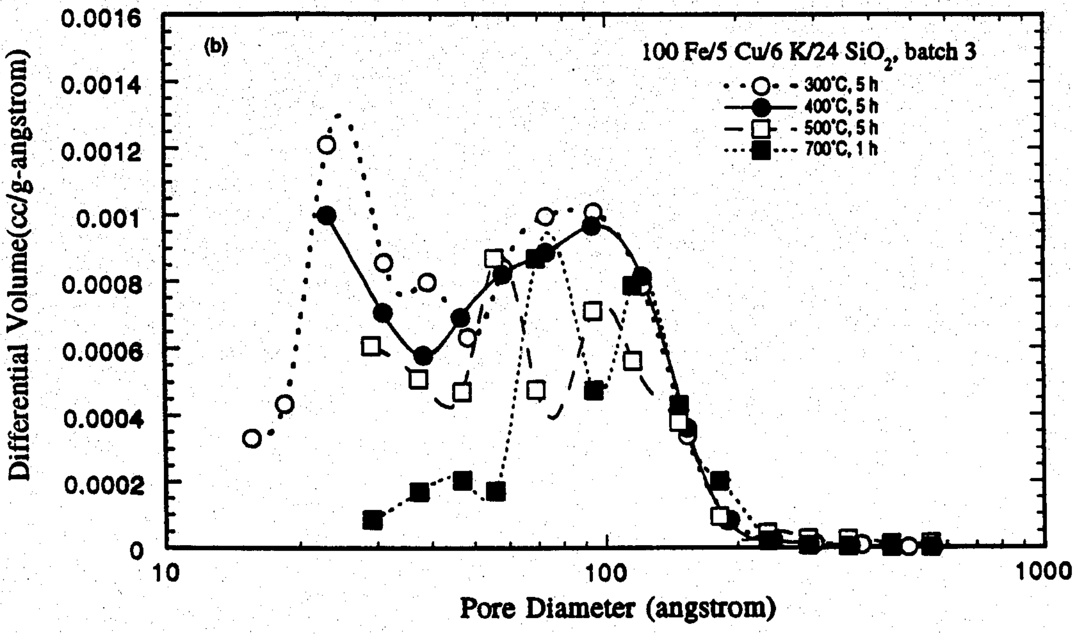

Figure VII-1.1b Effect of calcination temperature on the pore size distribution of catalyst B (100 Fe/5 Cu/6 K/24 SiO_2, batch-3).

Table VII-1.2 Iron Phases in Catalysts B and C from Fixed Bed and Slurry Reactor Tests

Run Number	Catalyst	Time on Stream (TOS), h	Iron Phases Identified by Mössbauer	Iron Phases Identified by XRD
FA-1605	100 Fe/3 Cu/4 K/16 SiO_2 (S3416-4, calcined at 300°C, 5 h)	120 top	49% (Spm) and 51% (ε'-$Fe_{22}C$)	ε'-$Fe_{22}C$
		120 bot	50% (Spm) and 50% (ε'-$Fe_{22}C$)	ε'-$Fe_{22}C$
FA-3305	100 Fe/3 Cu/4 K/16 SiO_2 (S3416-4, calcined at 400°C, 5 h)	120 top	55% (Spm) and 45% (ε'-$Fe_{22}C$)	ε'-$Fe_{22}C$
		120 bot	52% (Spm) and 48% (ε'-$Fe_{22}C$)	ε'-$Fe_{22}C$
FA-3095	100 Fe/3 Cu/4 K/16 SiO_2 (S3416-4, calcined at 500°C, 5 h)	120 top	58% (Spm) and 42% (ε'-$Fe_{22}C$)	ε'-$Fe_{22}C$
		120 bot	59% (Spm) and 41% (ε'-$Fe_{22}C$)	ε'-$Fe_{22}C$
FA-3495	100 Fe/3 Cu/4 K/16 SiO_2 (S3416-4, calcined at 700°C, 1 h)	116 top	45% (Spm) and 55% (ε'-$Fe_{22}C$)	ε'-$Fe_{22}C$
		116 bot	42% (Spm), 18% (Fe_3O_4) and 40% (ε'-$Fe_{22}C$)	Fe_3O_4 and ε'-$Fe_{22}C$
SB-0676	100 Fe/3 Cu/4 K/16 SiO_2 (S3416-4, calcined at 700°C, 1 h)	0	73% (Spm), and 27% (Fe_3O_4)	Fe_3O_4
		120	39% (Spm), 26% (Fe_3O_4) and 35% (ε'-$Fe_{22}C$)	Fe_3O_4 and ε'-$Fe_{22}C$
		221	26% (Spm), 19% (Fe_3O_4) and 55% (ε'-$Fe_{22}C$)	Fe_3O_4 and ε'-$Fe_{22}C$
		305	26% (Spm), 22% (Fe_3O_4) and 52% (ε'-$Fe_{22}C$)	Fe_3O_4 and ε'-$Fe_{22}C$
FB-1715	100 Fe/5 Cu/6 K/24 SiO_2 (S5624-3, calcined at 300°C, 5 h)	119	40% (Spm) and 60% (ε'-$Fe_{22}C$)	ε'-$Fe_{22}C$
			42% (Spm) and 58% (ε'-$Fe_{22}C$)	ε'-$Fe_{22}C$
FB-2975	100 Fe/5 Cu/6 K/24 SiO_2 (S5624-3, calcined at 400°C, 5 h)	142 top	54% (Spm) and 46% (ε'-$Fe_{22}C$)	ε'-$Fe_{22}C$
		142 bot	53% (Spm) and 47% (ε'-$Fe_{22}C$)	ε'-$Fe_{22}C$
FA-2925	100 Fe/5 Cu/6 K/24 SiO_2 (S5624-3, calcined at 500°C, 5 h)	140 top	60% (Spm) and 40% (ε'-$Fe_{22}C$)	ε'-$Fe_{22}C$
		140 bot	56% (Spm) and 44% (ε'-$Fe_{22}C$)	ε'-$Fe_{22}C$
FB-0236	100 Fe/5 Cu/6 K/24 SiO_2 (S5624-3, calcined at 700°C, 1 h)	120 top	39% (Spm) and 61% (ε'-$Fe_{22}C$)	ε'-$Fe_{22}C$
		120 bot	34% (Spm), 9% (Fe_3O_4) and 57% (ε'-$Fe_{22}C$)	Fe_3O_4 and ε'-$Fe_{22}C$
SB-1276	100 Fe/5 Cu/6 K/24 SiO_2 (S5624-3, calcined at 700°C, 1 h)	0	59% (Spm), 27% (Fe_3O_4), and 14% (α-Fe)	Fe_3O_4, and α-Fe
		138	44% (Spm), 30% (Fe_3O_4) and 26% (ε'-$Fe_{22}C$)	Fe_3O_4 and ε'-$Fe_{22}C$
		239	39% (Spm), 26% (Fe_3O_4) and 35% (ε'-$Fe_{22}C$)	Fe_3O_4 and ε'-$Fe_{22}C$
		311	33% (Spm), 24% (Fe_3O_4) and 43% (ε'-$Fe_{22}C$)	Fe_3O_4 and ε'-$Fe_{22}C$
		384	27% (Spm), 23% (Fe_3O_4) and 50% (ε'-$Fe_{22}C$)	Fe_3O_4 and ε'-$Fe_{22}C$

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 - 1.8 Nl/g-cat/h.

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 = 1.2 - 2.2 Nl/g-cat/h.

FTS process conditions for fixed bed tests with catalysts C and B were: T = 250°C, P = 1.48 MPa, $H_2/CO = 0.67$, SV = 2.0 Nl/g-cat/h.

After the reduction at 240°C for 2 h (run SB-0676, TOS = 0 h) catalyst C, calcined at 700°C for 1 h, was not reduced to metallic iron and only magnetite (Fe_3O_4) was identified by both XRD and MES analysis. In samples withdrawn from the slurry reactor at TOS = 120-305 h, both magnetite and pseudo-hexagonal iron carbide (ε'-$Fe_{2.2}C$) were found. The catalyst activity in run SB-0676 declined slowly with time on stream (see Figure VII-2.8b).

