

# **Development of Improved Fischer-Tropsch Catalysts – Part II**

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## **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 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. A detailed description of progress in each of these areas is given below.

## **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 on 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 supported). We plan to investigate 2-3 catalysts, and use (4-6) combinations of pretreatment conditions for each of the catalysts (see Table 1). Results from studies with the state-of-the-art Ruhrchemie catalyst (100 Fe/5 Cu/4.2 K/25 SiO<sub>2</sub>, in parts per weight) were reported at the last years' Review Meeting (Bukur et al. 1990d). During the past year we have completed three fixed bed tests, and one slurry reactor test with an unsupported iron catalyst with nominal composition 100Fe/0.3Cu/0.8K. The pretreatment conditions employed are listed in Table 2.

After the pretreatment, the catalyst was tested in a fixed bed reactor at 200 psig (1.48 MPa), 250°C, 2(Nl/g-cat/h) with the syngas with H<sub>2</sub>:CO molar ratio of 2:3. Test duration was between 130 and 200 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<sub>2</sub> + CO) conversion in all four tests was between 30 and 90%. The conversion increased slightly with time on stream in test FB-3480 (H<sub>2</sub> reduction at 250°C for 2h), whereas it decreased slightly in test FA-2780 (H<sub>2</sub> reduction at 220°C for 1h) and more rapidly in the test FB-0021 where CO activation was employed. These trends are in qualitative agreement with our results obtained in tests with unsupported 100 Fe/3 Cu/0.2 K catalyst and the Ruhrchemie catalyst (Bukur et al., 1988; 1989a; 1990d). H<sub>2</sub> reduction at 220°C for 1 h resulted in low (H<sub>2</sub>+CO) conversion, probably due to incomplete reduction of iron, whereas the (H<sub>2</sub>+CO) conversion was much higher following reduction at 250°C for 2 h. These results suggest that catalyst activity increases with degree of iron reduction. Catalyst characterization studies, which are in progress, will provide additional information leading to better understanding of pretreatment effects on the catalyst activity and stability.

The effect of pretreatment conditions on the water-gas-shift (WGS) activity, measured by H<sub>2</sub>/CO usage ratio, is shown in Figure 2. The WGS activity appears to be a function of (H<sub>2</sub>+CO) conversion, i.e. the usage ratio decreases with increase in conversion.

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<sub>12</sub><sup>+</sup> selectivity, whereas H<sub>2</sub> reduction at 250°C resulted in the highest methane and the lowest C<sub>12</sub><sup>+</sup> selectivity. Methane and C<sub>2</sub> - C<sub>4</sub> selectivities obtained using H<sub>2</sub> reduction at 220°C, were closer to values obtained using CO activation than to those obtained in the test where H<sub>2</sub> reduction at 250°C was employed.

This catalyst was tested also in a stirred tank slurry reactor (STSR) after reduction with H<sub>2</sub> at 250°C for 2 h. The catalyst was stable during 250 h of testing at 260°C, 200 psig, 1.2 Ni/g-cat/h and H<sub>2</sub>/CO = 0.67 as shown in Fig. 3. Hydrocarbon product distribution shifted gradually towards lower molecular weight products with time on stream. Selectivities of methane and gaseous hydrocarbons (C<sub>2</sub> - C<sub>4</sub>) varied between 5.5 - 6.8 and 19 - 24%, respectively. The average value of hydrocarbon product distribution is shown in Table 3 for comparison with results obtained in fixed bed reactor (FBR) test FB-3480. Selectivities of methane and gaseous hydrocarbons were markedly lower in the STSR than in the FBR, even though the reaction temperature was 10°C higher in the STSR.

Future activities in this area will include the following:

1. Continue pretreatment effect studies with the 100Fe/0.3Cu/0.8K catalyst in fixed bed and slurry reactors.
2. Initiate pretreatment effect studies with a silica containing precipitated iron catalyst (100Fe/xCu/yK/zSiO<sub>2</sub>).
3. Characterize catalysts after different pretreatment procedures and after FTS by BET (surface area and pore size distribution), XRD, TEM and Mössbauer spectroscopy.

## IRON/SILICA CATALYSTS

The performance of silica containing iron Fischer-Tropsch catalysts of composition 100 Fe/5 Cu/4.2 K/x SiO<sub>2</sub> (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 objective of the current contract is to determine optimal concentrations of promoters (CuO, K<sub>2</sub>O) and binders (SiO<sub>2</sub>) needed to achieve the specified catalyst performance (Figure 4).

