Fischer-Tropsch Synthesis Over Iron/Silica Catalysts

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DOE Contractors' Review Meeting
Pittsburgh, PA, November 6-8, 1990

Contract DE-AC22-89PC89868

INTRODUCTION

The objective of this three year contract (September 27, 1989 – September 26, 1992) is to develop catalysts with enhanced slurry phase activity and higher selectivity to fuel range products, through a better understanding and systematic studies of the effects of pretreatment procedures and promoters/binders (silica) on catalyst performance. Synthesized catalysts will be tested in automated fixed bed (screening tests, 5-7 days) and stirred tank slurry reactors (up to 30 days on stream). The most promising compositions will be characterized by a variety of physical, chemical and instrumental techniques with the objective to establish correlation between the physical/chemical properties of the catalyst and the corresponding catalytic behaviors for the Fischer-Tropsch synthesis. The two main research tasks for this contract are Pretreatment Effect Research and Development of Improved Iron/Silica Catalysts.

PRETREATMENT EFFECT RESEARCH

Prior studies in our laboratory (Bukur et al., 1987, 1988, 1989a) with a precipitated iron catalyst have shown that pretreatment conditions (nature of reductant, activation temperature, duration and pressure) have significant effect catalyst activity, stability and selectivity during Fischer-Tropsch synthesis (FTS). The objectives of the present study are to develop a better understanding of the role of pretreatment conditions on the catalyst performance, and establish optimal pretreatment conditions for two types of iron based catalysts (unsupported and silica supported). We plan to investigate 2-3 catalysts, and use (4-6) combinations of pretreatment conditions for each of the catalysts (see Table 1).

We have initiated these studies with the state-of-the-art Ruhrchemie catalyst (100 Fe/5 Cu/4.2 K/25 SiO_2, in parts per weight). Four fixed bed, and two slurry reactor tests have been completed. The pretreatment conditions employed are listed in Table 2.

After the pretreatment, the catalyst was tested at 200 psig (1.48 MPa), 250°C, 2(Nl/g-cat/h) with the syngas with H_2:CO molar ratio of 2:3. Test duration was between 160 and 1200 h.

Detailed description of our experimental apparatus, product analysis system and operating procedures can be found elsewhere (Bukur et al., 1989a; 1990 a, b, c; Zimmerman and Bukur, 1990).

The effect of pretreatment conditions on the catalyst activity, and stability is shown in Figure 1 (Fixed bed reactor tests). (H_2 + CO) conversion in all four tests was between 55 and 68% during the first 200 h on stream. The conversion increased with time on stream in the two tests with H_2 as reductant, whereas it decreased in the test where CO activation was employed. These trends are in qualitative agreement with our results obtained in tests with the unsupported 100 Fe/3 Cu/0.2 K catalyst (Bukur et al., 1988; 1989a). The activity of the syngas activated catalyst (H_2:CO = 2:1 at 310°C) was fairly stable between 50 and 160 h on stream. Following manufacturer's recommendation H_2 reductions were performed using high linear gas velocity (150 cm/s at reduction conditions) to prevent sintering. These results show that it is essential to maintain low water partial pressure during the reduction in order to achieve high catalyst activity. When the partial pressure of H_2O is low the reduction temperature has no effect on the activity. In our previous tests with the 100 Fe/3 Cu/0.2 K H_2 reductions were done using much lower H_2 flow rates and as a result the catalyst activity decreased with either increase in reduction temperature or with duration of the reduction (Bukur et al. 1987; 1988; 1989a).

The effect of pretreatment conditions on the water-gas-shift (WGS) activity, measured by H_2/CO usage ratio, is shown in Figure 2. The WGS activity was higher (lower usage ratio) with H_2 reductions. The WGS activity of the CO and syngas activated catalyst was the same. These observations are in agreement with results obtained from tests with the 100 Fe/3 Cu/0.2 K catalyst (Bukur et al., 1989a).

The effect of pretreatment conditions on hydrocarbon product distribution is illustrated in Table 3. The catalyst activated with CO had the lowest methane and the highest C_{12}^+ selectivity, whereas H_2 reduction at 280°C resulted in the highest methane and the lowest C_{12}^+ selectivity. Methane and C_2 - C_4 selectivities obtained using syngas activation at 310°C and the H_2 reduction at

220°C, were similar to those obtained using the CO activation. The reasons for differences in selectivities obtained are not known. Characterization of catalyst after the pretreatment and at the end of the test is required to assist in explanation of the results obtained in these tests.

The catalyst reduced at 220°C for 1 h was tested over a long period of time in both fixed bed and stirred tank slurry reactors. In the fixed bed reactor test FA-3509 (H_2+CO) conversion increased with time on stream during the first 240 h (60-68%), and then remained stable at 68% over the next 200 h. The (H_2+CO) conversion increased to 80% when the gas space velocity was lowered to 1.3 (N*l*/g-cat/h) and to 84% when the temperature was raised to 258°C from 250°C (Figure 3). The (H_2+CO) conversion was high (~85%) and very stable between 550 and 1050 h on stream. However, upon returning to the baseline conditions (250°C, 2 N*l*/g-cat/h, 200 psig, H_2/CO=0.67) a significant loss in activity was observed (H_2+CO conversion was 46-50% at the end of the run, 1100-1200 h).

Variation of the (H_2+CO) conversion with time on stream during the slurry reactor test SB-1370 is shown in Figure 4. The catalyst activity reached the steady state after about 40 h on stream, and remained stable during the next 320 h of testing at baseline process conditions: 250°C, 200 psig, 2 N*l*/g-cat/h , H_2/CO=0.65. Following the stability portion of the test process conditions were varied between 360 and 620 h on stream (mass balances 6-9). The catalyst had not deactivated during the process variable studies, and its activity at 620-670 h on stream was essentially the same as that observed during the first 360 h of testing (H_2+CO conversion of 38-40%). The (H_2+CO) increased to 48-52%, when the syngas feed composition was changed to H_2:CO=1:1 (670-770 h on stream). The test was terminated voluntarily after 770 h on stream.