Figure VII-1.2 illustrates the XRD patterns of catalyst samples withdrawn from slurry test SB-1276 with catalyst B calcined at 700°C for 1 h, and reduced at 250°C in H_2 for 4 h. Magnetite (Fe_3O_4) and metallic iron (α-Fe) were found in the sample withdrawn immediately after the hydrogen reduction (TOS = 0 h) as shown in Figure VII-1.2A. Both magnetite (Fe_3O_4) and pseudo-hexagonal iron carbide (ε'-$Fe_{22}C$) were found in the samples withdrawn during F-T synthesis (Figure VII-1.2B to VII-1.2E). These results are in qualitative agreement with the MES analysis (Table VII-1.2). From the MES results of used catalyst samples from run SB-1276 it appears that the fraction of iron phase(s) exhibiting superparamagnetic behavior decreases from 44% (at TOS = 138 h) to 27% (at TOS = 384 h), and the fraction of iron in the form of magnetite decreases from 30 to 23% during the same time period. Also, the fraction of pseudo-hexagonal iron carbide increased from 26 to 50% as the time on stream increased from 138 to 384 h (Table VII-1.2). Catalyst activity was continually decreasing with time during run SB-1267 (see Figure VII-2.5b).

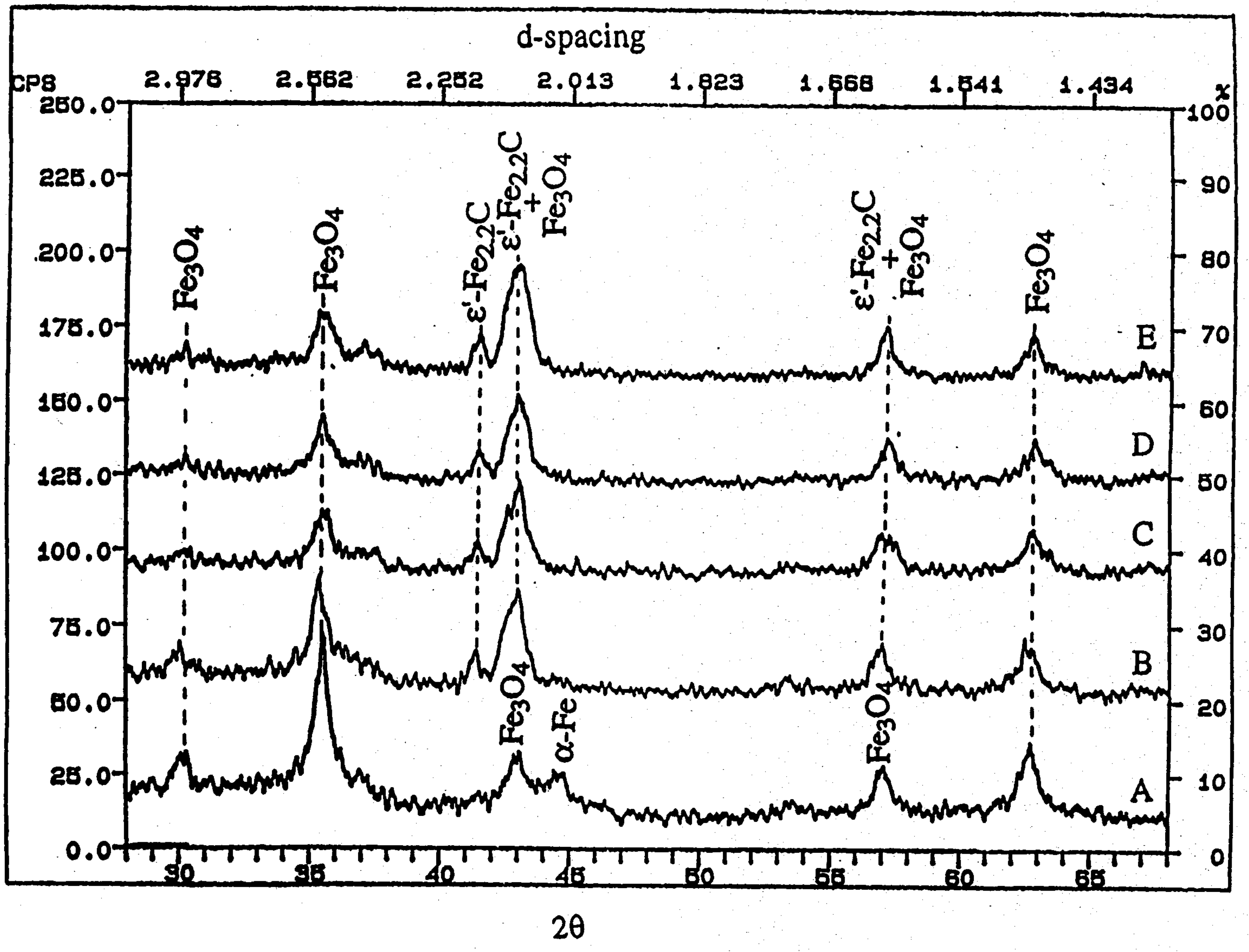

Figure VII-1.2 Changes in bulk iron phases with time on stream during run SB-1276 with catalyst B (100 Fe/5 Cu/6 K/24 SiO_2, batch-3) calcined at 700°C for 1 h and reduced at 250°C in H_2 for 4 h: (A) TOS = 0 h; (B) TOS = 138 h; (C) TOS = 239 h; (D) TOS = 311 h; (E) TOS = 384 h.

VII-2 Reaction Studies

In this section we report results on the effect of calcination temperature on performance of catalysts B (from batch-3) and C (from batch-4) during F-T synthesis. Both catalysts were calcined in air at 400°C, 500°C and 700°C, to study the effect of calcination temperature relative to our standard (baseline) calcination temperature of 300°C for 5 hours.

Six fixed bed tests were completed and results from these tests are compared with those obtained in tests carried out with catalysts calcined at 300°C. Test identification and calcination conditions are listed in Table VII-2.1. Two tests with catalysts B and C calcined at 700°C for 1 h were conducted in a STSR to determine whether the trends found in fixed bed reactor tests remain the same during F-T synthesis in slurry phase. Results from these two tests are compared with tests SA-1665 (catalyst C) and SB-1295 (catalyst B) made with catalysts calcined at 300°C. Slurry tests identifications are also listed in Table VII-2.1.

VII-2. 1 Fixed Bed Reactor Tests

About 3 g of the catalyst sized to 30/60 mesh (250-600 μm) was diluted 1:7 (reactor B) or 1:9 (reactor A) by volume with glass beads of the same size range and charged into the reactor. The catalyst was reduced with hydrogen at atmospheric pressure, gas flow rate of 7500 cm^3/min either at 250°C for 4 hours (catalyst B) or at 240°C for 2 hours (catalyst C), and then tested at 250°C, 1.48 MPa (200 psig), 2 Nl/g-cat/h using syngas with H_2/CO molar ratio of 0.67. Test durations were 120-140 h, including 30 hour conditioning period to reach the reaction temperature of 250°C.

Table VII-2.1. Calcination Temperatures and Test Designations

Test ID	Catalyst used	Calcination temperature, (°C)
FB-1715	100 Fe/5 Cu/6 K/24 SiO_2	300
FB-2975		400
FA-2925		500
FB-0236		700
SB-1295		300
SB-1276		700
FA-1605	100 Fe/3 Cu/4 K/16 SiO_2	300
FA-3095		400
FA-3905		500
FA-3495		700
SA-1665		300
SB-0676		700

FA, FB = Fixed bed reactor test; SB = Slurry phase reactor test

Fixed Bed Reactor Tests of Catalyst B (100 Fe/5 Cu/6 K/24 SiO_2)

Changes in synthesis gas conversion with time-on-stream are shown in Figure VII-2.1. Before the feed interruption at about 70 h on stream, the catalyst calcined at 400°C (run FA-2975) had the highest conversion (~70%). Upon resumption of this test, the conversion increased gradually with time and approached 60% at 140 hours. The catalyst B calcined at 500°C (run FB-2925) had the same activity and deactivation trends as the catalyst calcined at