Since March 1, 1990 we have performed seven screening tests in fixed bed reactors, and six tests in stirred tank slurry reactors. Results from two of the slurry reactor tests were presented

at the previous DOE Contractor's Review Meeting (Bukur et al., 1990d) whereas results from the remaining four tests are discussed in this paper.

Variations in (H<sub>2</sub>+CO) conversion with time on stream (TOS) for different catalysts tested are shown in Figure 5. Process conditions in all tests were: 260°C, 200 psig, H<sub>2</sub>/CO = 0.66 – 0.70, whereas gas space velocity varied between 2.2 and 3.2 Nl/g-Fe/h (see Fig. 5 for details). In two of the tests (catalysts A and B) process conditions were varied during the test, however results from these periods are not shown in Fig. 5. In three of the four tests the gas space velocity was nearly constant, whereas in the test of catalyst C the gas space velocity was decreased twice to obtain higher conversion. Catalyst D had the highest deactivation rate (~3.3% per day), whereas deactivation rates in tests of other catalysts varied between 1.1 and 1.7% per day (Table 4). Catalyst deactivation rate was estimated using the following expression

$$DR = [1 - k(t)/k(t_0)] \times 100/t \quad (1)$$

where: DR – deactivation rate in (%/day); k(t) and k(t<sub>0</sub>) – reaction rate constants at time t and t<sub>0</sub>, respectively; t – duration of test in days; t<sub>0</sub> – time at which the first mass balance was conducted (usually, after about 40 h on stream). Reaction rate constants were calculated from experimental data by assuming that the reaction rate has a first-order dependence on hydrogen pressure.

The above procedure provides a conservative estimate, since the deactivation rate is based on the initial catalyst activity. In some cases the catalyst activity goes through a maximum (induction period) before it starts decreasing or leveling off. Test of catalyst B represents an example of the latter type of behavior as shown in Figure 5. Initially the (H<sub>2</sub>+CO) conversion was between 81 and 82%, and then began to decrease gradually, dropping to 76% at 150 h on stream. Between 160 and 240 h the catalyst was tested at 265°C (results are not shown in Fig. 5) and it continued to deactivate. Upon returning to the baseline conditions (260°C) the activity became stable as evidenced by nearly constant values of (H<sub>2</sub>+CO) conversion (66 – 68%) between 240 and 530 h on stream. Catalyst deactivation rate during this time period (240 – 530 h) was virtually nil;

whereas the average deactivation rate for the entire test (0 – 530 h), calculated from Eq. (1), was 1.2% per day (Table 5).

Activities of all four catalysts were somewhat lower than the specified target values shown in Fig. 4. For example, the (H<sub>2</sub>+CO) conversion values were between 52 and 88% and catalyst productivities varied between 1.5 and 2.5 Nm<sup>3</sup> (H<sub>2</sub>+CO) converted/h·kg-Fe, whereas the corresponding target values are 88% and 2.6, respectively. The WGS activity of all four catalysts was high and (H<sub>2</sub>/CO) usage ratios (0.54 – 0.62) in all tests were lower than the corresponding feed ratios (Table 4).

Selectivities of methane and (C<sub>1</sub>+C<sub>2</sub>) hydrocarbons obtained in tests with these four FTS catalysts are shown in Figure 6. In tests with catalysts A, C, and D selectivities of methane and (C<sub>1</sub>+C<sub>2</sub>) hydrocarbons increased gradually with TOS, whereas in the test with catalyst B these two selectivities passed through a maximum. The highest methane and (C<sub>1</sub>+C<sub>2</sub>) selectivities were obtained with catalyst D, which also had the highest deactivation rate. In tests with catalysts A, B, and C methane and (C<sub>1</sub>+C<sub>2</sub>) selectivities were low. (C<sub>1</sub>+C<sub>2</sub>) selectivities of catalysts A and B were within the specified target (less than 7%) throughout the entire test. The performance of catalyst C was within the target during the first 420 h of testing, and slightly above the target during the last 100 h on stream. Selectivities of other hydrocarbons (lumped into groups by carbon numbers) are given in Table 4. For each catalyst a range of values obtained is shown in this table.

