

V. Task 2 SLURRY CATALYST DEVELOPMENT

Activation / Reduction Procedure Research

V.1.1. Literature Review

The most common catalysts for CO hydrogenation (Fischer-Tropsch synthesis) are group VIII elements: cobalt, nickel, ruthenium and iron. Before synthesis a catalyst precursor is subjected to a pretreatment, the purpose of which is to bring the catalyst into an active form for synthesis. Cobalt, nickel and ruthenium are almost always reduced in flowing H_2 at 200 - 450°C to the zero-valent metallic state. During the synthesis, under a variety of process conditions, these catalysts remain in the zero-valent state (Anderson, 1956). However, the purpose of pretreatment for iron catalysts is not so clear. Reduction in H_2 may lead to the zero-valent state, but during the synthesis the metallic iron is rapidly converted to a carbide phase or phases (e.g., Amelse et al., 1978; Raupp and Delgass, 1979; Dry, 1981). At high ($H_2 + CO$) conversions, the reaction mixture becomes more oxidizing (relatively high H_2O/H_2 and CO_2/CO ratios) and magnetite (Fe_3O_4) is also formed (e.g., Anderson, 1956; Dry, 1981; Satterfield et al., 1986). Other pretreatments have also been employed, such as CO reduction (activation), synthesis gas treatment (induction), and/or H_2 reduction followed by CO or vice-versa. These activations often yield a better catalyst than that obtained by H_2 reduction, but the catalyst composition still changes during synthesis. Numerous studies have been published concerning correlations between phases present in the iron catalyst and its reaction behavior, as summarized, for example, by Dwyer and Hardenbergh (1984) and Satterfield et al. (1986a). However, there is no clear consensus as to which of the phases is responsible for catalyst activity. The two extreme views are that the active phase(s) is (are) either (a) iron carbides (e.g., Amelse et al., 1978; Raupp and Delgass, 1979; Niemantsverdriet et al., 1980); or (b) iron oxides (Reymond et al., 1982; Blanchard et al., 1982). Based on the extensive studies at the U. S. Bureau of Mines and the previous German work, the following iron phases were found to be catalytically active: metallic α -Fe, various carbides, nitrides and carbonitrides, and Fe_3O_4 (Hofer 1956, p. 434). During synthesis, industrial catalysts consist of mixtures of carbides and magnetite, and in general there is no clear correlation between the catalyst bulk composition and its activity and/or selectivity (Dry, 1981, p. 197; Anderson, 1984, p. 56). Thus, the objectives of the catalyst pretreatment in the case of iron are not clear. The general goals of a successful pretreatment are to obtain high activity, the desired selectivity, and long life (high stability). The effective activation procedures for iron catalysts have been developed

empirically. There have been only a few studies on the effect of activation parameters on subsequent catalyst activity, selectivity, and stability during the synthesis.

In early work with alkalized precipitated catalysts at Kaiser Wilhelm Institute in Germany, it was found that reduction with H_2 at $360^\circ C$ was not effective, and further studies focused on activations with carbon monoxide and CO rich synthesis gas, (Anderson, 1956 pp. 176-180). They investigated the effects of activation temperature ($255-450^\circ C$) and pressure (0.01 - 1.5 MPa) on catalyst activity and stability. The optimal activation parameters were: CO at 0.01 MPa (subatmospheric pressure) and $325-345^\circ C$. These activation conditions gave high (H_2 -CO) conversions and constant catalyst activity for 80-120 days in fixed bed reactor tests.

In studies with a precipitated iron catalyst at the U. S. Bureau of Mines, several activation procedures were employed with different reducing agents: H_2 , CO, and $H_2/CO=1$ or 2 (Anderson, 1956, p. 183-184; Anderson, 1984, pp. 56-58). It was found that catalysts activated with syngas or CO had higher activity and produced less light hydrocarbons than H_2 reduced catalysts.

Recent work at the Pittsburgh Energy Technology Center has focused on the effect of catalyst pretreatment on the catalyst's synthesis behavior in a stirred tank slurry reactor (Pennline et al., 1987; Zarochak and McDonald, 1986, 1987). In studies with a precipitated iron-manganese catalyst, Pennline et al. found that pretreatment with H_2 or $H_2/CO=1$ syngas at $275^\circ C$ resulted in completely inactive catalysts during the synthesis. Activations with CO were more successful, and changes in activation temperature or pressure had some effect on the catalyst activity and selectivity. Zarochak and Anderson employed activations with syngas ($H_2/CO=0.7$ or 1) and CO in studies with Fe-Cu- K_2O catalyst. Following activation the catalyst deactivated, sometimes rather rapidly, during the synthesis. The rate of deactivation was affected both by pretreatment and by reaction conditions during the synthesis. In Mobil's work on development of the two-stage process for synthesis gas conversion to gasoline, in-situ activations, in a slurry bubble column reactor, with syngas ($H_2/CO=2/3$) at $280^\circ C$, 1.1-1.5 MPa for 2-10 h, were found to be effective in producing an active and stable catalyst (Kuo, 1983).

The information on the effect of reduction parameters on catalytic behavior during the synthesis for H_2 reductions is rather scarce. Reductions at relatively high temperatures were not successful as noted earlier. Dry (1981, p. 179) states that low temperatures ($180-220^\circ C$) and high linear velocities are needed to achieve high surface areas after the reduction.

In this section we present results of a comprehensive study on the effect of activation pa-

rameters (temperature, pressure, duration and nature of the reducing gas) on catalyst activity, selectivity, and stability. Eleven different activation procedures were employed, and the catalyst (100Fe/3Cu/0.2K) was subsequently tested in a fixed bed reactor. Two tests were also conducted in a stirred tank slurry reactor to determine whether the same trends are observed in both types of reactors.

V.1.2. Experimental Procedure

Typically, 3.5 g of the catalyst (3 cc) was diluted 1:8 by volume with glass beads of the same size range (30/60 mesh) and charged into the reactor. All tests were conducted with a catalyst from a single batch, having a composition of 100Fe/3Cu/0.2K (expressed in parts of metal by weight) as determined by atomic absorption spectroscopy (Varian Spectra AA 30). Eleven sets of activation conditions were employed to evaluate the effect of activation parameters (gas type, temperature, duration and pressure) on subsequent catalyst performance. All activations were conducted at a gas space velocity of 3 NI/g-cat.h and atmospheric pressure, except in test A-3517 where the activation was conducted at 1.48 MPa (200 psig). Test identifications and activation conditions are shown in Table V.1-1.

Following activation (reduction), the flow was switched to helium and the bed was cooled down to 190°C. The system was then pressurized to 1.48 MPa, the helium flow was cut off, and synthesis gas ($H_2:CO = 1:1$) was introduced at a gas space velocity of 2NI/g-cat.h. The bed temperature was gradually increased to 250° C following the time temperature schedule listed in Table V.1-2 (conditioning period). During the conditioning period, the bed temperature was monitored frequently to prevent development of hot spots, and the volumetric gas contraction was recorded periodically. After achievement of the final reaction temperature, 250°C, the tests were conducted over a 120 h period, during which time two mass balances were made at approximately 40 and 90 h on stream. The tail gas was analyzed frequently throughout the entire test.

V.1.3. Results

Selected results from catalytic tests are summarized in Table V.1-3 (activations with CO) and Table V.1-4 (activations with H_2 and syngas). Activation parameters investigated were: temperature (250 vs. 280°C for both H_2 and CO, and 310°C with CO only), duration (8 and 24 h), pressure (0.1 vs. 1.48 MPa, with CO only), and gas composition (CO, H_2 and $H_2/CO=0.68$).