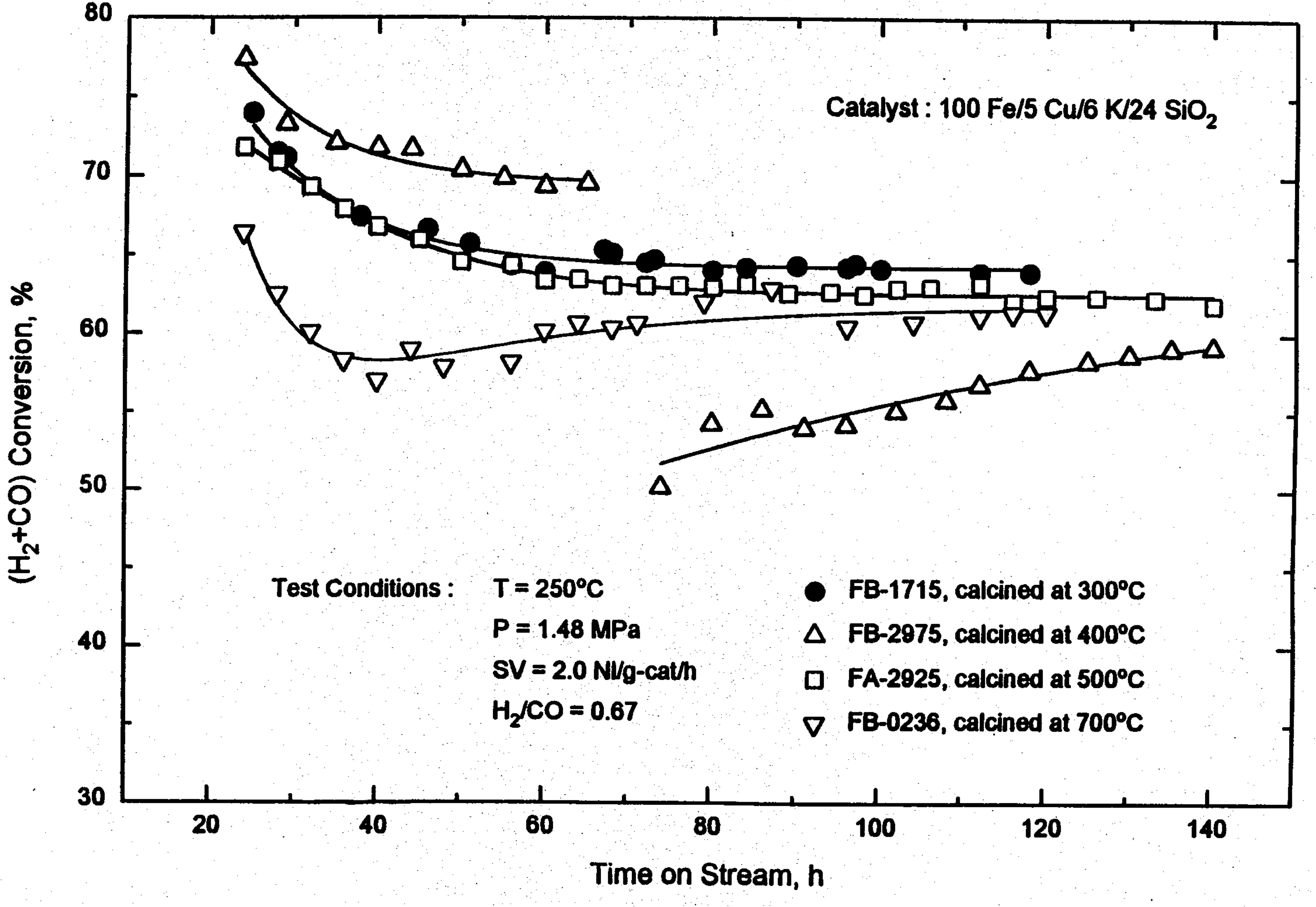

Figure VII-2.1 · Synthesis gas conversion as a function of time for fixed bed reactor tests of catalyst B calcined at different temperatures.

300°C (run FB-1715). Initially, conversions in run FB-0236 with the catalyst calcined at 700°C for 1 h were lower than in other tests, which was partly due to fluctuations in reactor temperature. However, after about 80 h on stream, the syngas conversions in this run were similar to those obtained with catalysts calcined at lower temperatures (300 to 500°C). The usage ratios in all four tests were similar (0.58-0.60) and stable with time.

Gaseous hydrocarbon selectivities as a function of time on stream for all four tests are shown in Figure VII-2.2. Catalysts calcined at 400°C (before interruption of the feed flow) and at 700°C produced more methane than the ones calcined at 300°C or 500°C (Figure VII-2.2a). Gaseous hydrocarbon selectivity (C_2-C_4 hydrocarbons) of the catalyst calcined at 700°C (run FB-0236) was higher than that obtained in other tests (Figure VII-2.2b).

Fixed Bed Reactor Tests of Catalyst C (100 Fe/3 Cu/4 K/16 SiO_2)

As shown in Figure VII-2.3, the initial syngas conversion of the catalysts calcined at 400°C (run FA-3305) and 500°C (run FA-3095), were the same as that of the catalyst calcined at 300°C (run FA-1605). However, the catalysts calcined at 400°C and 500°C deactivated faster than the catalyst calcined at 300°C, and at 100 h on stream the conversions in these two tests were about 8% less than those obtained in run FA-1605. The synthesis gas conversion in run FA-3495 with the catalyst calcined at 700°C was significantly lower than that obtained with catalysts calcined at 300-500°C. The usage ratios in all four tests were about the same, 0.57-0.60 indicating similar WGS activity.

Gaseous hydrocarbon selectivities in all four tests were similar. For example, methane selectivity was generally between 5% and 6%, (Figure VII-2.4a), and C_2-C_4 selectivities were between 21% and 25% (Figure VII-2.4b).

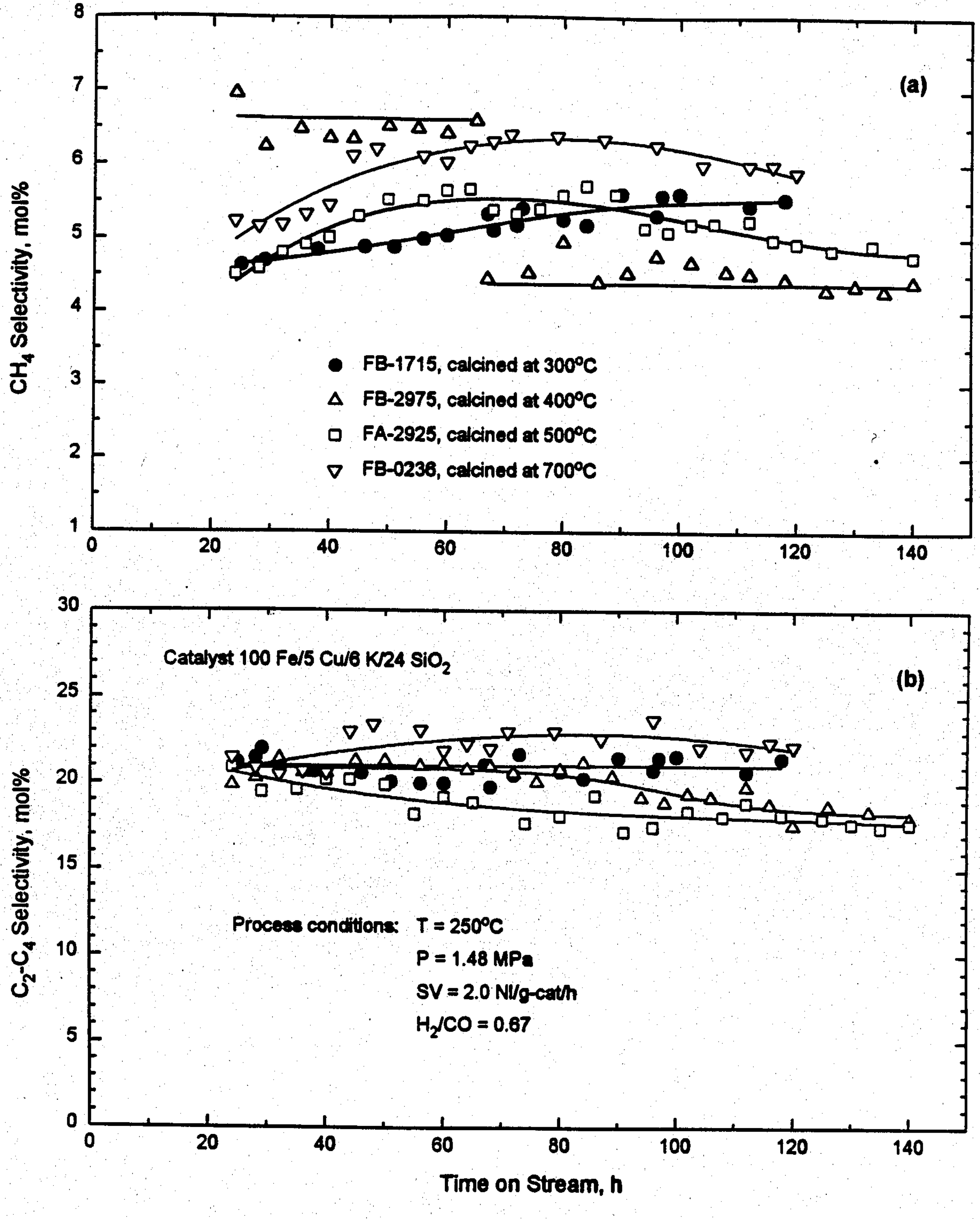

Figure VII-2.2 Methane selectivity (a) and (C_2- C_4) hydrocarbon selectivity (b) as a function of time for fixed bed reactor tests of catalyst B calcined at different temperatures.