Also, results from Mobil's run CT-256-13 with a precipitated iron catalyst (100Fe/xCu/yK) in a bubble column slurry reactor (BCSR) are listed in Table 4 for comparison with our data. This particular run has been used as a benchmark for comparison of catalysts designed to minimize methane selectivity while producing large quantities of wax (wax mode of production). Data shown in Table 4 are from mass balance 18 at 23.8 days on stream (Kuo, 1985). Process conditions employed in Mobil's study and the present one are very similar. It can be seen that performance (activity and selectivity) of our catalysts A, B and C, is similar to that of Mobil's

catalyst. However, catalysts synthesized at TAMU are more active than the Mobil's catalyst, since our data are obtained in the STSR reactor, which approaches perfectly mixed reactor behavior, whereas Mobil's data are from the BCSR (which approaches plug flow reactor behavior).

In summary, two of iron FTS catalysts synthesized in our laboratory (catalysts B and C) have met specified performance targets for hydrocarbon selectivity and catalyst stability, whereas catalyst's A performance was within the selectivity target but its deactivation rate was higher than 1% per day. None of the catalysts tested have met the activity targets (i.e. 88% syngas conversion, and productivity greater than  $2.6 \text{ Nm}^3/\text{kg-Fe/h}$ ). It should be noted that performance criteria in Figure 4 are based on data obtained in bubble column slurry reactors (plug flow type of reactor). It is considerably more difficult to achieve these targets (particularly the activity target) in a stirred tank slurry reactor (perfectly mixed flow type of reactor).

Future activities related to this task will include the following:

1. Testing of new catalysts in fixed bed and stirred tank slurry reactors.
2. Characterization of selected catalysts after pretreatment, during and after FTS reaction by XRD, TEM and Mössbauer spectroscopy.

## ACKNOWLEDGEMENT

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## **Table 1. Catalyst Pretreatment Research Plan**

**(a) Catalysts (2-3):**

- |            |  |   |
|------------|--|---|
| <b>(1)</b> | <b>100 Fe/x Cu/y K/z SiO<sub>2</sub></b> | <b>iron/silica catalyst</b>                 |
| <b>(2)</b> | <b>100 Fe/0.3 Cu/0.5-1.0 K</b>           | <b>unsupported catalyst</b>                 |
| <b>(3)</b> | <b>Ruhrchemie catalyst</b>               | <b>commercial state-of-the-art catalyst</b> |

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

- **Reductant type (H<sub>2</sub>, 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	DURATION (h)	PRESSURE (MPa)
FB-0021	280	CO	8	0.1
FB-2800	220	H <sub>2</sub>	1	0.1
FB-3480	250	H <sub>2</sub>	2	0.1
SA-0791	250	H <sub>2</sub>	2	0.8

FB = Fixed Bed Reactor Tests

SA = Slurry Reactor Tests

CATALYST: 100Fe/0.3Cu/0.8K

Table 3. Comparison of Pretreatment Procedures

Run ID	FB-2800	FB-3480	FB-0021	SA-0791
Red. Cond.	H <sub>2</sub> , 1h 220°C	H <sub>2</sub> , 2h 250°C	CO, 8h 280°C	H <sub>2</sub> , 2h 250°C
TOS(h)	30-170	26-134	30-126	40-250
% CO conv.	28-40	80.5-86.8	60.2-95.7	82.8-86.1
%H <sub>2</sub> +CO conv.	28-41	75.7-83.4	58-91	79.5-82.1
Hydrocarbon Selectivities:				
CH <sub>4</sub>	6.2	10.6	3.4	6.2
C <sub>2</sub> - C <sub>4</sub>	19.4	30.6	18.2	21.8
C <sub>5</sub> - C <sub>11</sub>	29.3	40.2	23.0	37.1
C <sub>12</sub> <sup>+</sup>	45.1	13.6	55.4	34.9

Conditions: 200 psig; 2 NI/h.g-cat; H<sub>2</sub>/CO = 0.67; 250°C (FB = Fixed Bed Reactor Tests)  
 200 psig; 1.2 NI/h · g-cat; H<sub>2</sub>/CO = 0.69; 260°C (SA = Slurry Reactor Test)  
 CATALYST: 100Fe/0.3Cu/0.8K