Hydrocarbon selectivities from these two tests are shown in Table 4, together with results from runs FB-1588 and SA-0888 in which the Ruhrchemie catalyst was pretreated with CO. The results from the latter two tests have been described in detail elsewhere (Bukur et al., 1989b; 1990c) and only selected results are shown here to illustrate the effect of pretreatment procedure on the catalyst performance. As discussed earlier in the paper the activity of the H_2 reduced catalyst (measured by (H_2+CO) conversion) was greater than that of the CO pretreated catalysts, whereas methane and (C_2-C_4) selectivities in the fixed bed reactor tests were not markedly affected by differences in the pretreatment procedures (see Figure 1 and Tables 3 and 4). However, in the slurry tests the activity of the H_2 reduced catalyst was lower than that of the CO activated catalyst. The H_2 reduced catalyst produced less (C_2-C_4) hydrocarbons than the CO activated catalyst, whereas the methane selectivities were similar (see Table 4).

The (H_2+CO) conversions in the fixed bed reactor tests were higher than those in the slurry reactor tests for both pretreatments, because the former approaches the plug flow behavior whereas the latter is closer to the perfectly mixed flow reactor. The reactor type did not have a strong effect on hydrocarbon product distribution with CO pretreated catalyst (Table 4, Runs FB-1588 and SA-0888), whereas in tests where H_2 reduction was employed less gaseous (CH_4 and C_2-C_4) and more C_{12}^+ hydrocarbons were produced in the slurry reactor than in the fixed bed reactor.

Major results from the pretreatment effect studies are summarized in Figure 5.

IRON/SILICA CATALYSTS

The performance of silica containing iron Fischer-Tropsch catalysts of composition 100 Fe/5 Cu/4.2 K/x SiO_2 (x=0, 8, 24, and 100) was evaluated in our laboratory (Bukur et al., 1989b; 1990b). It was found that these catalysts are suitable for production of transportation fuels, by minimizing methane and gaseous hydrocarbon selectivities. The FTS activity of these catalysts decreased with increasing amount of silica, whereas the addition of silica was found to have beneficial effect on the catalyst stability. The objective of the current contract is to determine optimal concentrations of promoters (CuO, K_2O) and binders (SiO_2) needed to achieve the specified catalyst performance (Figure 6).

The work on this task has begun on March 1, 1990. 17 silica containing catalysts have been synthesized by controlled - pH, continuous precipitation method developed in our laboratory.

Two catalysts were evaluated in fixed bed and slurry reactor tests. Results from the slurry reactor tests, which lasted about 400 h each, are described below.

FTS activity, measured by volumetric gas contraction, of catalyst with nominal composition 100 Fe/5 Cu/4.2 K/8 SiO_2 as a function of time is shown in Figure 7. The catalyst was tested initially at 250°C, 200 psig (1.48 MPa), $H_2/CO=0.70$, and the gas space velocity of 2 N*l*/g-cat/h (i.e. gas flow rate of 1 N*l*/min). During the first 110 h the volumetric contraction (VC) increased slightly with TOS but after slurry withdrawal at about 110 h, the VC decreased by 10%. Some of the decline in activity may be attributed to loss of catalyst with wax removed from an external settling vessel used to separate the catalyst from excess wax produced during synthesis. Drops in activity were observed after each slurry withdrawal as shown in Figure 7. The slurry withdrawals in this figure are denoted by vertical lines, and the amounts withdrawn are also indicated. Upon increasing the reaction temperature to 258°C, the VC increased significantly but it dropped sharply after the second slurry withdrawal and subsequent temporary stoppage of the syngas flow at about 230 h, due to plugging of the gas inlet line. Baseline conditions were established at about 360 h on stream, and at this time the volumetric contraction was ~30%, compared to 34-38% between 20 and 100 h on stream. At this time about 9g of the catalyst, out of 30g charged initially was removed with the wax from the settler.

In the test of 100 Fe/5 Cu/4.2 K/16 SiO_2 catalyst only 10g of catalyst was charged initially to the reactor, and the wax produced during synthesis was removed through an internal cylindrical filter element with an average pore diameter of 2 μm. The catalyst was tested initially (first 250 h) at 260°C, 1.48 MPa, 1.4 N*l*/g-cat/h and $H_2/CO=0.69$. The volumetric gas contraction decreased slowly with TOS during the first 180 h, as shown in Figure 8. After the wax withdrawal (no catalyst was found in the wax withdrawn through the filter) at 184 h, the volumetric contraction decreased markedly from 41% to 31%; and then remained fairly stable during the next 40 h. Although, the reasons for this sharp drop in activity are not shown, we suspect that it might have been caused by removal of some of the catalyst from the synthesis zone. After removal of 194g of wax (~280 cm^3 at reaction conditions), it is possible that part of the catalyst remained above the slurry level (e.g. deposited on the reactor wall, or on the internal filter element which was placed vertically). It appears that this catalyst is not as active as the one in the slurry.

At about 230 h the reaction pressure and the gas space velocity where increased simultaneously to 300 psig (2.17 psig) and 2.3 Nl/g-cat/h; respectively. During the next 60 hours, the activity remained fairly stable (VC=21-23%), while the space-time-yield increased by nearly 50%. At about 250 h on stream an attempt was made to improve the catalyst activity by adding 65 g of wax to raise liquid level in the reactor. However, this did not result in increased catalyst activity.

At about 300 h, the catalyst was regenerated in-situ with H_2 at 220°C and 200 psig for 2 hours, and the catalyst activity increased markedly. At 311 h the volumetric contraction was 34%. However, the activity declined with time on stream, and at 400 h the volumetric contraction was only 23.5%.

The WGS activity of both catalysts was high, as shown in Table 5 (Usage ratios varied between 0.54 and 0.66). Initially, hydrocarbon selectivities of both catalysts were within the specified target performance (i.e. C_1+C_2 selectivity less than 8 wt%), but the distribution shifted gradually towards lower molecular weight hydrocarbons with catalyst aging (particularly with the catalyst containing 16 parts of SiO_2). The catalyst deactivation rate was greater than the target rate (see Table 6). It appears that the deactivation rate was accelerated by wax (slurry) withdrawals. Further improvements in the wax (slurry) withdrawal procedures are required to remedy this problem.