Table V.1-1. Activation conditions and test designations.

Conditions				
Test	Temperature (°C)	Pressure (MPa)	Reductant	Duration (h)
A-2737	250	0.10	CO	8
B-2857	250	0.10	CO	24
A-3077	280	0.10	CO	8
A-2967	280	0.10	CO	24
A-2847	310	0.10	CO	8
A-3517	280	1.48	CO	24
B-3087	250	0.10	H ₂	8
A-3237	250	0.10	H ₂	24
B-2957	280	0.10	H ₂	8
B-3227	280	0.10	H ₂	24
B-3377	280	0.10	H ₂ /CO = 0.68	24

^(a) Space velocity = 3.0 Nl/g-cat·h for all tests

Table V.1-2. Start-up time/temperature schedule used during conditioning period following activation treatment.

Time on stream (h)	Temperature (°C) ^(a)	Duration (h)
0	Reduction-190	1
1	190	1
2	190-200	1
3	200	1
4	200-210	1
7	210	3
8	210-220	1
11	220	3
12	220-230	1
23	230	11
24	230-240	1
28	240	4
30	240-250	2

^(a) 1.48 MPa, 2.0 NI/g-cat·h, H₂/CO = 1.0

Table V.1.3. Results summary of catalyst tests using CO activations.

T _{test} ^(a)	A-2737	H-2857	A-3077	A-2067	A-2847	A-3517
Time on stream (h)	43 91	43 91	43 92	44 93	43 81	43 91
CO conversion (%)	91.4 86.9	63.6 56.0	76.6 68.6	88.6 84.1	85.1 77.7	76.5 68.6
H ₂ +CO conversion (%)	78.6 73.1	56.9 50.0	68.6 61.2	76.2 74.5	71.4 64.8	65.1 58.5
r _{CO₂} /(-r _{CO})	0.44 0.44	0.39 0.40	0.42 0.43	0.41 0.41	0.44 0.45	0.47 0.45
Weight % of hydrocarbons						
CH ₄	11.2 10.8	5.5 8.2	7.2 6.7	7.1 7.7	6.1 6.0	6.5 5.8
C ₂ -C ₄	31.9 32.9	20.6 29.1	27.0 26.8	25.8 27.8	24.8 23.8	26.4 26.1
C ₅ -C ₁₁	29.8 30.3	38.4 30.6	30.7 33.2	22.7 30.4	30.7 28.9	26.3 24.9
C ₁₂ +	27.1 26.0	35.5 32.1	35.1 33.3	44.4 34.1	38.4 41.3	40.8 43.2
Olfin content (Weight %)						
C ₂ -C ₄	63 64	70 72	70 71	69 68	77 78	78 76
C ₅ -C ₁₁	49 53	58 62	60 61	56 59	60 66	67 68
2 Butene/1-Butene ratio	0.49 0.45	0.26 0.21	0.24 0.22	0.27 0.30	0.06 0.06	0.06 0.06

^(a) Nominal process conditions: 250 °C, 1.48 MPa, 2.0 NI/g-cat-h, H₂/CO = 1.0

Table V.1-4 Results summary of catalyst tests using H_2 or $H_2 + CO$ activations.

Test ^(a)	D-3087	A-3237	B-2057	B-3227	D-3377
Time on stream (h)	43	42 90	45 92	42 91	40 86
CO conversion (%)	81.1	79.0 85.7	61.2 67.5	31.0 33.1	76.0 67.2
$H_2 + CO$ conversion (%)	65.2	62.9 70.2	48.0 53.3	26.0 27.1	04.0 58.4
$r_{CO_2}/(-r_{CO})$	0.49	0.50 0.50	0.54 0.54	0.50 0.51	0.45 0.46
Weight % of hydrocarbons					
C_{H_4}	14.2	12.4 14.7	14.0 12.9	10.7 11.7	7.1 0.5
C_2-C_4	39.9	38.9 42.8	45.2 39.6	39.3 38.4	30.5 27.0
C_5-C_{11}	39.4	42.2 32.7	36.9 33.0	39.6 34.3	31.8 32.7
$C_{12}+$	6.5	6.5 9.8	3.9 14.5	10.4 15.6	30.6 33.8
Olefin content (Weight %)					
C_2-C_4	65	70 68	75 77	72 75	76 76
C_5-C_{11}	58	65 64	63 64	66 68	72 69
2-Butene/1 Butene ratio	0.09	0.05 0.07	0.03 0.02	0.03 0.03	0.07 0.06

^(a) Nominal process conditions: 250 °C, 1.48 MPa, 2.0 NI/g-cat-h, $H_2/CO = 1.0$

Activations with CO

Catalyst activity, measured by volumetric gas contraction, as a function of time on stream during the conditioning period is shown in Figure V.1-1. Volumetric contraction, defined as: $100 \times (\text{Inlet flow rate} - \text{Outlet flow rate}) / (\text{Inlet flow rate})$ varies nearly linearly with respect to syngas ($\text{H}_2 + \text{CO}$) conversion and is a convenient measure of catalyst activity. At a given temperature and time on stream, the volumetric gas contraction is essentially independent of activation procedure employed. Any differences in results may be attributed to non-uniformity in the bed temperature and/or fluctuations in the tail gas flow rate, since the system was not at steady state during these measurements. At the end of the conditioning period the catalyst activity was nearly the same for all six activation procedures employed.

The catalyst activity, measured by ($\text{H}_2 + \text{CO}$) conversion, as a function of time on stream during the steady state period (250°C, 1.48 MPa, 2NI/g- cat.h and $\text{H}_2/\text{CO}=1$) is shown in Figure V.1-2. The initial activity of the catalyst was high and similar for all CO activation procedures employed. The syngas and CO conversions for different activation procedures at 1-2 h at the process conditions were: 75-84% and 87-97%, respectively. The activations at 250°C for 8 h and 280°C for 24 h (both at atmospheric pressure) resulted in the highest catalyst activity and stability during the catalytic tests, however the activity declined with time on stream for all CO activations. The loss in activity expressed as a percentage of the initial ($\text{H}_2 + \text{CO}$) conversion, over the 120 h test period, ranged from 10% (test A-2967) to 45% (test B-2857). The activation at 250°C for 24 h resulted in the most rapid catalyst deactivation at the synthesis conditions, but the underlying reasons for this behavior are not yet understood. This activation procedure and subsequent catalytic testing were repeated in run B-0098. Similar results were obtained during this test: the ($\text{H}_2 + \text{CO}$) conversion declined from an initial value of 75.4% to 51.5% at 120 h on stream, which represents a 32% loss in activity. The latter value is lower than that obtained in test B-2857, but is still high in comparison to the other activations with CO at atmospheric pressure.

The ratio of CO_2 production (r_{CO_2}) to total CO consumption ($-r_{\text{CO}}$) represents a measure of the water gas shift (WGS) activity and is listed in Table V.1-3. This ratio did not vary much with time on stream nor with the activation procedures. The catalyst activated at 1.48 MPa and 280°C for 24 h (A-3517) had the highest WGS activity, whereas the lowest WGS activity was observed in test B-2857. However, the difference between these two extreme cases was only 15%.