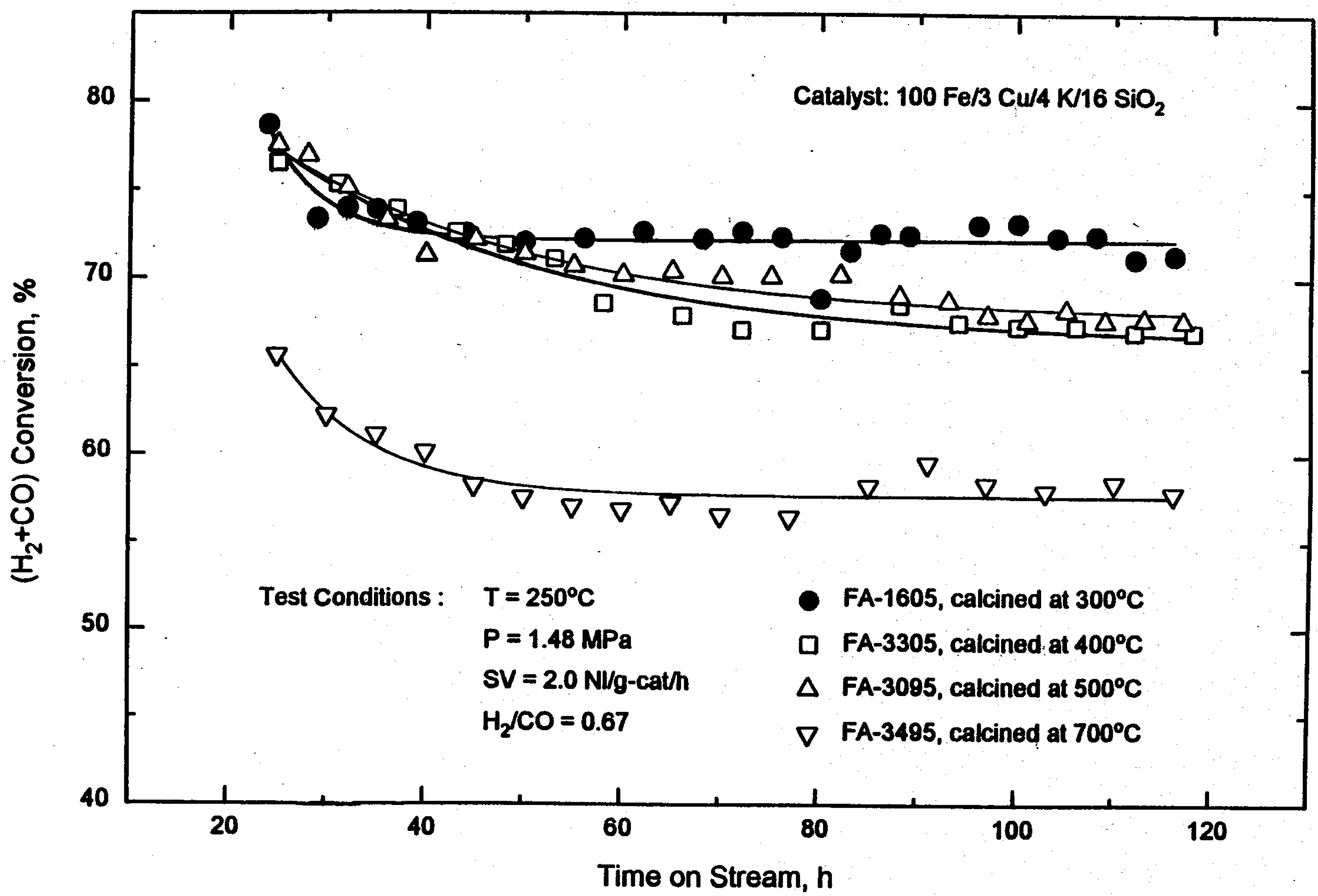

Figure VII-2.3 Synthesis gas conversion as a function of time for fixed bed reactor tests of catalyst C calcined at different temperatures.

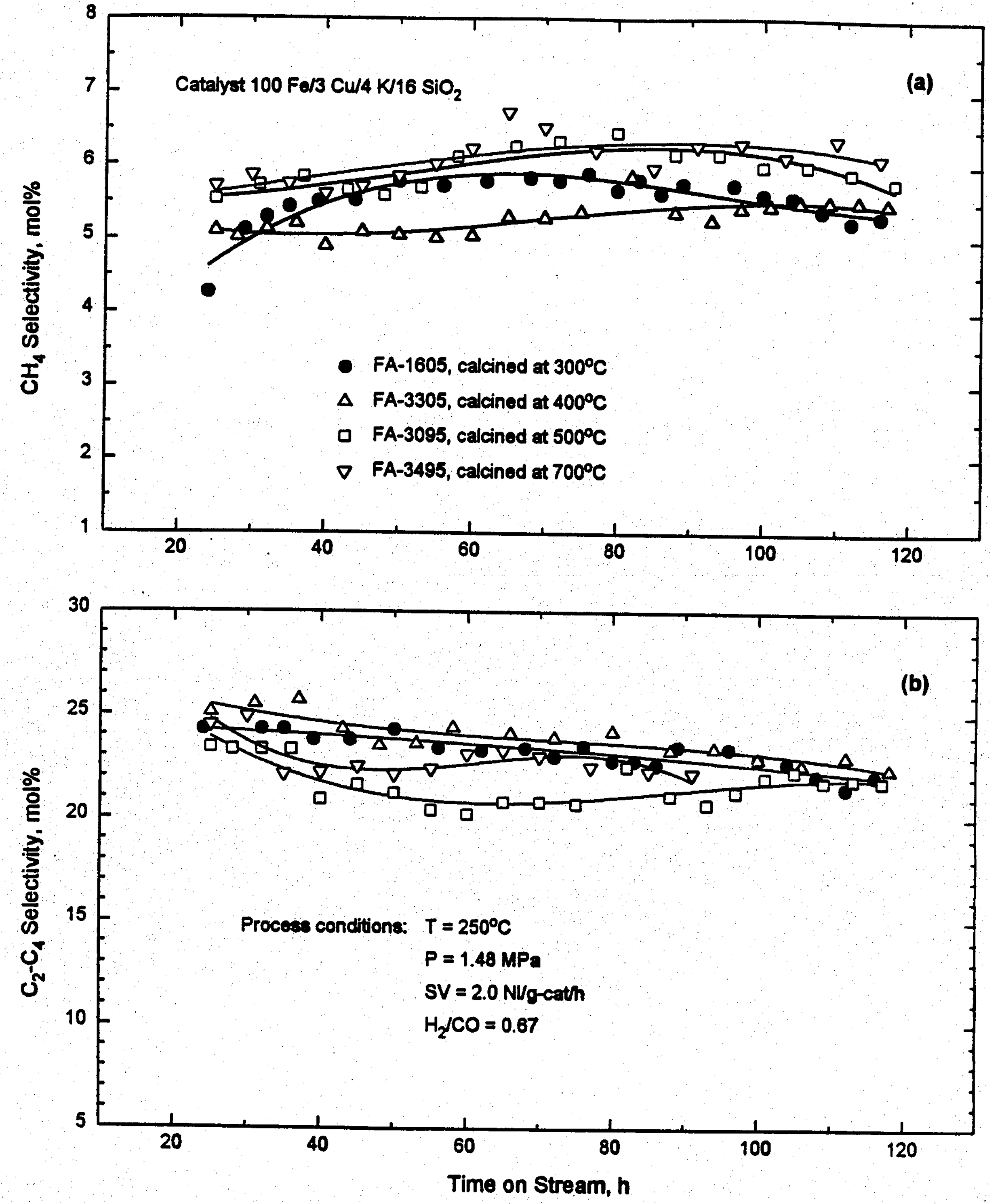

Figure VII-2.4 Methane selectivity (a) and (C_2- C_4) hydrocarbon selectivity (b) as a function of time for fixed bed reactor tests of catalyst B calcined at different temperatures.