Table 4. Catalyst Performance in a Stirred Tank Slurry Bed Reactor

CATALYST	A	B	C	D	Mobil's Run CT-256-13
Process Conditions					
Temp. (°C)	260	260	260	260	257
Press. (MPa)	1.48	1.48	1.48	1.48	1.48
SV (NI/h.g-Fe)	2.4 - 2.5	2.2-2.4	2.2-3.4	2.9-3.2	2.3
(H <sub>2</sub> /CO) <i>feed</i>	0.66-0.70	0.68-0.70	0.66-0.69	0.68-0.70	0.73
TOS(h)	40-560	40-530	40-520	40-350	475
%H <sub>2</sub> +CO <i>conv.</i>	71-88	63-83	74-84	52-83	82.2
STY (Nm <sup>3</sup> /kg-Fe·h)	1.8-2.2	1.5-2.0	1.8-2.5	1.6-2.5	1.9
Usage ratio (H <sub>2</sub> /CO)	0.54-0.60	0.54-0.62	0.56-0.62	0.54-0.58	0.59
Deactivation rate (%/day)	1.7	1.2	1.1	3.3	?
Hydrocarbon Selectivity(wt%)					
CH <sub>4</sub>	2.5-3.7	2.1-2.8	2.5-3.7	4.6-6.4	2.7
C <sub>2</sub> - C <sub>4</sub>	10.6-12.5	9.3-13.0	10.2-14.6	18-21	11.1
C <sub>5</sub> - C <sub>11</sub>	17.0-21.7	12.3-15.5	13.2-19.6	30-36	18.1
C <sub>12</sub> <sup>+</sup>	65.2-69.6	68.1-76.4	62.1-73.0	37-45	68.1
C <sub>1</sub> + C <sub>2</sub>	5.3-7.1	4.9-6.4	5.4-8.2	9.1-12.3	5.6