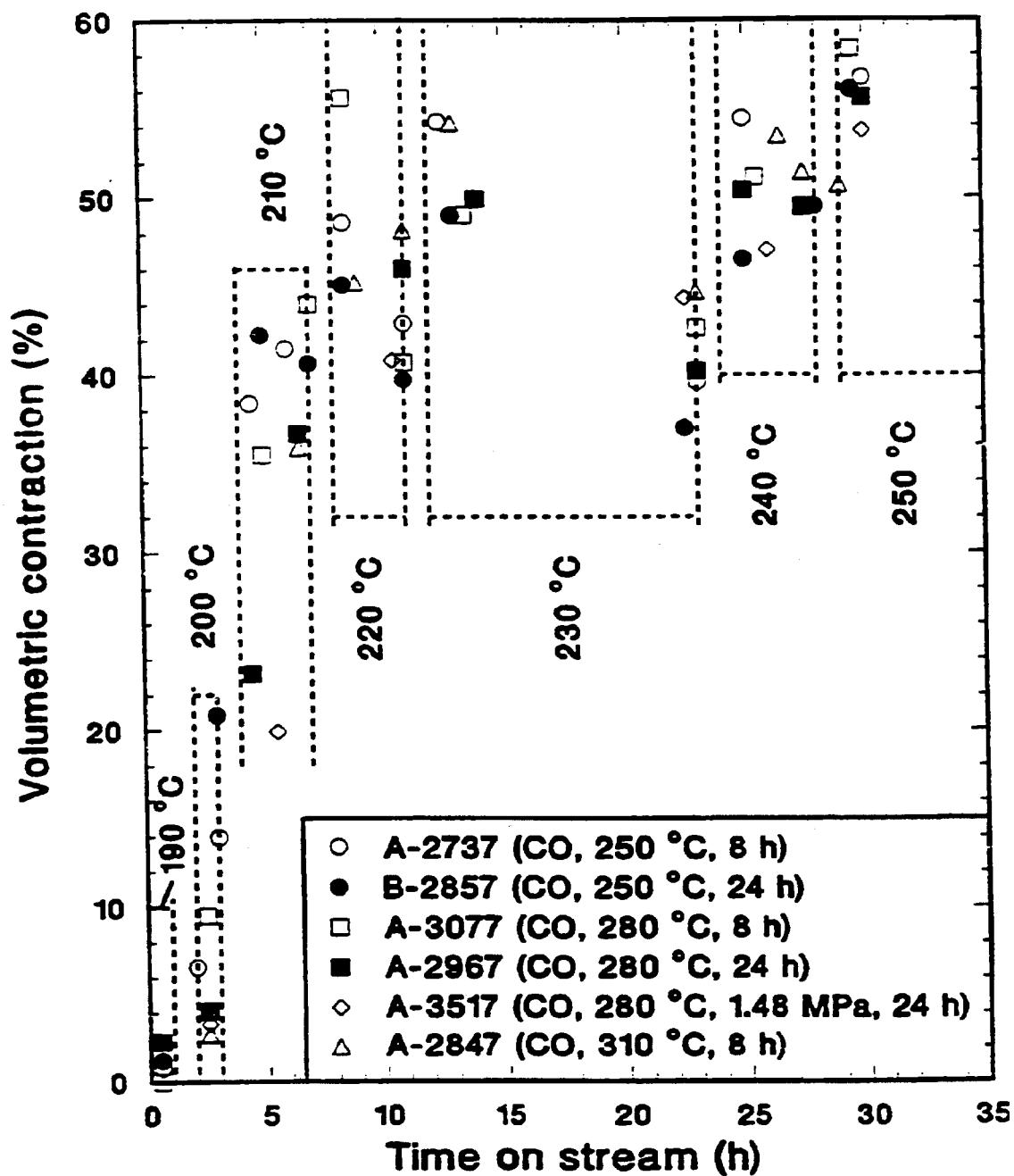


Figure V.1-1. Volumetric contractions during conditioning period for the CO activation procedures.

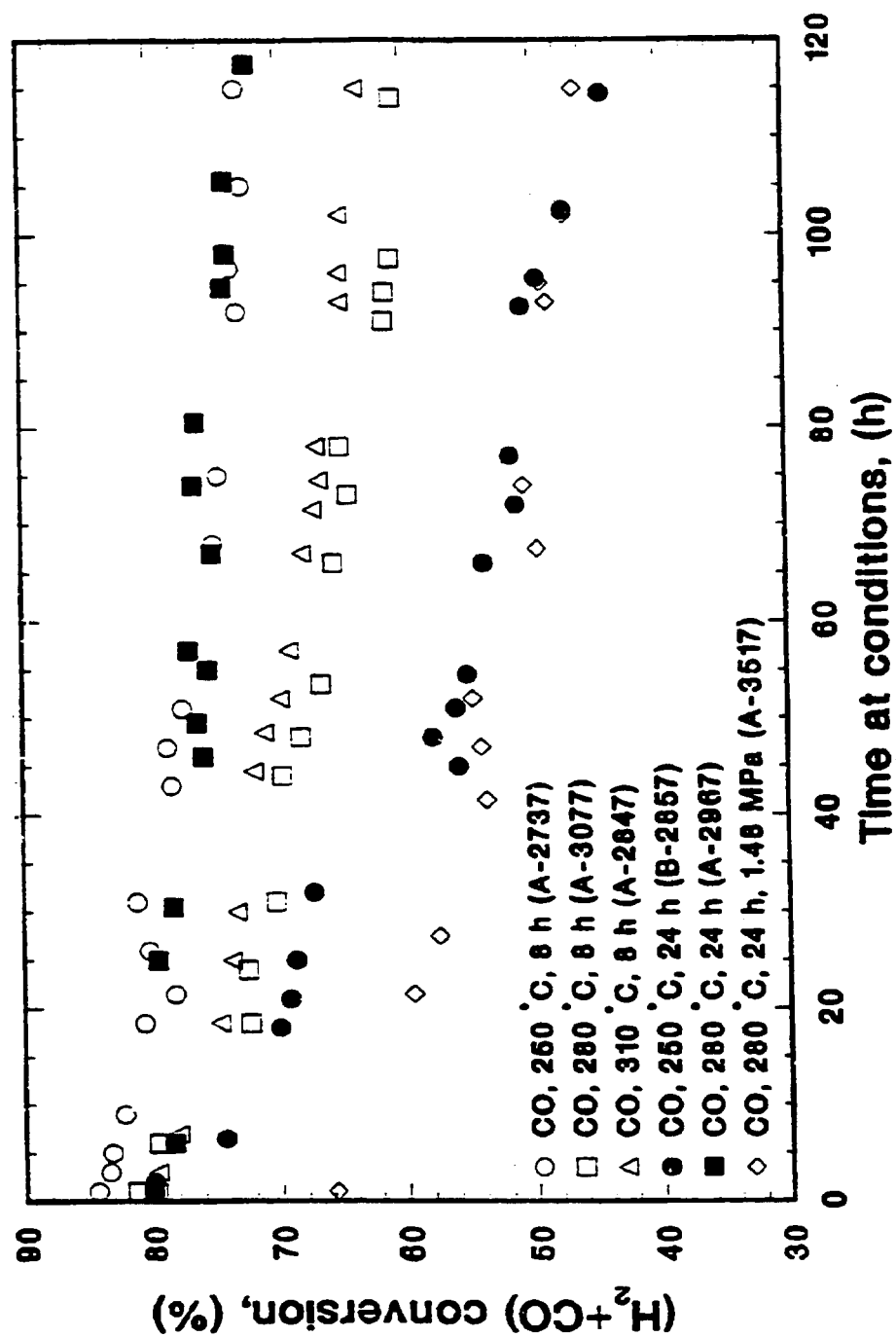


Figure V.1-2. Comparison of activity and stability for the CO activation procedures.