VII-2. 2 Stirred Tank Slurry Reactor Tests

For slurry reactor tests 14 to 16 g of catalyst B and C (particle size less than 53 μm) calcined at 700°C for one hour was charged to a reactor, and Durasyn 164 oil was used as the initial slurry liquid. The initial concentration of slurry was 4.8-5.4 wt%. The catalyst was reduced with hydrogen, at 7500 cm^3/min, 0.8 MPa and 250°C for 4 hours (catalyst B), or 240°C for 2 hours (catalyst C). The same reduction conditions were used for catalysts B and C calcined at 300°C.

Slurry Reactor Tests of Catalyst B

After the pretreatment, the catalysts were tested at 260°C, 1.48 MPa, synthesis gas molar feed ratio of 0.67 and gas space velocity of 2.2 Nl/g-cat/h for 48 h, and then at 1.8 Nl/g-cat/h for the next 138 hours. The syngas conversion in run SB-1276 with the catalyst calcined at 700°C was significantly lower than that obtained in the test of the catalyst calcined at 300°C (SB-1295) under the same process conditions (Figure VII-2.5a). For example at 260°C, 1.48 MPa, gas space velocity of 1.8 Nl/g-cat/h the syngas conversion was about 70% for the catalyst calcined at 300°C, whereas the syngas conversion with the catalyst calcined at 700°C was 57%. To get higher conversions with the catalyst calcined at 700°C, higher reaction pressure (2.17 MPa) and lower gas space velocity (1.2 Nl/g-cat/h) were used.

Comparison of catalyst activity in terms of the apparent reaction rate constant is shown in Figure VII-2.5b. The catalyst deactivated with time in both tests, but during the first 150 hours on stream the rate of deactivation was much higher on the catalyst calcined at 300°C (run SB-1295). The deactivation rate of the catalyst calcined at 700°C (run SB-1276)

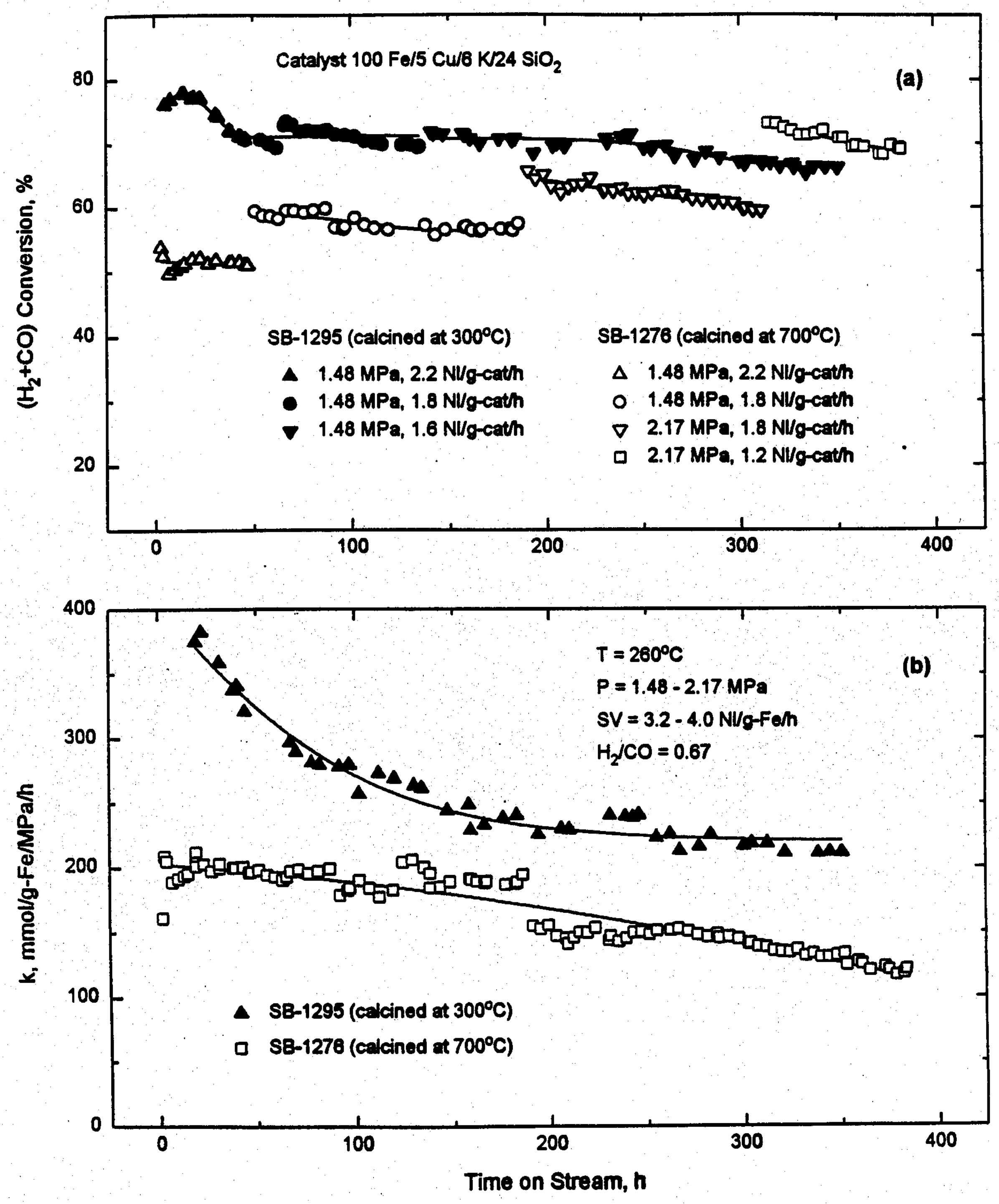

Figure VII-2.5 Synthesis gas conversion (a) and apparent reaction rate constant (b) as a function of time for STSR tests of catalyst B calcined at different temperatures.

was nearly constant regardless of the test conditions, and its activity was lower than that of the catalyst calcined at 300°C.

The catalyst calcined at 700°C had also lower WGS activity than the catalyst calcined at 300°C. The H_2/CO usage ratio obtained for this catalyst was about 0.56 in run SB-1295, whereas in run SB-1276 it was 0.60 (see Table VII-2.2).

The catalyst calcined at 700°C had relatively high initial methane selectivity (Figure VII-2.6a). However, after 60-70 hours on stream, the methane selectivity started to decrease, and after about 200 hours it was nearly the same as methane selectivity obtained with the catalyst calcined at 300°C (about 4 mol%). The same trend was observed for C_1+C_2 selectivity (Figure VII-2.6b).

Olefin selectivity for the catalyst B in tests SB-1295 and SB-1276 is shown in Figure VII-2.7. The olefin content obtained with the catalyst calcined at 700°C is almost independent of carbon number (for C_5+ hydrocarbons). Ethene selectivity in run SB-1276 was high (~72%), and the maximum olefin content (~ 82%) was obtained for propene. The olefin content was approximately 70 % for C_8+ hydrocarbons. The olefin content in run SB-1295 (catalyst calcined at 300°C) decreased from 82% (propene) to about 50% (at C_{15}). 2-olefin content obtained in run SB-1276 was lower then that in run SB-1295 with the catalyst calcined at 300°C. The catalyst calcined at 700°C had markedly higher selectivity to alpha olefins for C_{10}+ hydrocarbons.

Lumped hydrocarbon distribution, activity parameters and product yields obtained in runs SB-1295 and SB-1276 at 120-160 hours on stream are shown in Table VII-2.2. The catalyst calcined at 700°C had higher selectivity to lower molecular weight hydrocarbons than the catalyst calcined at 300°C, and produced much more oxygenates (30 g/Nm^3 in run SB-1276 vs. 6.9 g/Nm^3 in run SB-1295).