Finally, we report results from a test of silica containing iron catalyst which is still in progress. This work is conducted in our laboratory with financial support from the Texas Higher Education Coordinating Board as a part of the Texas Advanced Technology Program.

During first 250 h on stream the catalyst was tested at 260°C, 1.48 MPa, 2.5 Nl/g-Fe/h and H_2/CO=0.66. The (H_2+CO) conversion as a function of time is shown in Figure 9. Initially (10-

40 h on stream) the conversion was about 88%, and it decreased slowly to 76% at 250 h on stream (Loss in conversion of about 1% per day). The initial activity and stability of this catalyst satisfied several performance criteria (Table 6). Also, hydrocarbon selectivity of this catalyst was within the target performance. It should be noted that the performance criteria listed in Table 6, were established on the basis of results obtained in the slurry bubble column reactors (Kölbel and Ralek, 1980; Kuo, 1985), whereas our tests were conducted in a stirred tank slurry reactor. For a given catalyst one would expect to obtain higher activity and more favorable hydrocarbon selectivity (less gaseous hydrocarbons) in the bubble column reactor than in the stirred tank reactor.

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Table 1. Catalyst Pretreatment Research Plan

(a) Catalysts (2-3):

(1)	100 Fe/x Cu/y K/z SiO_2	iron/silica catalyst
(2)	100 Fe/0.3 Cu/0.5-1.0 K	unsupported catalyst
(3)	Ruhrchemie catalyst	commercial state-of-the-art catalyst

(b) Activation parameters (4-6 per catalyst)

- Reductant type (H_2, CO, syngas)
- Activation temperature (220-310°C)
- Duration (1-24 h)
- Flow rate (?)

Table 2. Pretreatment Conditions and Test Designations

TEST (ID)	TEMP. (°C)	REDUCTION TYPE	DURATION (h)	PRESSURE (MPa)
FB-1588	280	CO	12	0.1
FA-3509	220	H_2	1	0.1
FB-1920	280	H_2	1	0.1
FB-2290	310	H_2:CO=2:1	6	0.1
SA-0888	280	CO	16	0.8
SB-1370	220	H_2	1	0.8

(FA, FB) – Fixed Bed Reactor Tests

(SA, SB) – Slurry Reactor Tests

Table 3. Comparison of Pretreatment Procedures

Run ID	FA-3509	FB-1920	FB-1588	FB-2290
Red. Cond.	H_2, 1h 220°C	H_2, 1h 280°C	CO, 12h 280°C	H_2/CO(2:1), 6h 310°C
TOS(h)	50-200	71-197	70-198	49-162
% CO conv.	55.0-63.1	58.0-70.6	51.9-56.8	56.8-61.7
%H_2+CO *conv.*	60.2-64.4	61.4-67.6	54.9-59.1	60.4-64.3
Hydrocarbon Selectivities:				
CH_4	6.2	9.2	5.4	7.0
C_2 - C_4	20.4	24.4	21.9	23.0
C_5 - C_{11}	29.2	46.6	18.7	23.1
C_{12}+	44.2	19.8	54.0	46.9

Conditions: 200 psig; 2 Nl/h.g-cat; H_2/CO = 0.67; 250°C
Ruhrchemie LP 33/81 Catalyst

Table 4. Catalyst Performance in Fixed Bed and Slurry Bed Reactors

Run ID	FA-3509	SB-1370	FB-1588	SA-0888
Red. Cond.	H_2, 1h 220°C	H_2, 1h 220°C	CO, 12h 280°C	CO, 16h 280°C
TOS(h)	50-200	66-186	70-198	45-163
% CO conv.	55.0-63.1	32.3-38.4	51.9-56.8	42.1-46.5
%H_2+CO *conv.*	60.2-64.4	36.9-40.1	54.9-59.1	43.7-46.4
Hydrocarbon Selectivities:				
CH_4	6.2	4.3	5.4	4.7
C_2 - C_4	20.4	14.7	21.9	19.8
C_5 - C_{11}	29.2	25.6	18.7	21.2
$C_{12}{}^+$	44.2	55.4	54.0	54.3

Conditions: 200 psig; 2 N*l*/h.g-cat; H_2/CO = 0.67; 250°C
Ruhrchemie LP 33/81 Catalyst

Table 5. Comparison of Iron/Silica Catalysts - Slurry Bed Reactor Tests

CATALYST	$100Fe/5Cu/4.2K/8SiO_2$			$100Fe/5Cu/4.2K/16SiO_2$			
Process Conditions							
Temp. (°C)	250	250	258	260	260	260	260*
Press. (MPa)	1.48	1.48	1.48	1.48	1.48	2.17	2.19
SV (Nl/h.g-Fe)	3.30	3.50	3.90	2.40	2.40	4.00	3.75
$(H_2/CO)_{feed}$	0.75	0.64	0.75	0.69	0.69	0.69	0.66
TOS(h)	55	103	247	45	94	285	332
%H_2+CO *conv.*	54.1	56.1	45.7	65.7	64.2	34.5	44.2
Usage ratio (H_2/CO)	0.60	0.54	0.66	0.61	0.61	0.66	0.58
Hydrocarbon Selectivities:							
CH_4	3.1	3.3	3.8	3.3	4.0	4.6	4.4
C_2 - C_4	13.2	13.2	13.7	12.7	15.0	19.5	20.1
C_5 - C_{11}	21.4	26.0	24.1	12.5	16.4	19.0	18.6
C_{12}^+	62.4	57.5	58.4	71.5	64.6	57.0	56.9
$C_1 + C_2$	6.7	6.7	7.4	6.7	8.6	9.7	10.0