Selectivity

The hydrocarbon product distribution, the fraction of olefins in light hydrocarbons, and the olefin isomerization activity (expressed as 2-butene/ 1-butene ratio) obtained during the two mass balances for each of the six activation treatments are given in Table V.1-3. Although the catalyst activity decreased with time on stream, selectivities remained relatively stable between the two balances performed at approximately 43 and 91 h on stream. Thus, the average values for the hydrocarbon product distribution and the (1+2)-olefins/n-paraffin ratios (or the olefin content in a given carbon number range) from balances 1 and 2 can be used for comparison of different activation procedures (Figure V.1-3).

Hydrocarbon product selectivity improved with the increase in activation temperature at 8 h activation durations. The catalyst activated at higher temperature produced less methane and C₂-C₄ products. The (1+2)-olefins/n-paraffin ratios (Fig.V.1.3) and the olefin content of C₂-C₄ and C₅- C₁₁ hydrocarbons (Table V.1.3) increased, whereas the 2-butene/1-butene ratio decreased as the activation temperature increased. Since paraffins and β -olefins are produced primarily via secondary reactions, this means that activations at higher temperature (280 and 310°C) tend to suppress these secondary reactions. At 24 h reduction durations, comparisons can be made at 250 and 280° C. With the longer duration, higher activation temperature favors a more stable catalyst, while the selectivities were similar (Table V.1.3 and Fig.V.1.3). These trends are not the same as those observed at 8 h durations, indicating that the effects of activation temperature and duration can not be separated.

The effect of activation duration can be seen at 250 and 280 °C. At 250° C, the 24 h duration (B-2857) produced the least stable of all the catalysts, however, the selectivity is better than with the 8 h activation as less methane and C₂-C₄ products are produced. The stability with a 280°C reduction is superior when a longer duration (24 h) is used (Fig. V.1-1), whereas the selectivity is not strongly affected by duration (A-3077 vs. A- 2967). On the basis of the overall catalyst performance (stability and product selectivity) the activation at 280 °C for 24 h (A-2967) produced the best results of all five activations with CO at atmospheric pressure.

The effect of pressure during activation was determined at these optimal values of activation temperature and duration in test A-3517. Higher pressures are needed for in-situ activations in slurry reactors to reduce losses of liquid medium due to evaporation. The catalyst activated at ambient pressure was found to be more active and more stable than the catalyst activated at

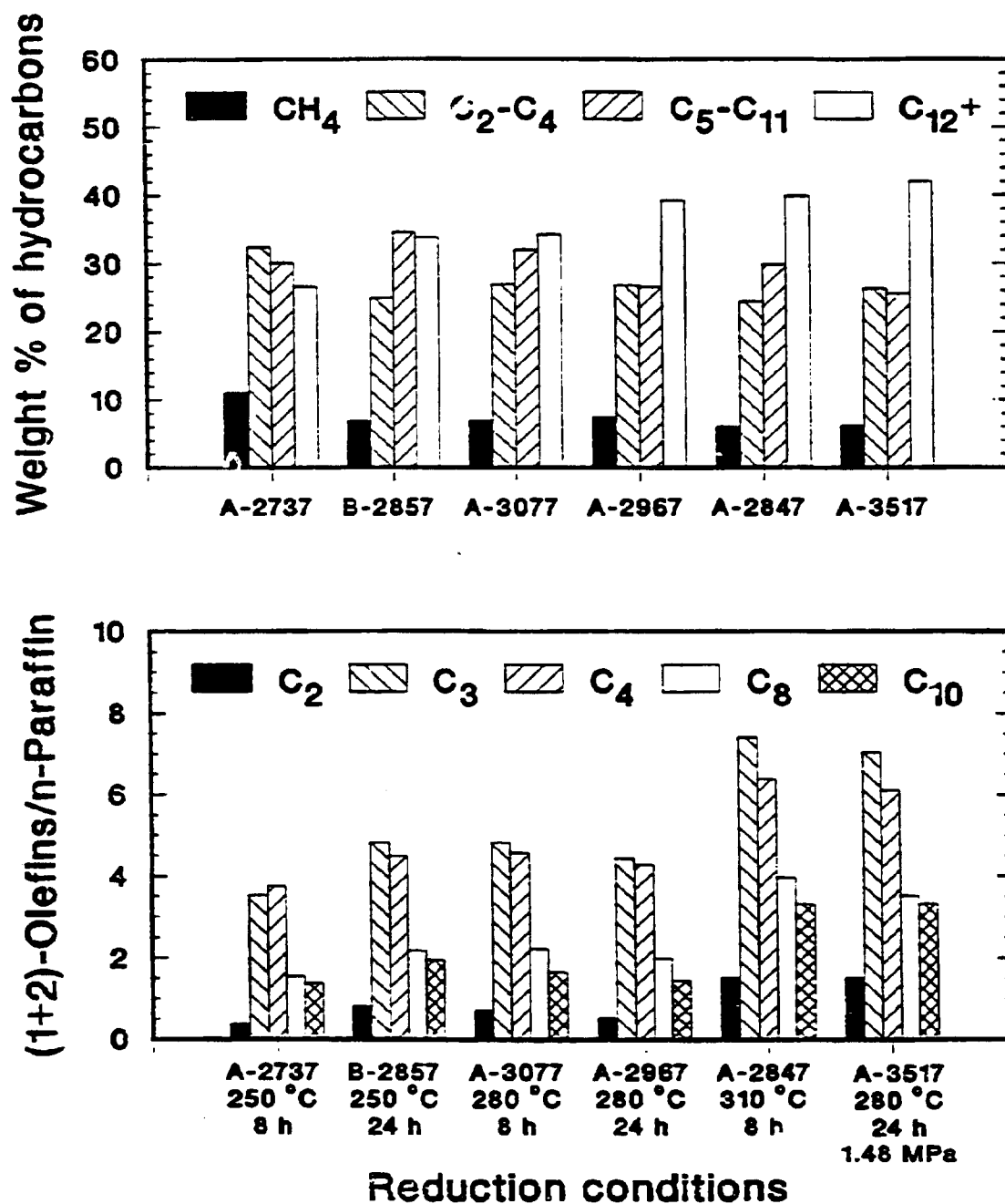


Figure V.1-3. Comparison of hydrocarbon distribution and olefin selectivity for the CO activation procedures.

high pressure (Fig. V.1-2). The activation pressure did not have a strong effect on hydrocarbon product selectivity, as shown in Figure V.1-3 and Table V.1-3. The weight percent hydrocarbon distribution obtained using different activation pressures was nearly the same for both procedures, although some shifting between higher molecular weight products (C_5 - C_{11} , C_{12} -) is evident. The (1+2)-olefins/n-paraffin ratios and the olefin content in C_2 - C_4 and C_5 - C_{11} hydrocarbons were higher for the catalyst activated at higher pressure, however, this may have been caused in part by the significantly higher conversions obtained with the ambient pressure reduction. As the (H_2 -CO) conversion increases, the partial pressure of H_2 relative to CO also increases (as long as the usage ratio is lower than the feed ratio). Also, higher conversions lead to longer residence times in the reactor due to gas contraction upon reaction. Both of these effects (the increase in the H_2 /CO partial pressure ratio and the longer residence time) favor hydrogenation of olefinic products at high (H_2 -CO) conversion, decreasing the (1+2)-olefins/n-paraffin ratio. The isomerization activity (2-butene/1-butene) was significantly lower for the catalyst activated at 1.48 MPa.