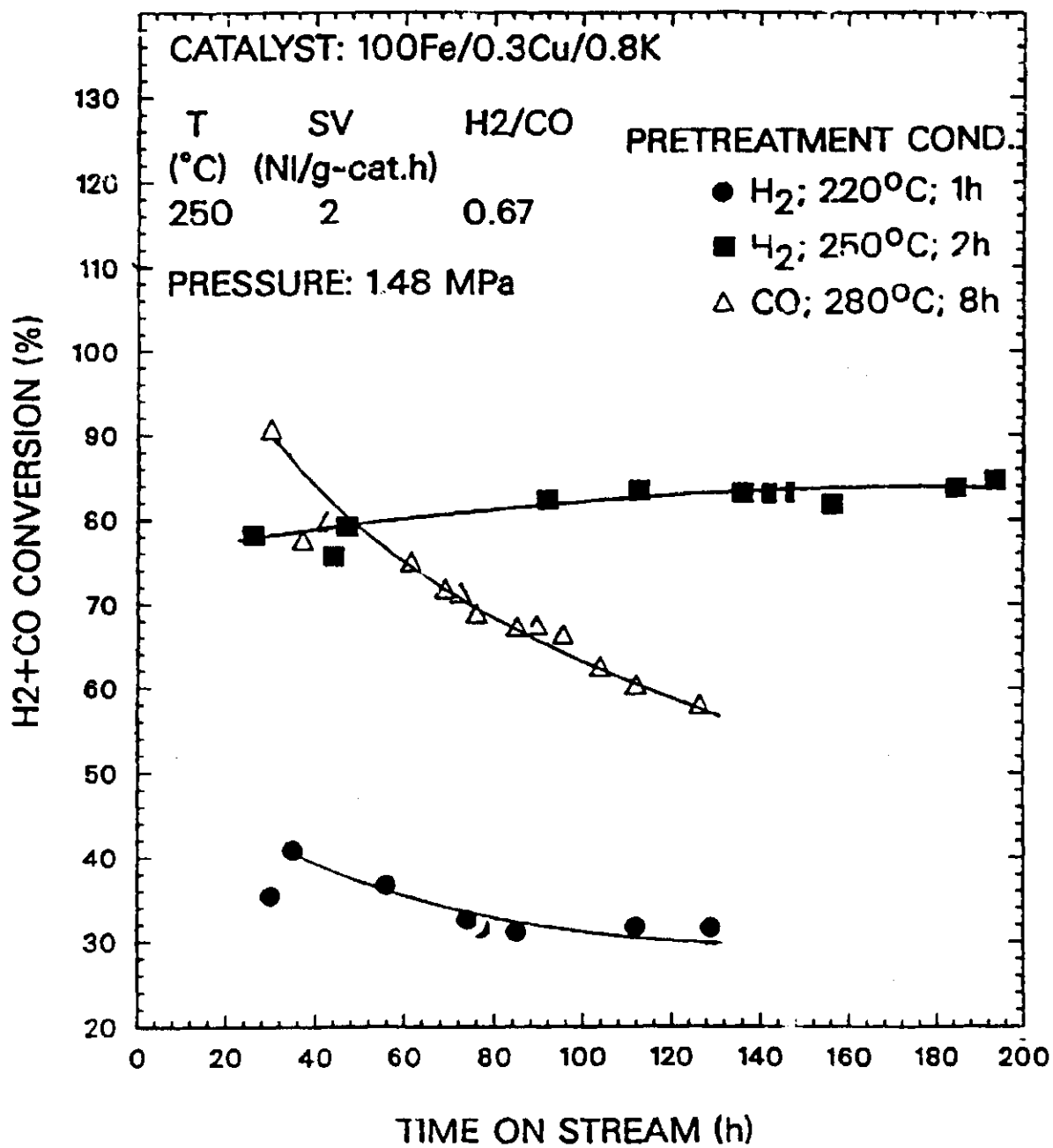


Figure 1. Effect of pretreatment procedures on catalyst activity and stability (Fixed bed reactor tests)

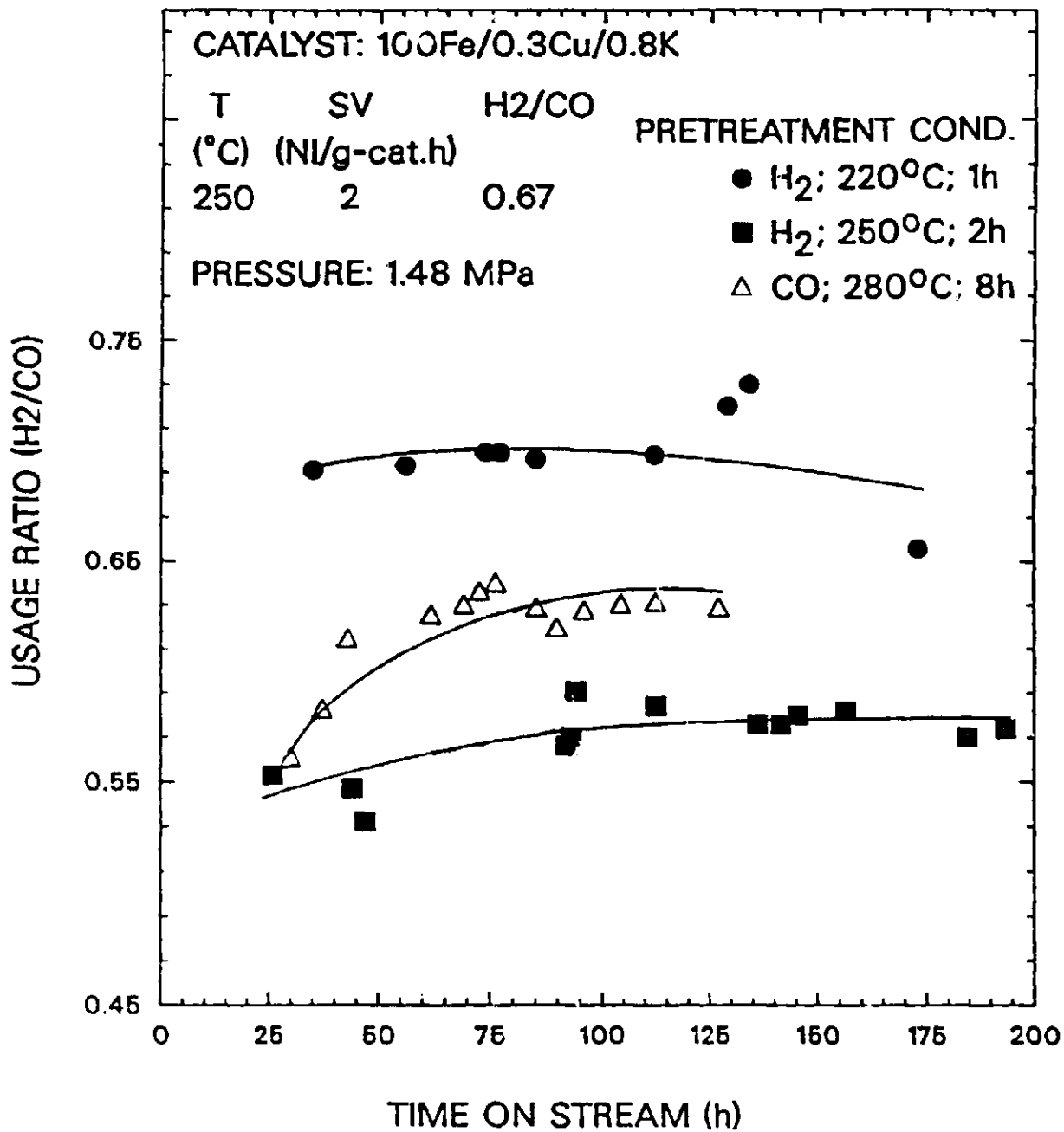


Figure 2. Comparison of usage ratio for different activation procedures in a fixed bed reactor