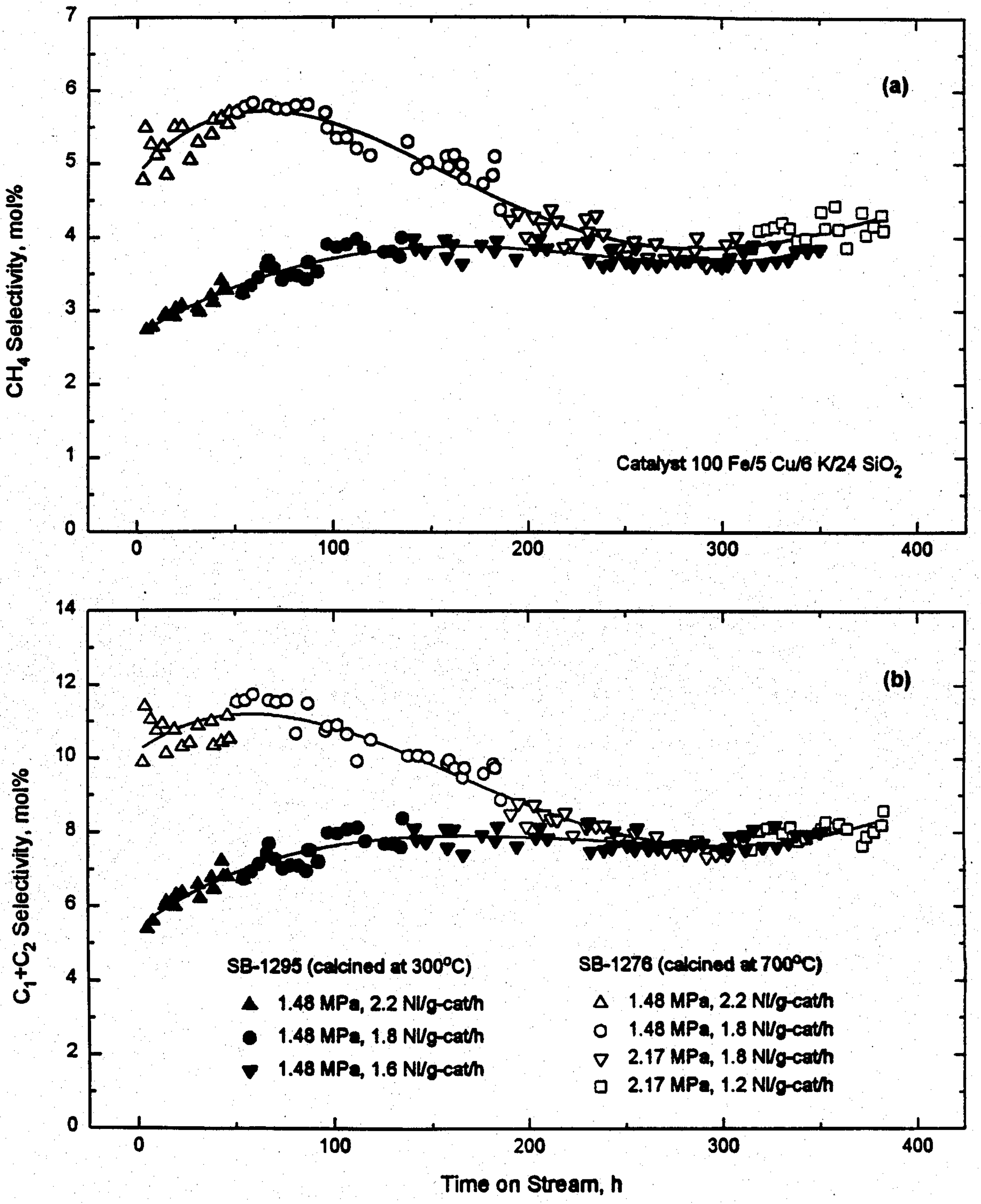

Figure VII-2.6 Methane selectivity (a) and ($C_1 + C_2$) hydrocarbon selectivity (b) as a function of time for STSR tests of catalyst B calcined at different temperatures.

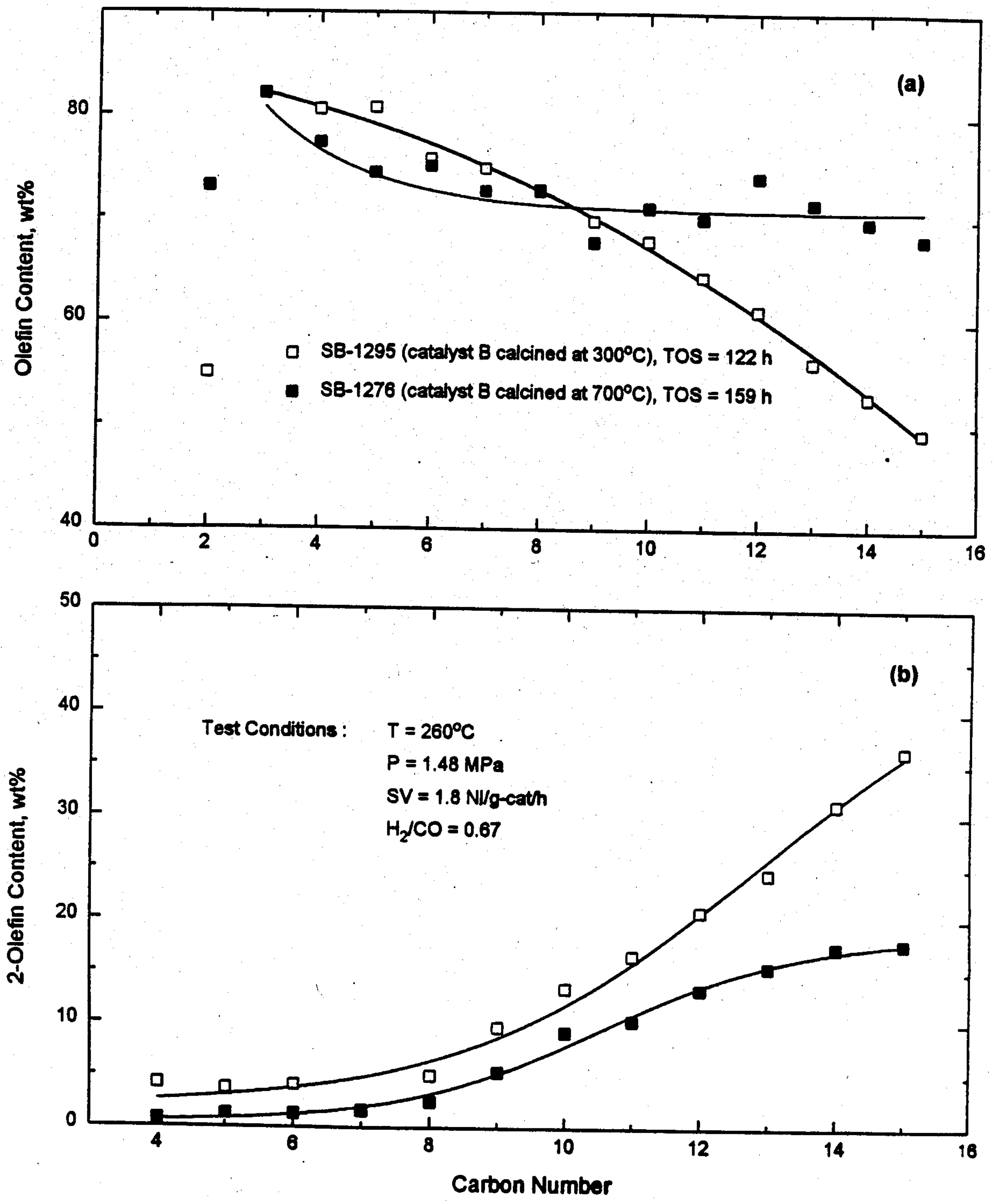

Figure VII-2.7 Olefin content (a) and 2-olefin content (b) dependence on carbon number for catalyst B calcined at different temperatures.