The products of the Fischer-Tropsch synthesis follow the Anderson-Schulz-Flory (ASF) distribution, which may be characterized either by a single value of the chain growth probability factor or by two values (Huff and Satterfield, 1984). We found that whenever all products collected were analyzed, including those in the high pressure trap, at least two chain growth probabilities are needed to characterize the product distribution. An example of the ASF plot is shown in Fig. V.1-4, for the data from test A- 3077, balance 2. The two- α model of Huff and Satterfield was found to accurately represent these data:

$$x_n = \beta(1 - \alpha_1)\alpha_1^{n-1} - (1 - \beta)(1 - \alpha_2)\alpha_2^{n-1} \quad (V.1-1)$$

where x_n is the mole fraction of products containing n carbon atoms (hydrocarbon and oxygenate), β is the fraction of type I sites on the catalyst and α_1 and α_2 are the chain growth probabilities associated with the type I and type II sites, respectively. The negative deviations from the ASF distribution in the C_6 - C_8 range are caused by product loss due to evaporation, while positive deviations at C_{46} - are due to errors in the GC peak integration (high base-line shift).

Activations with H_2

The changes in catalyst activity with time on stream during the unsteady state conditioning period and the steady state synthesis period are shown in Figures V.1-5 and V.1-6, respectively.

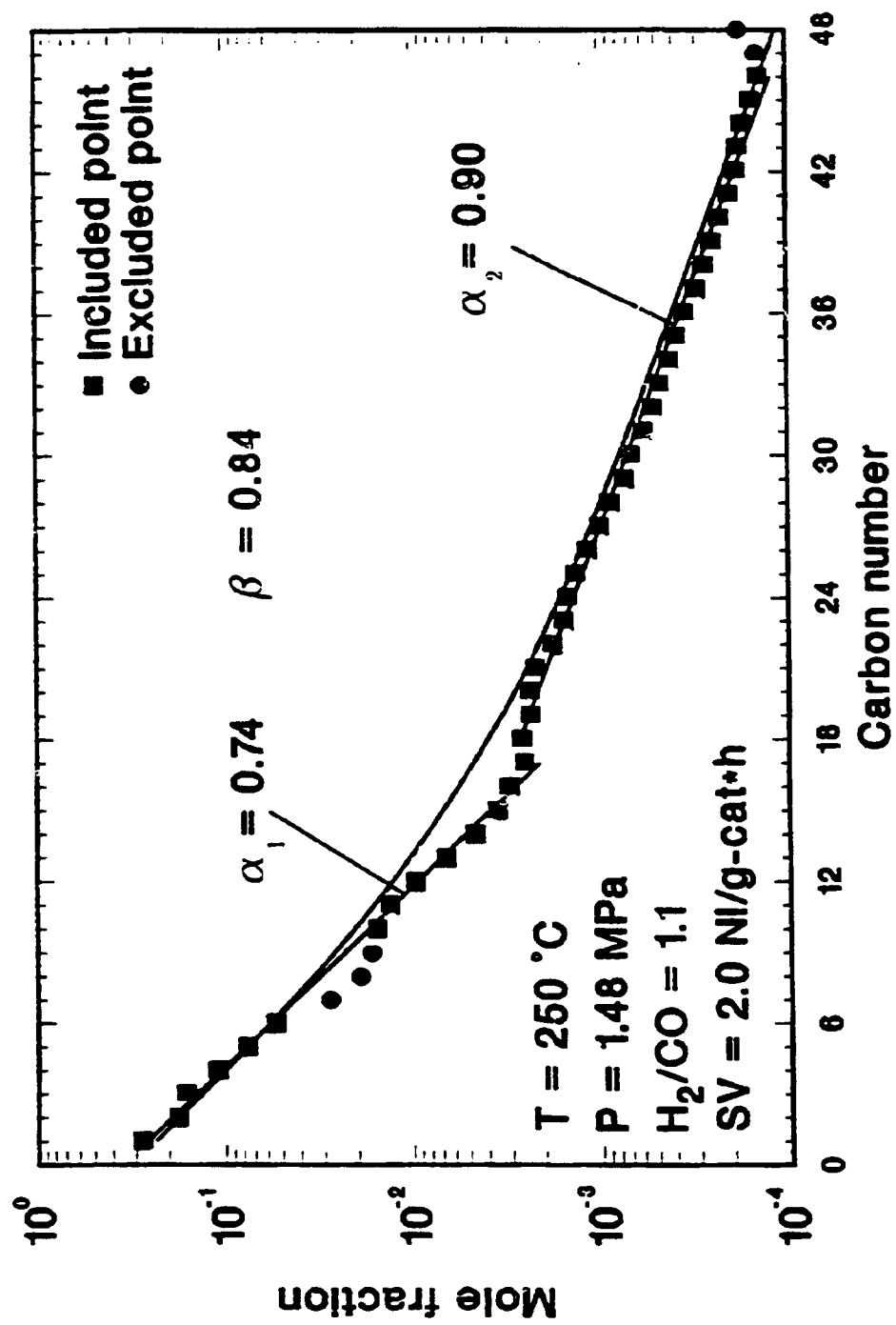


Figure V.1.4 . Anderson-Schultz Flory plot for the products obtained in test A 3077 at 92 h on stream.

In contrast to the behavior of CO reduced catalyst, the activities of the H₂ reduced catalyst, measured by volumetric contraction, during the conditioning period were strongly influenced by activation conditions (temperature and/or duration) and increased in the following order (280°C, 24 h) < (280°C, 8 h) < (250°C, 24 h) < (250°C, 8 h). This order continued throughout the steady state period (Fig. V.1-6), but the activity of the catalyst reduced at 250°C for 24 h approached that of the catalyst reduced at 250°C for 8 h. The latter test (B-3087) was prematurely terminated due to a flow interruption which occurred at approximately 80 h on stream (before the second mass balance was completed). All four reductions with H₂ lead to either a constant or a gradually increasing activity during the synthesis. The activities of the catalyst reduced at 250°C (8 and 24 h durations) were significantly higher than those resulting from activation at 280°C. Also, the shorter 8 h reduction at 280°C (B-2957) produced a significantly more active catalyst than the 24 h reduction at the same temperature.

As with the CO activated catalyst, selectivity did not change significantly between the two mass balances (See Table V.1-4). The effects of reduction temperature and duration on catalyst selectivity may be studied in Figure V.1-7 (the average values from the two mass balances were used for this comparison) and in Table V.1-4. The hydrocarbon weight percent distribution was not strongly affected by the H₂ reduction procedure followed, regardless of the reduction conditions. The (1+2)-olefins/n-paraffin ratios did not change significantly with the duration of the reduction, however, the ratios decreased as the reduction temperature decreased from 280 to 250°C, at both 8 and 24 h reduction durations. This trend may be caused, in part, by the significantly higher (H₂+CO) conversions obtained with the catalysts reduced at 250°C.

WGS activity was not affected much by differences in reduction parameters, and the ratio $(r_{CO_2})/(-r_{CO})$ only varied between 0.49 and 0.54. The olefin isomerization activity decreased with the increase in reduction temperature, but again this could have been caused at least in part by the decreased α -olefin concentration at lower (H₂+CO) conversions (i.e., higher reduction temperature).