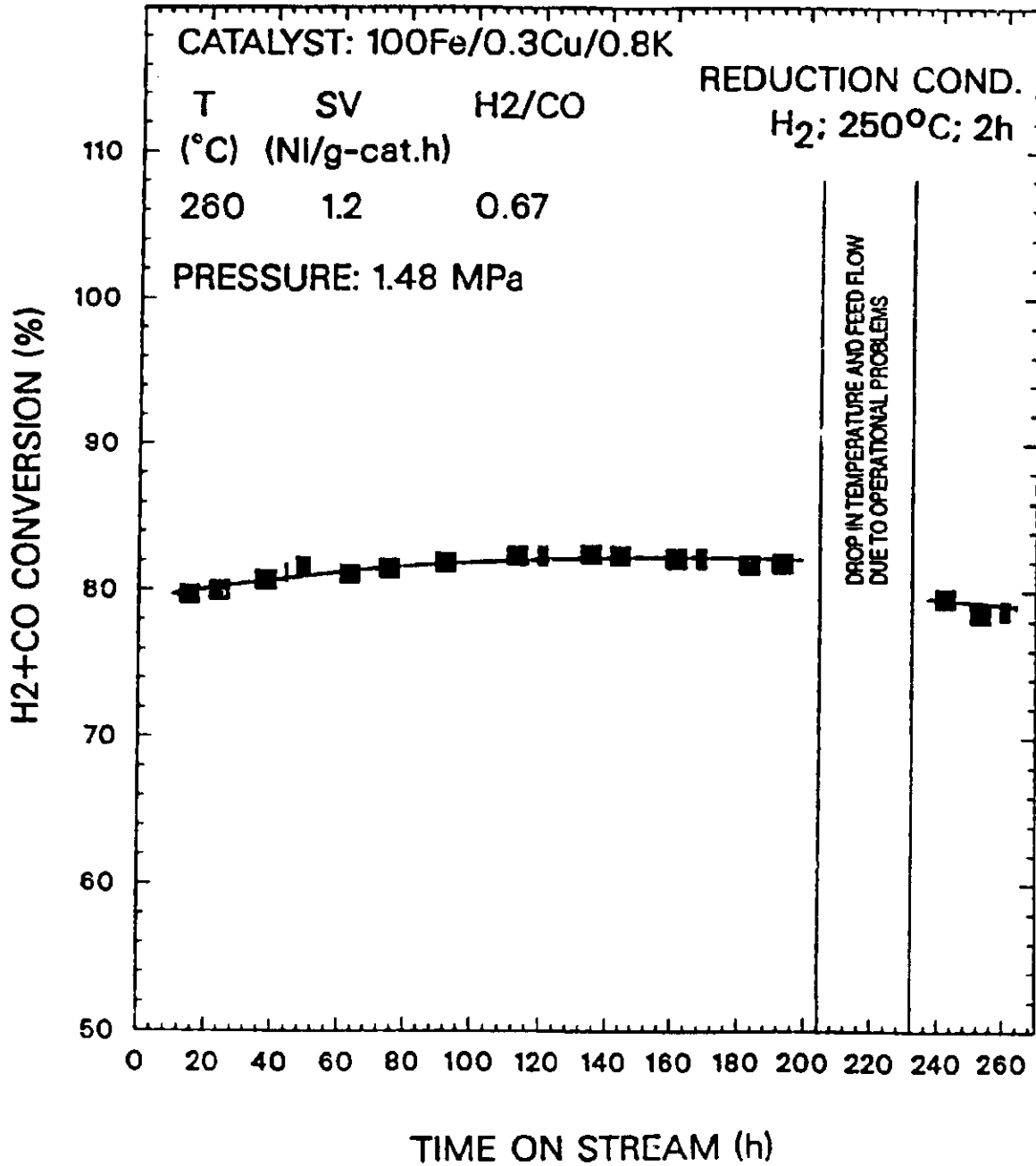


Figure 3. (H<sub>2</sub>+CO) conversion as a function of time-on-stream for a slurry reactor test SA-0791