* After in-situ regeneration with H_2 at 220°C and 1.5 MPa for 2 h

Table 6. Catalyst Performance in a Stirred Tank Slurry Bed Reactor

CATALYST	$100Fe/xCu/yK/zSiO_2$			
Process Conditions				
Temp. (°C)	260	260	260	260
Press. (MPa)	1.48	1.48	1.48	1.48
SV (Nl/h.g-Fe)	2.45	2.48	2.49	2.52
$(H_2/CO)_{feed}$	0.66	0.66	0.66	0.66
TOS(h)	49	109	171	244
%H_2+CO *conv.*	86.3	84.3	83.9	76.8
Usage ratio (H_2/CO)	0.55	0.57	0.57	0.52
k(mol (H_2+CO)/MPa.h.g-cat)	0.19	0.19	0.19	0.14
Hydrocarbon Selectivity(wt%)				
CH_4	2.6	2.8	3.3	3.2
C_2 - C_4	11.3	11.7	13.4	13.3
C_5 - C_{11}	23.1	20.8	18.4	17.6
C_{12}^+	62.9	64.8	65.0	65.9
C_1 + C_2	5.6	6.1	7.2	7.1

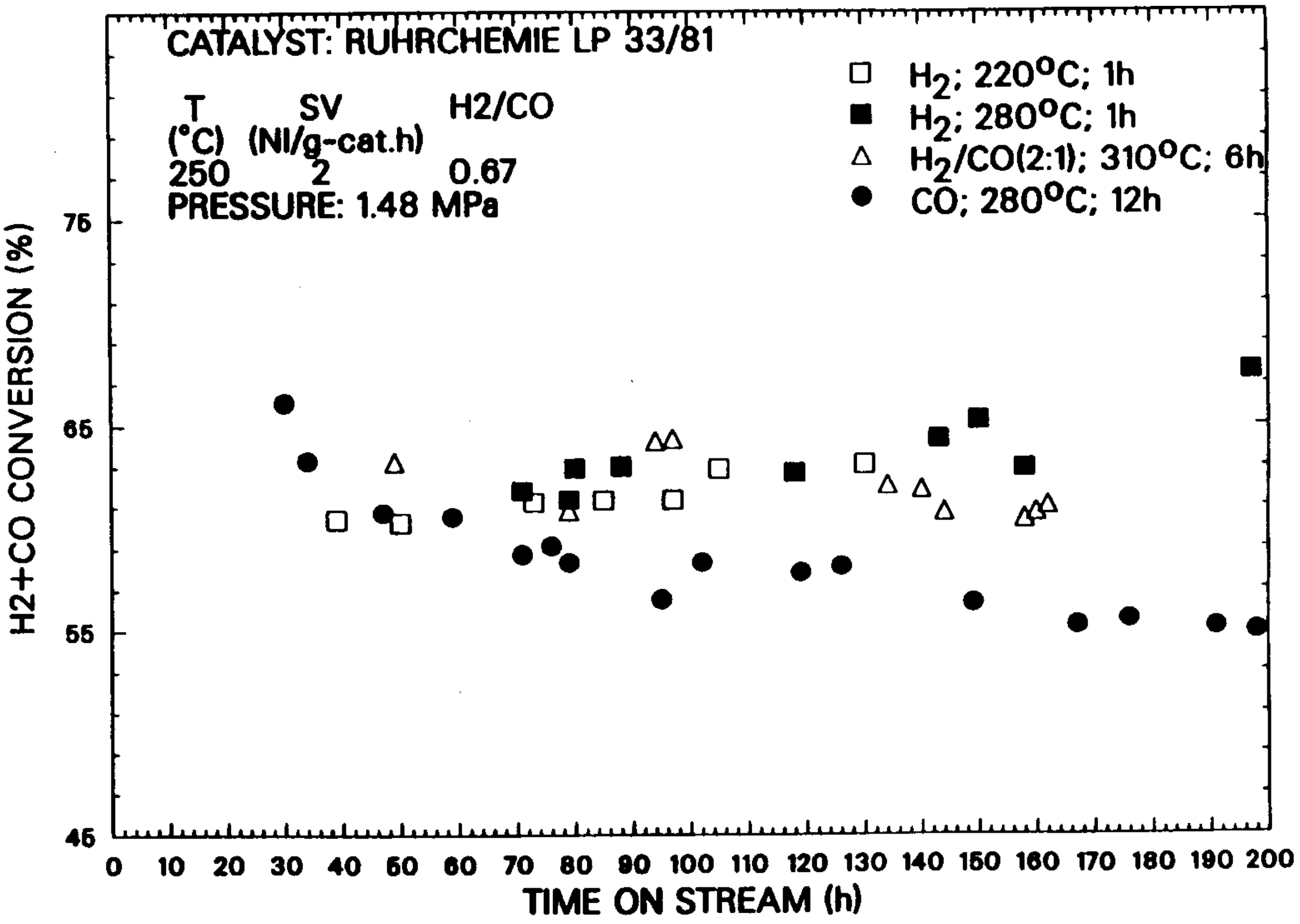

Figure 1. Comparison of activity and stability for different activation procedures in fixed bed reactor