Comparison of Activations with CO, H₂ and Syngas

The activities of the catalyst activated with CO, H₂ and syngas (H₂/CO=0.68) at atmospheric pressure and 280° C for 24 h are compared in Figure V.1-8. The CO activated catalyst was more active and stable than the catalyst activated with the CO rich syngas, whereas the H₂ reduced catalyst showed high stability but a very low activity, about 30% (H₂+CO) conversion throughout the run. The change in activity with time on stream for the H₂ reduced catalyst

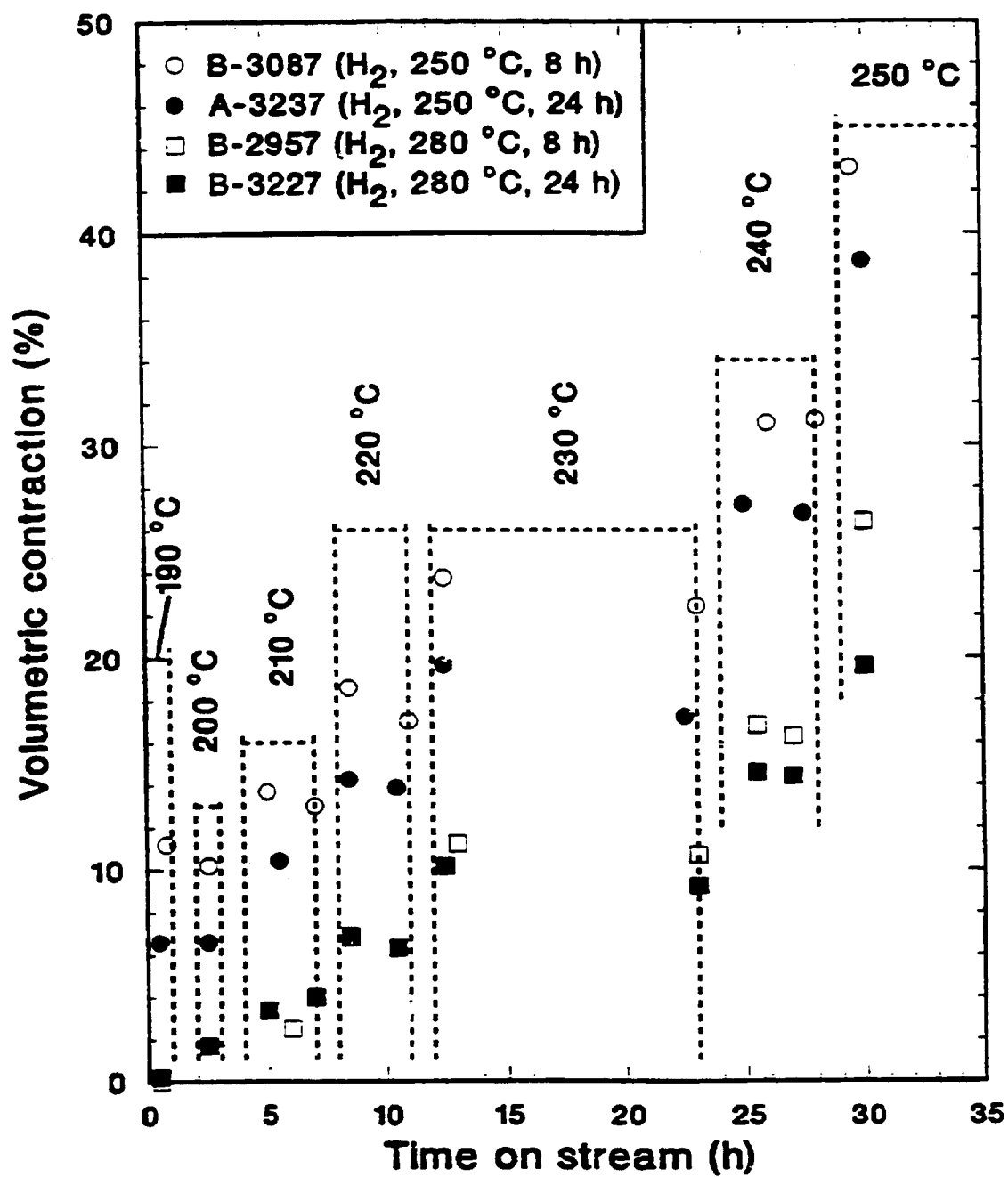


Figure V.J-5. Volumetric contractions during conditioning period for the H_2 activation procedures.

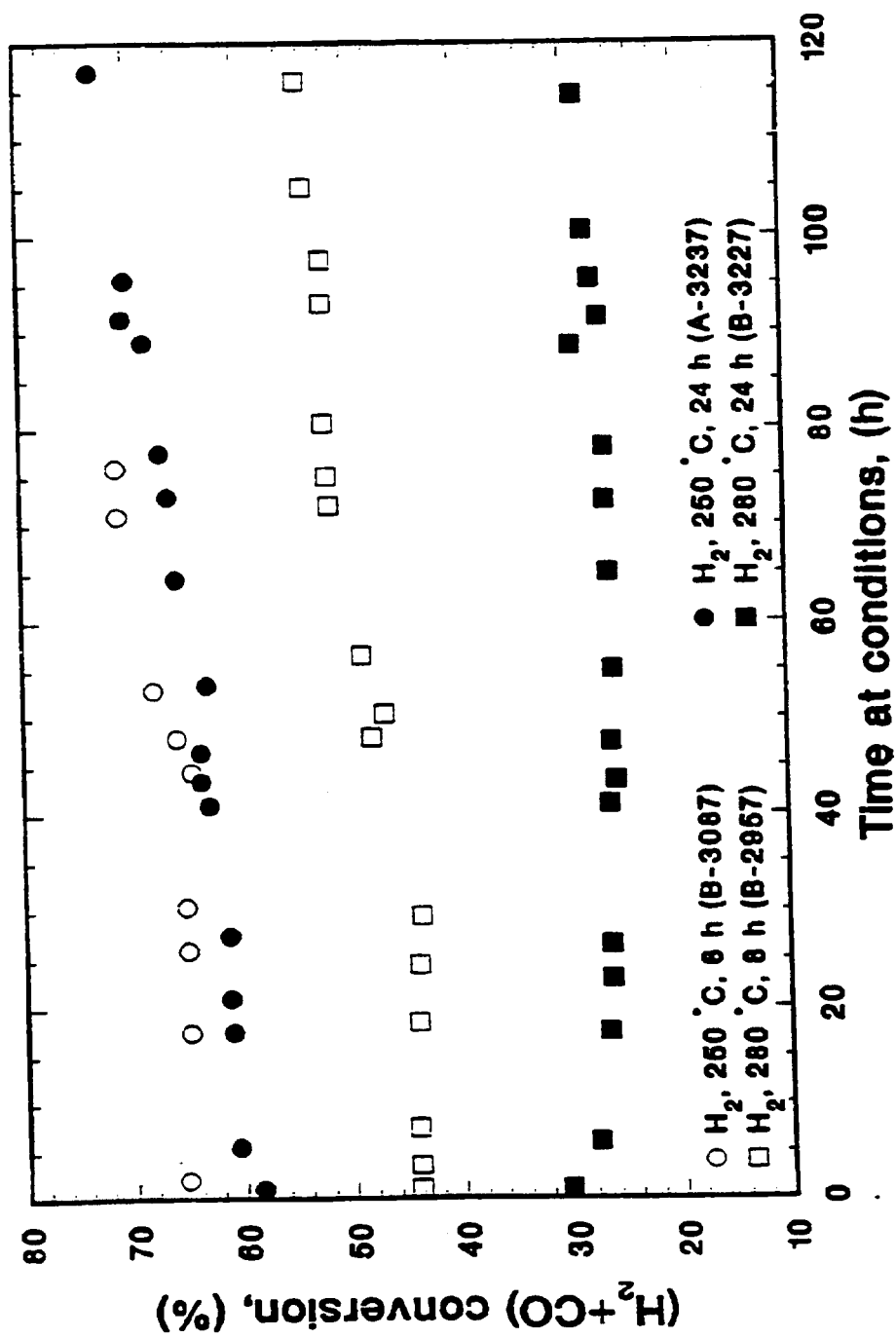


Figure V.1.6. Comparison of activity and stability for the H_2 activation procedures.