Table VII-2.2 Effect of Calcination Temperature on the Performance of Catalysts B and C in Slurry Reactor Tests

Test designation	SB-1295	SB-1276	SA-1665		SB-0626	
Catalyst	100 Fe/5 Cu/6 K/24 SiO_2[a]		100 Fe/3 Cu/4 K/16 SiO_2[b]			
Calcination temperature, °C	300	700	300		700	
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	1.8	1.4	2.0	1.4	1.8
Feed H_2/CO ratio	0.67	0.67	0.67	0.67	0.67	0.67
Time on stream, h	122	159	112	485	113	281
CO conversion, %	74.3	59.1	84.1	70.9	65.6	61.4
(H_2+CO) conversion, %	69.6	56.6	79.0	67.4	60.8	57.4
STY, mmol (H_2+CO)/g-cat/h	57	43	49	61	38	46
k, mmol/g-Fe/h/MPa[c]	259	181	238	176	148	117
(H_2/CO) usage ratio	0.56	0.60	0.57	0.58	0.56	0.56
$K_p = P_{CO2} \cdot P_{H2} / P_{CO} / P_{H2O}$	39		33	23	55	24
% CO converted to CO_2	48.9	49.4	48.9	48.2	49.1	49.0
Hydrocarbon selectivity, wt%						
CH_4	4.4	6.1	3.2	3.2	4.7	4.0
C_2-C_4	15.6	20.1	12.3	15.2	15.1	14.3
C_5-C_{11}	21.8	36.7	12.0	15.7	27.0	30.6
C_{12}-C_{18}	18.4	24.2				27.4
C_{12}+	59.2	37.0	72.5	66.0	53.2	51.2
C_1+C_2	8.3	11.2	6.6	7.2	8.9	7.4
Yield, g/Nm^3(H_2+CO) Converted						
Hydrocarbons	205	186	204	201	195	198
Oxygenates	6.9	30	2.4	4.2	17	15
Catalyst productivity, g HC/g-cat/h	0.26	0.18	0.22	0.27	0.17	0.20

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

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

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

Slurry Reactor Tests of Catalyst C

The catalysts were tested initially at 260°C, 1.48 MPa, synthesis gas molar feed ratio of 0.67 and gas space velocity 1.4 Nl/g-cat/h, and then the pressure was increased to 2.17 MPa, and the gas space velocity was increased to either 2.0 Nl/g-cat/h in run SA-1665 or to 1.8 Nl/g-cat/h in run SB-0626. The syngas conversions on the catalyst calcined at 700°C (run SB-0626) were lower than those obtained in run SA-1665 with the catalyst calcined at 300°C (Figure VII-2.8a).

The apparent reaction rate constants for these two tests are shown in Figure VII-2.8b. The initial value of k in run SA-1665 was about 250 mmol/g-Fe/h/MPa and then it decreased to 240 mmol/g-Fe/h/MPa at 270 hours.. The activity of the catalyst C calcined at 700°C also decreased with time, and its deactivation rate was fairly constant. The reaction rate constant decreased from initial value of 150 mmol/g-Fe/h/MPa to 117 mmol/g-Fe/h/MPa at 380 hours. The WGS activity of the catalyst C was not affected by calcination temperature, and varied between 0.56 and 0.57 in both tests (Table VII-2.2).

Initially, the catalyst calcined at 700°C (SB-0626) had higher methane and C_1+C_2 selectivity than the catalyst calcined at 300°C (SA-1665) (Figure VII-2.9). For example, at about 100 h on stream the methane selectivities were 4 mol% and 2.8 mol% for the catalysts calcined at 700°C and 300°C, respectively. However, methane and C_1+C_2 hydrocarbon selectivity of the catalyst calcined at 700°C decreased with time, and became more similar to those obtained in run SA-1665. For example, at 250 hours the methane selectivities were 3.5 mol% and 2.8 mol% for the catalyst calcined at 700°C and 300°C, respectively.

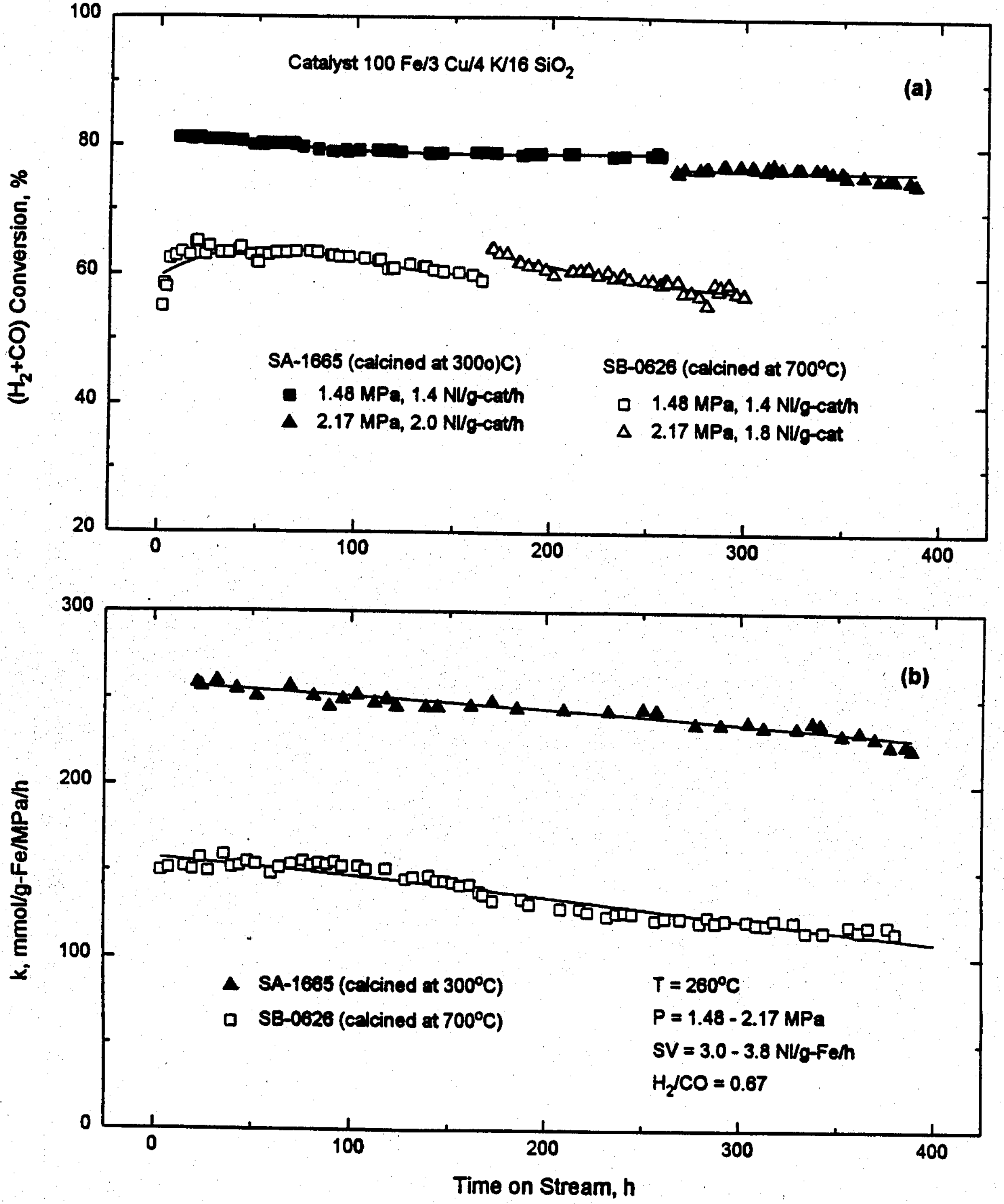

Figure VII-2.8 Synthesis gas conversion (a) and apparent reaction rate constant (b) as a function of time for STSR tests of catalyst C calcined at different temperatures.