## Figure 4. TARGET PERFORMANCE

### ACTIVITY

(H <sub>2</sub> +CO) conversion, %	≥ 88
Nm <sup>3</sup> (H <sub>2</sub> +CO) reacted/(kg-Fe·h)	≥ 2.6

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### HYDROCARBON SELECTIVITY

(C <sub>1</sub> +C <sub>2</sub> ), wt%	≤7.0
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**DEACTIVATION RATE:** ≤ 1% per day during 30 days of continuous testing

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### PROCESS CONDITIONS

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



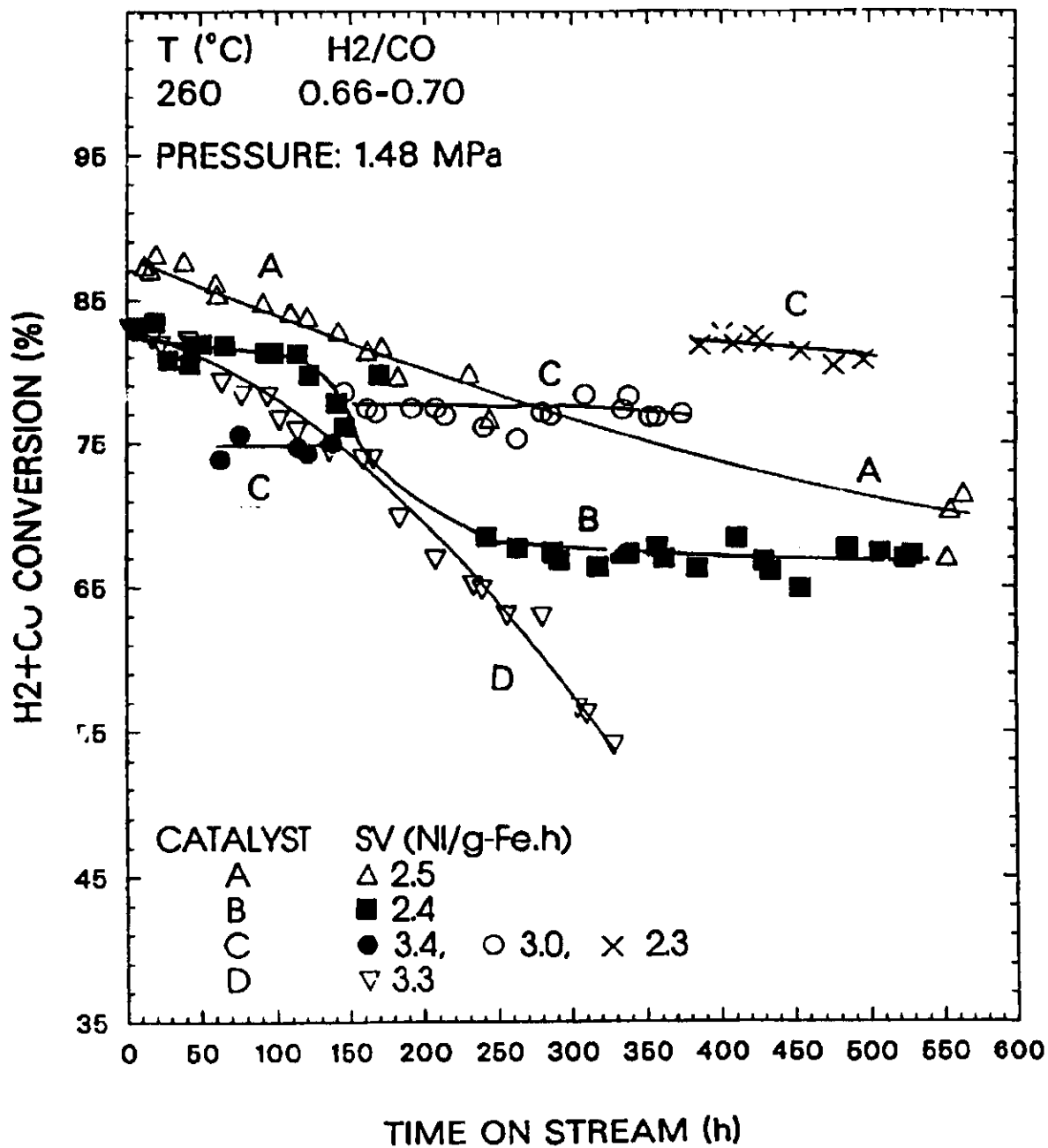


Figure 5. Effect of time-on-stream on (H<sub>2</sub>+CO) conversion in slurry reactor tests of iron/silica FTS catalysts