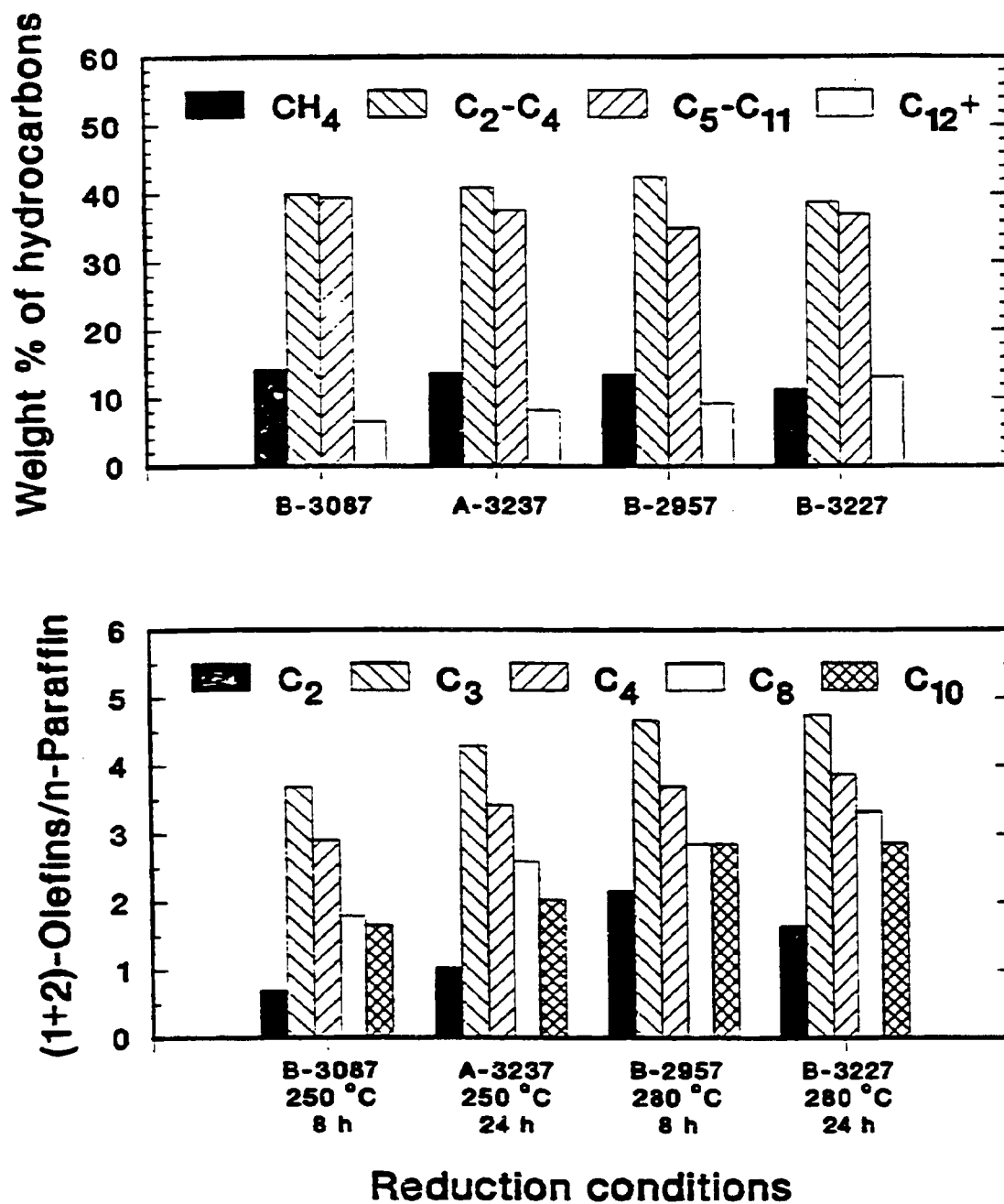


Figure V.1-7. Comparison of hydrocarbon distribution and olefin selectivity for the H₂ activation procedures.

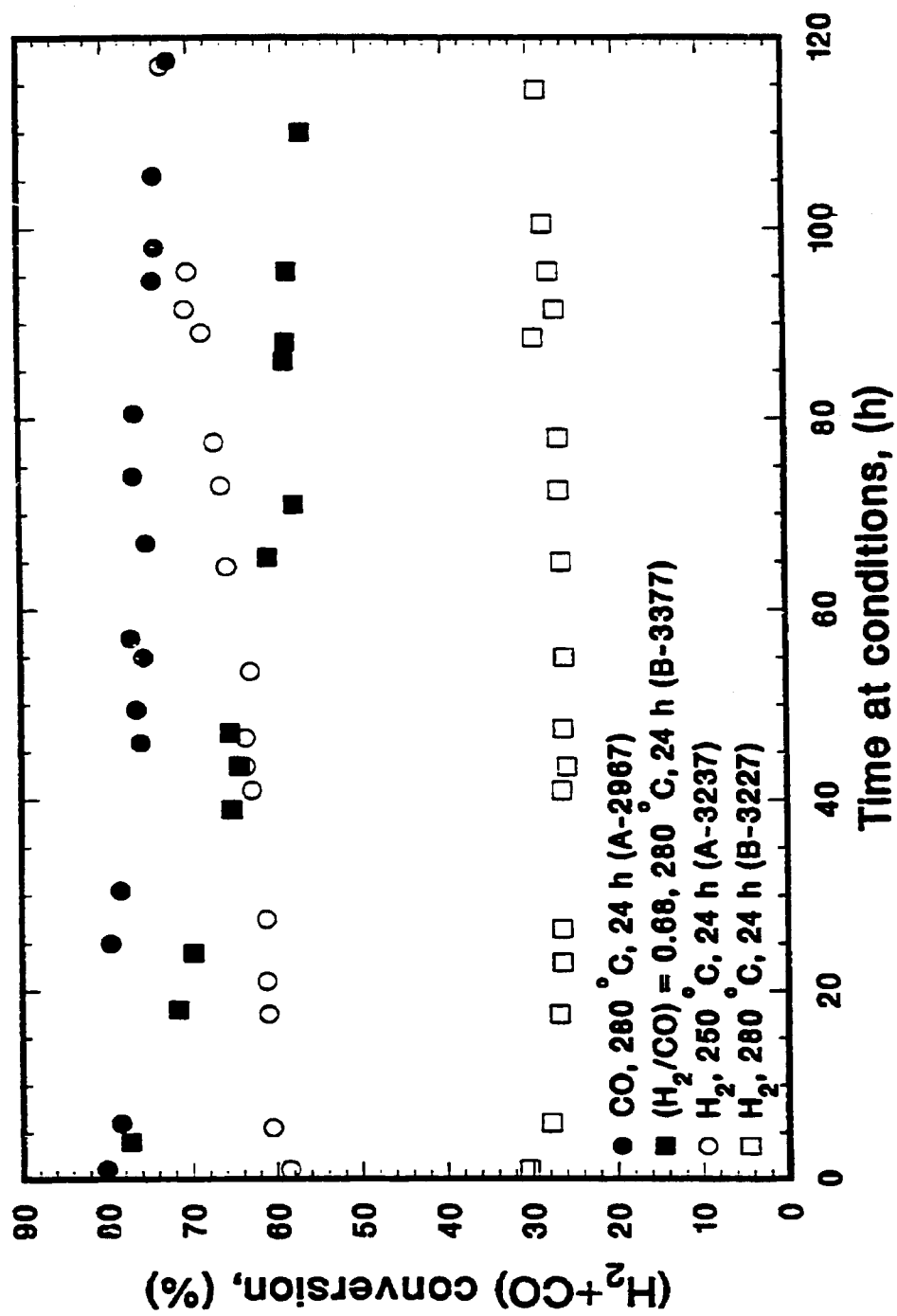


Figure V.1-8. Comparison of activity and stability for selected activation procedures.