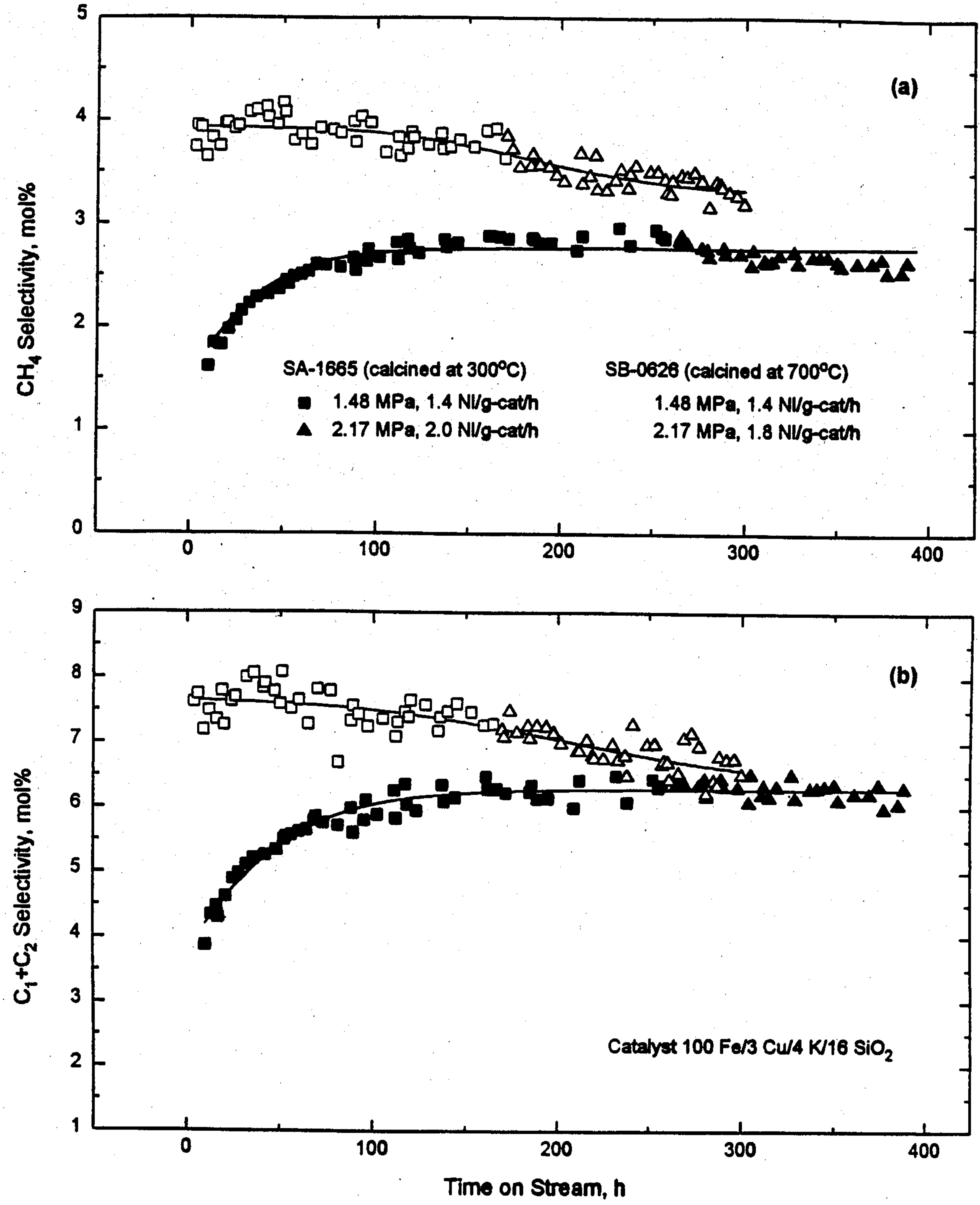

Figure VII-2.9 Methane selectivity (a) and (C_1+C_2) hydrocarbon selectivity (b) as a function of time for STSR tests of catalyst C calcined at different temperatures.

Total olefin and 2-olefin contents of catalyst C calcined at two different temperatures are shown in Figure VII-2.10. As in the case of catalyst B, the olefin content of the catalyst calcined at 700°C is almost independent of carbon number for C_5+ hydrocarbons, and its 2-olefin content is lower then that obtained with the catalyst calcined at 300°C (SA-1665).

Lumped hydrocarbon distribution at different times on stream is shown in Table VII-2.2. Catalyst calcined at 700°C had higher selectivity to lower molecular weight products, and its gasoline fraction is 27-31% of total hydrocarbon products. Also, the catalyst calcined at 700°C had much higher yield of oxygenates than the catalyst calcined at 300°C.

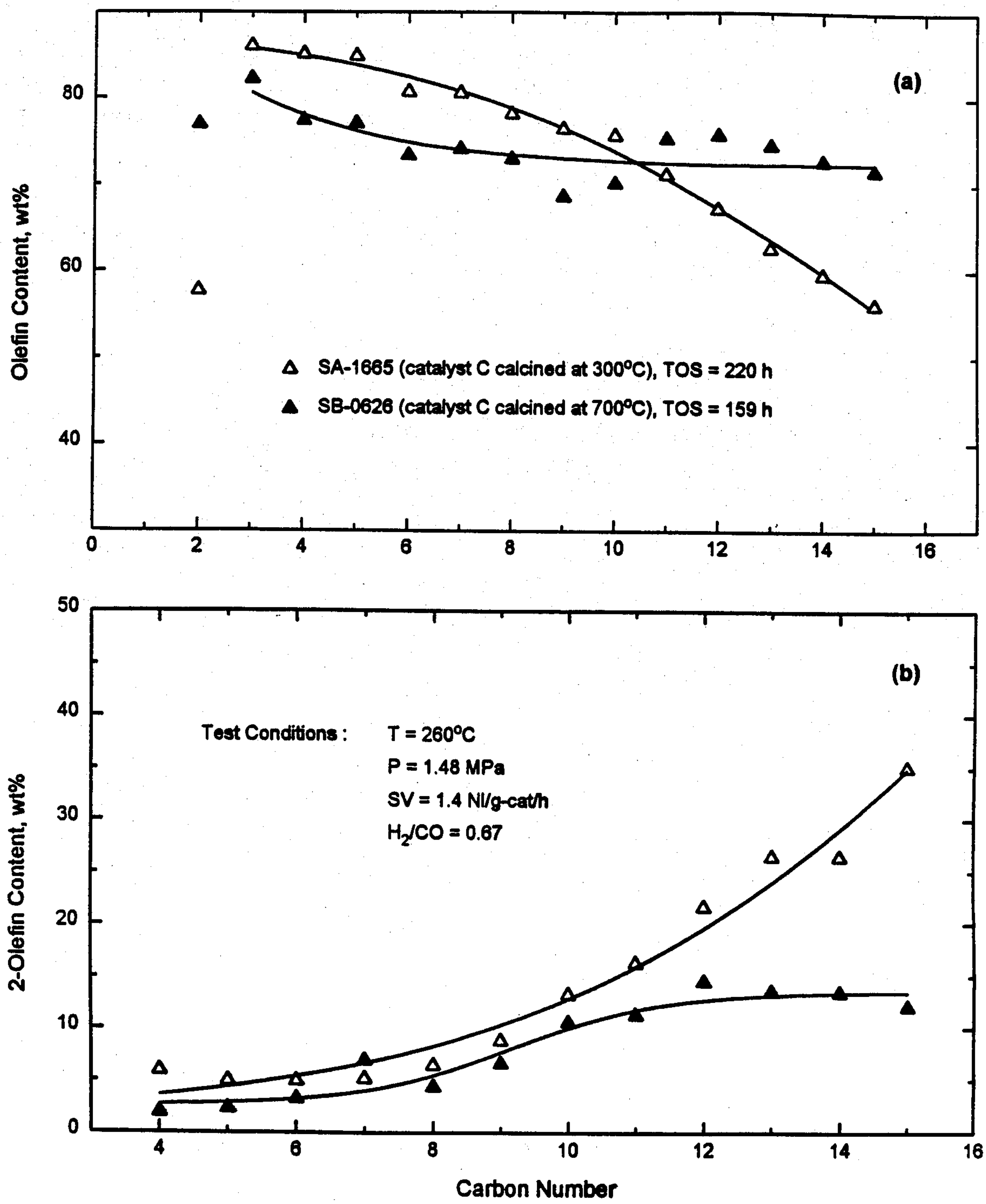

Figure VII-2.10 Olefin content (a) and 2-olefin content (b) dependence on carbon number for catalyst C calcined at different temperatures.

Concluding Remarks on the Calcination Effect Research

We have conducted six fixed bed reactor tests, and two slurry reactor tests under this task. Both catalyst B (100 Fe/5 Cu/6 K/24 SiO_2) and C (100 Fe/3 Cu/4 K/16 SiO_2) were tested in fixed bed reactors after calcinations at 400°C and 500°C for 5 h, and after flash calcination at 700°C for 1 h, and in a stirred tank slurry reactor after flash calcination at 700°C for 1 h.

In fixed bed reactor tests, activities, as well as gaseous hydrocarbon selectivities, of catalysts B and C calcined at 400°C and 500°C, were similar to those of catalysts calcined at 300°C. Catalysts calcined at 700°C for 1 h had lower activity, than the catalysts calcined at temperatures of 300-500°C. Gaseous hydrocarbon selectivity of catalyst C, was not strongly affected by the use of different calcination temperatures, whereas the catalyst B calcined at 700°C had higher gaseous hydrocarbon selectivity than the catalysts calcined at lower temperatures.

The main findings from slurry reactor tests are: (1) The activity of catalysts B and C calcined at 700°C is lower than that of these two catalysts calcined at 300°C; (2) Gaseous hydrocarbon selectivities are higher on catalysts calcined at 700°C; (3) Alpha olefin selectivity of C_{10}+ hydrocarbons was markedly higher on catalysts calcined at 700°C; and (4) Oxygenate yields were about four times higher on the catalysts B and C calcined at 700°C, than on the catalysts calcined at 300°C.

VII-3 References

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