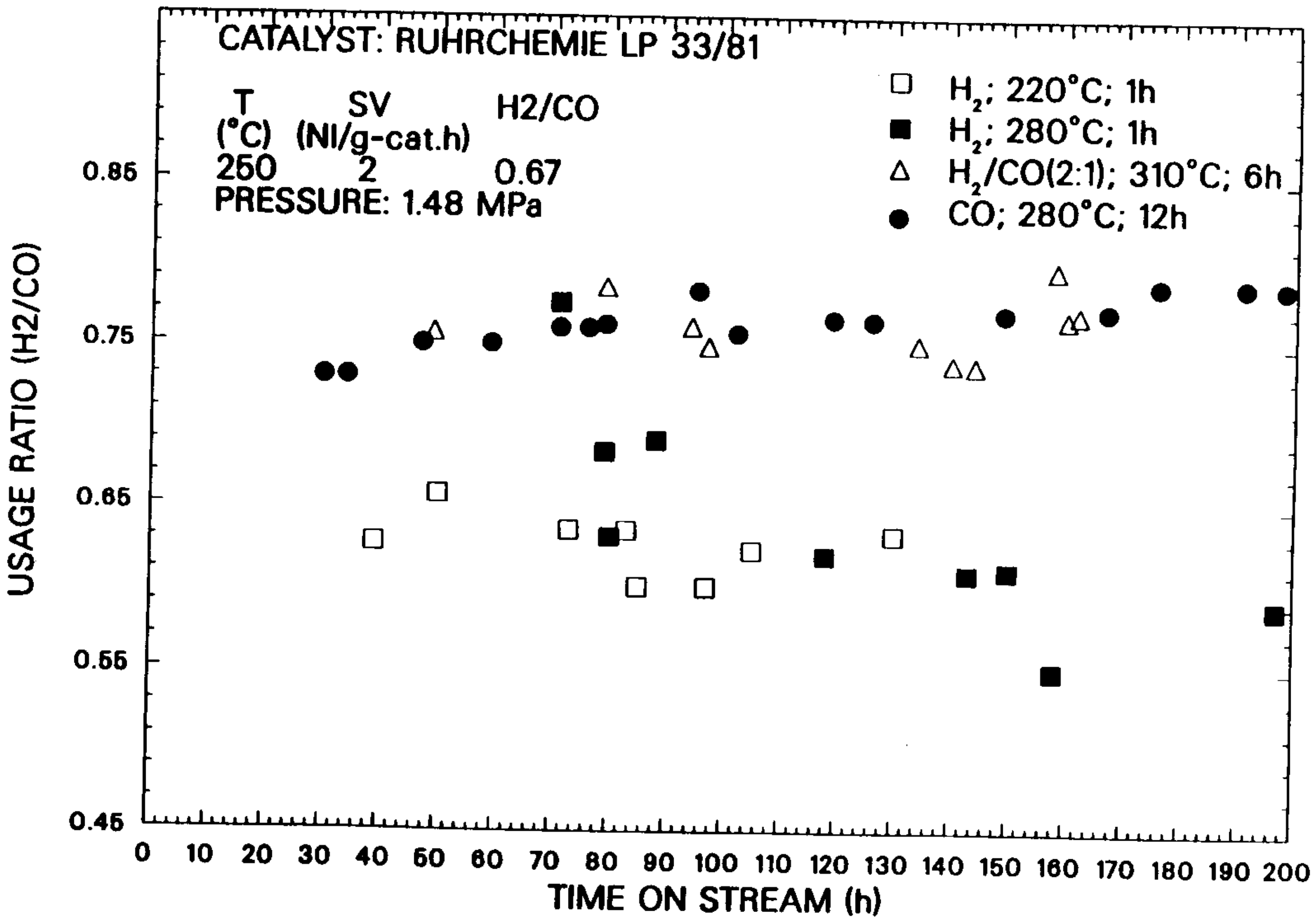

Figure 2. Comparison of usage ratio for different activation procedures in fixed bed reactor

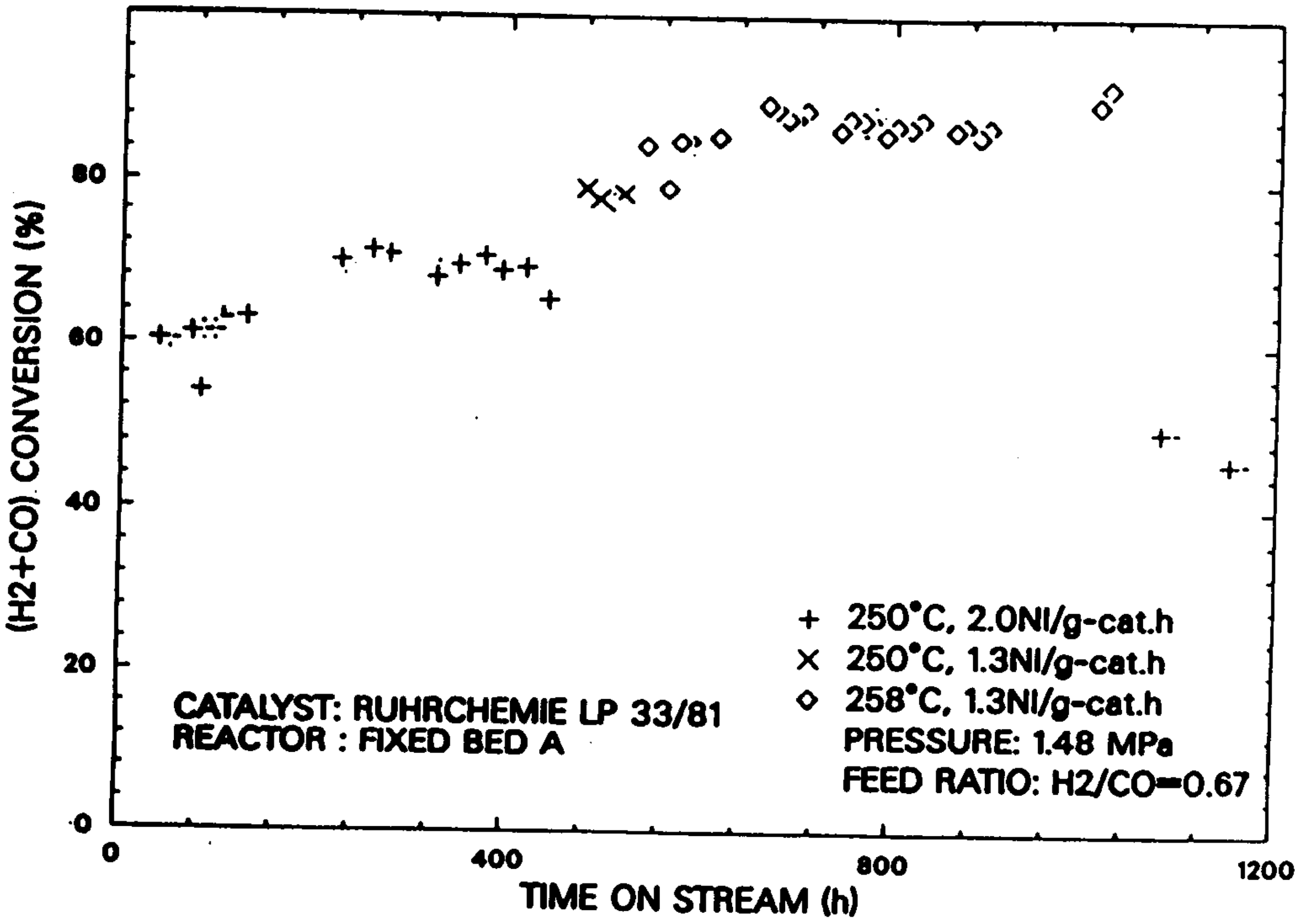

Figure 3. (H_2+ CO) conversion as a function of time and process conditions for fixed bed reactor run FA-3509