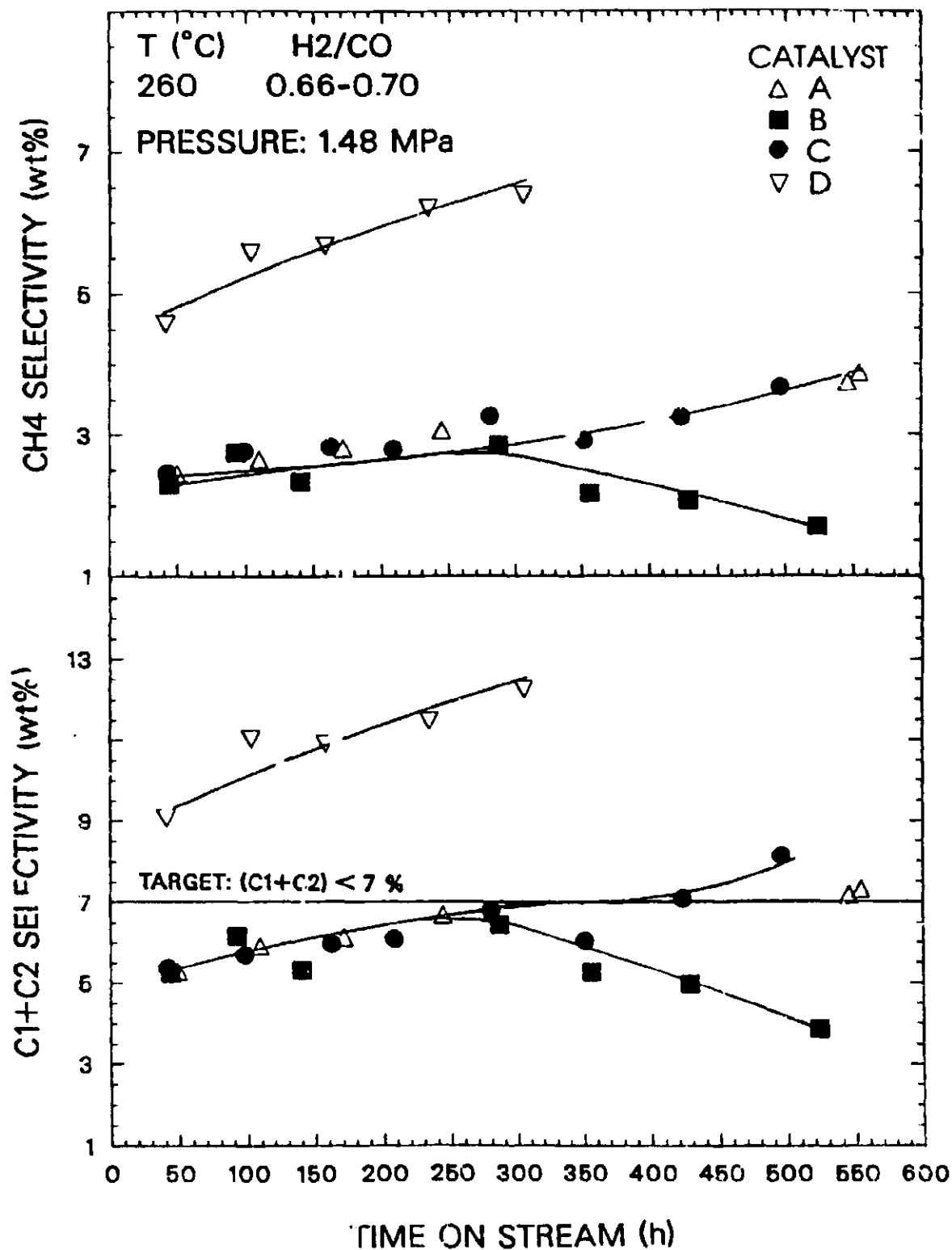


Figure 6. Effect of time-on-stream on methane and (methane+ethane+ethylene) selectivities in slurry reactor tests of iron/silica FT<sub>2</sub> catalysts (Gas space velocities are the same as in Figure 5)