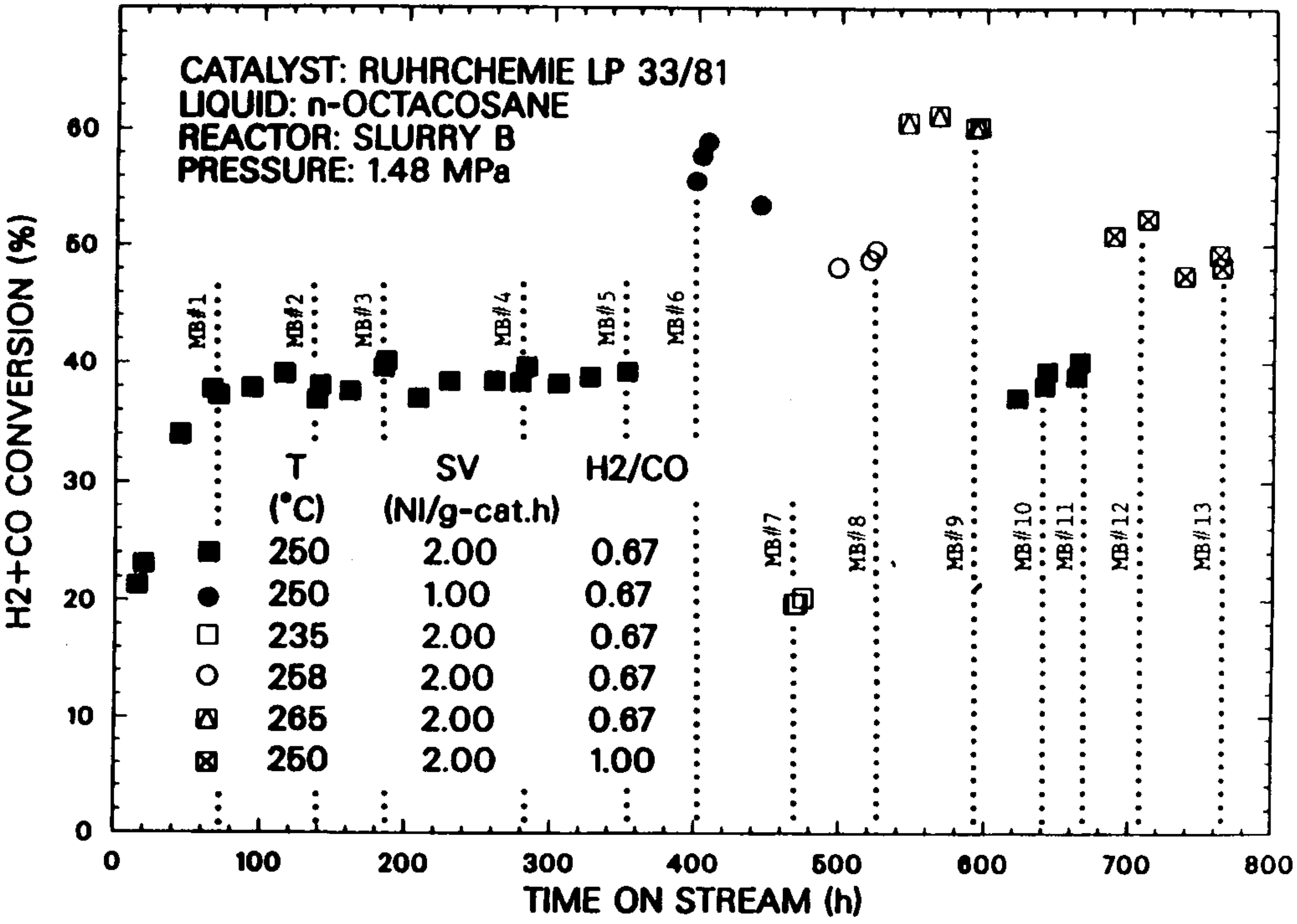

Figure 4. (H_2+ CO) conversion as a function of time and process conditions for slurry reactor run SB-1370

Figure 5. Summary of Results – Pretreatment Effect Research with the Ruhrchemie Catalyst

- FTS AND WGS ACTIVITY
  - Not strongly affected by pretreatment conditions (H_2 reduced catalysts more stable, and have higher WGS activity).
- HYDROCARBON SELECTIVITY (Fixed Bed Reactor Tests)
  - H_2 reduction at 280°C gave the highest yield of CH_4 and the lowest yield of C_{12}^+ hydrocarbons, whereas the other 3 activation procedures gave similar selectivities for CH_4 and (C_2-C_4) gaseous hydrocarbons.
- SLURRY VS. FIXED BED REACTOR
  - CH_4 and (C_2-C_4) hydrocarbon selectivities were somewhat lower in the slurry reactor.

Figure 6. Catalyst Target Performance

ACTIVITY

(H_2+CO) conversion, %	88
CO conversion, %	90
$Nm^3(H_2+CO)$ reacted/(g-Fe·h)	2.6
STY (kg C_3^+/m^3 reactor/day)	900

HYDROCARBON SELECTIVITY

(g $HC/Nm^3(H_2+CO)$ reacted)	≥178
(g $C_3^+/Nm^3(H_2+CO)$ reacted)	≥166
(C_1+C_2), wt%	6.7-8.0

PROCESS CONDITIONS

(H_2/CO) feed ratio = 0.6-1.0
Temperature (°C) = 230-300
Pressure (bar) = 1-20
Space velocity = 2-4 (Nm^3/kg-Fe·h)

DEACTIVATION RATE: ≤ 1% per day during 30 days of continuous testing

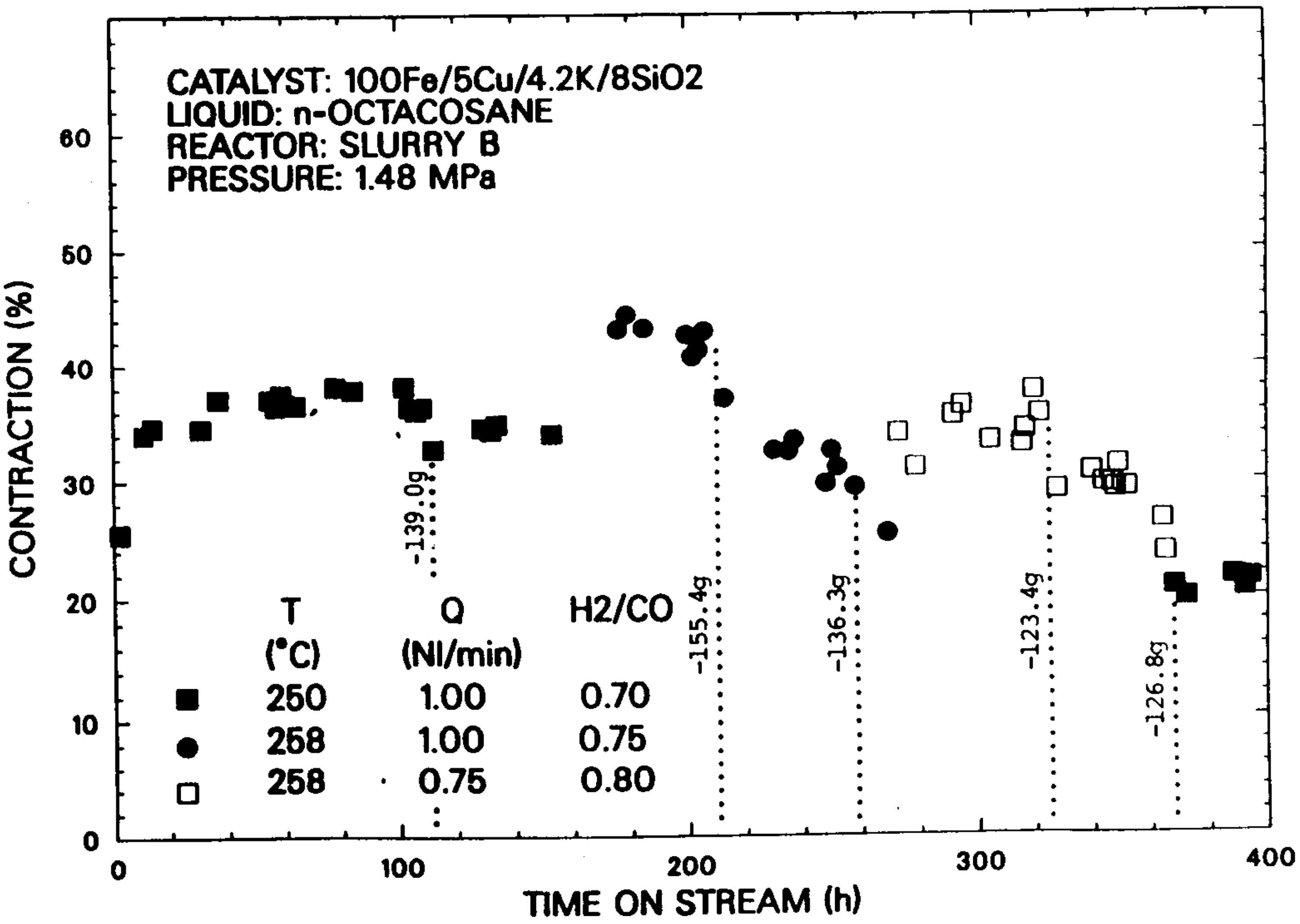

Figure 7. Volumetric contraction versus time on stream for run SB-1910

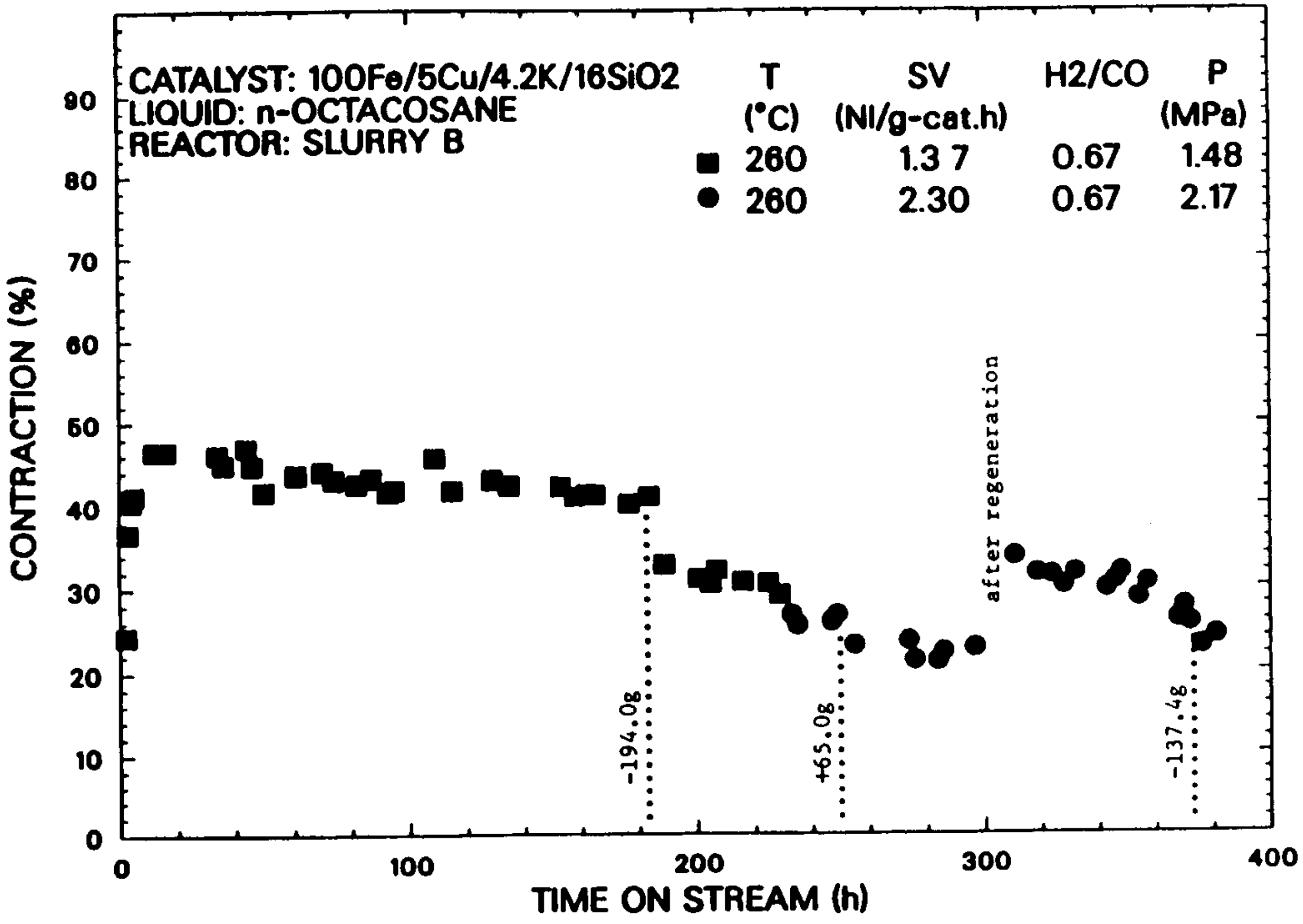

Figure 8. Volumetric contraction versus time on stream for run SB-2270

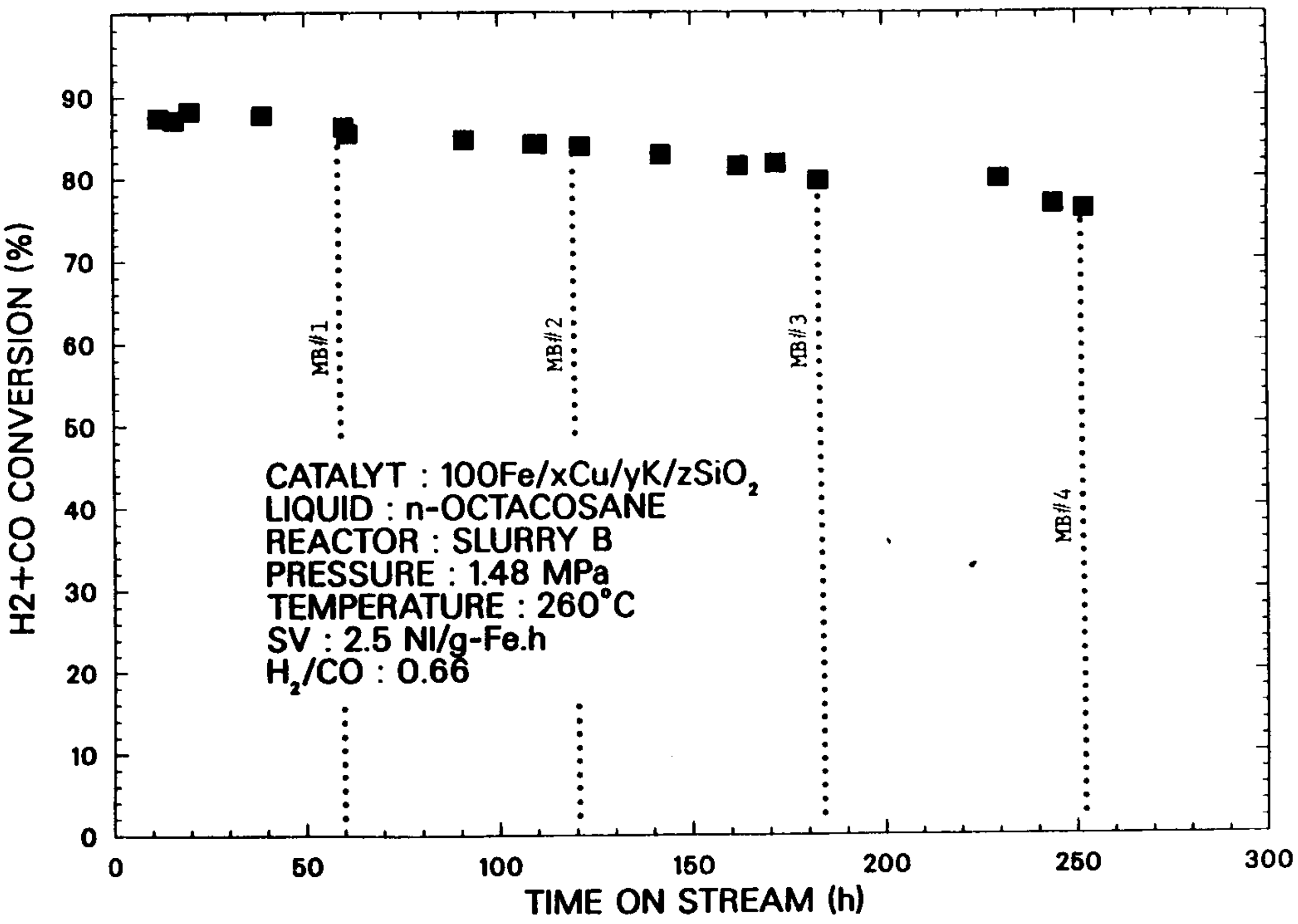

Figure 9. Effect of time on stream on catalyst activity and stability for run SB-2670