at 250°C for 24 h (A-3237) is also included for comparison. The activity of the catalyst during the latter test was initially lower than that of the CO activated catalyst, but after about 100 h at conditions the two activities were nearly the same. By referring to Tables V.1-3 and V.1-4, it may be seen that activations with H₂ give the highest $r_{\text{CO}_2} / (r_{\text{CO}})$ ratios (i.e., the highest WGS activity) followed by H₂/CO=0.68 and CO activations.

A comparison of the effect of reductant (gas) type on catalyst selectivity is given in Figure V.1-9 for the same four tests shown in Figure V.1-8. The weight percent hydrocarbon distribution obtained in tests following the CO and syngas activations were similar, with some minor shifting of products between the C₅-C₁₁ and C₁₂+ product ranges. The catalyst reduced with H₂ favored the formation of methane and C₂-C₄ products, with correspondingly lower weight percents of the higher molecular weight products (C₅-). The (1+2)-olefins/n-paraffin ratios were higher for the catalyst activated with synthesis gas, compared to the catalyst activated with either H₂ or CO, particularly the CO activated catalyst. These ratios are somewhat enhanced by the low conversions obtained in tests with the synthesis gas or H₂ (280°C, 24 h) activated catalyst, which may be seen by comparing olefin selectivities from tests A-2967 and A-3237 at approximately equal (H₂+CO) conversions. In this case the olefin selectivity of the H₂ activated catalyst is only slightly greater (C₅-C₁₁ fraction only) than that of the CO activated catalyst. The olefin isomerization activity of the CO activated catalyst is significantly greater than that of the catalyst activated by either H₂ or syngas regardless of the conversion level (see Tables V.1-3 and V.1-4).

On the basis of catalyst activity, stability, and selectivity, CO activation at atmospheric pressure, and 280°C for 24 h was found to be the most desirable of the eleven activations that were employed in this study.

Slurry Bed Reactor Tests

In order to determine whether the trends found in fixed bed reactor tests remain the same during the synthesis in slurry phase, two tests were conducted in a 1 liter stirred tank slurry reactor (Autoclave Engineers). A precipitated catalyst with composition 100Fe/0.3Cu/0.5K was employed in both tests. The catalyst was activated in H₂ for 24 h (test SB-0458) or in CO for 16 h (test SA-0468) both at 280°C, 0.79 MPa and 3 NI/g-cat.h. (see Section V.2.3) Following activation, the catalyst was tested at 250°C, 1.48 MPa, 2 NI/g-cat.h and H₂/CO=1.0 (the same process conditions used in the fixed bed reactor tests). The (H₂+CO) conversions at about 40 h on stream were 24.8 and 74.8% for the H₂ and CO reduced catalysts,

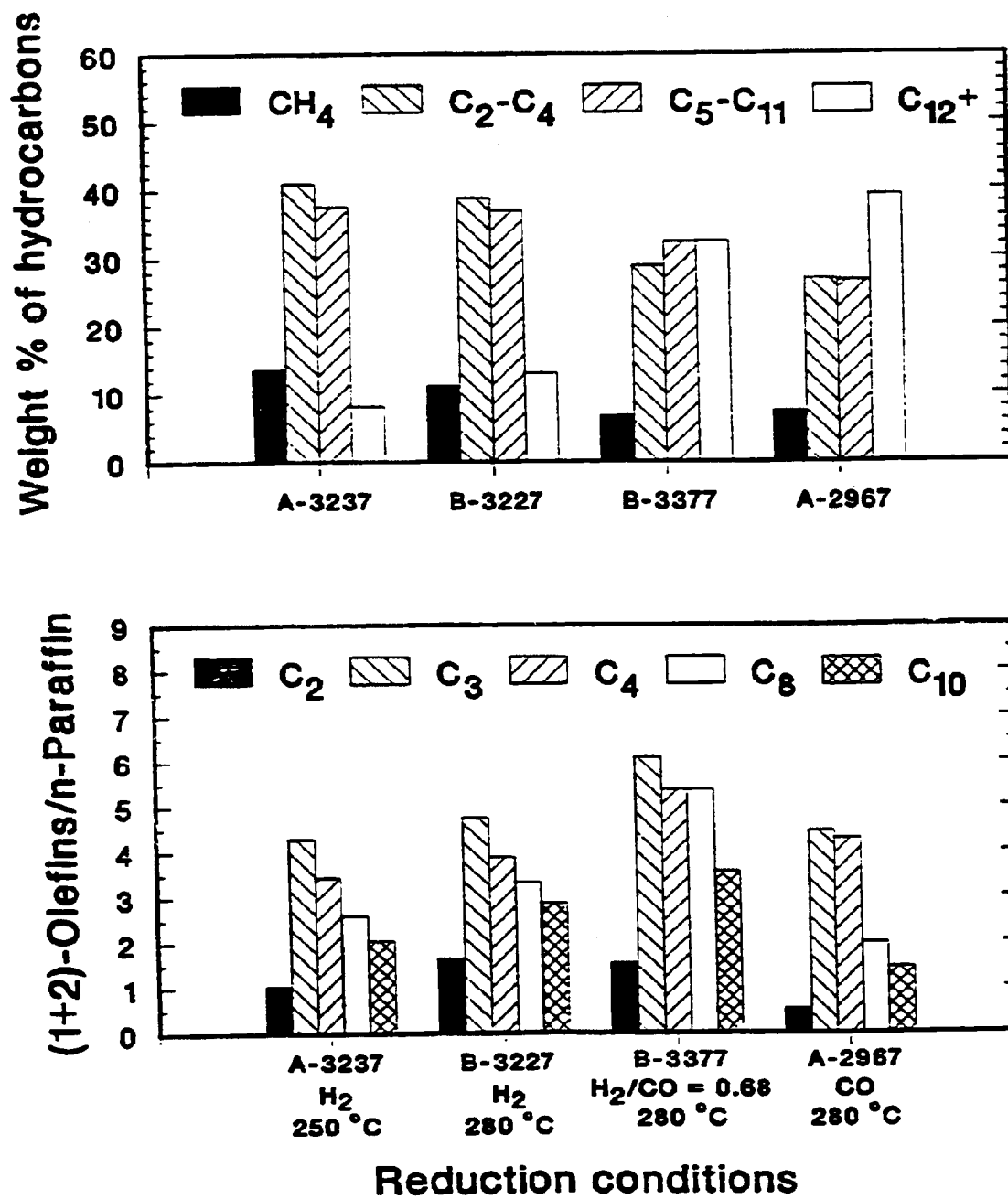


Figure V.1-9 . Comparison of hydrocarbon distribution and olefin selectivity for selected activation procedures.

respectively. These conversions are similar to those obtained in fixed bed tests when similar activations procedures were employed. After the first mass balance, the process conditions (temperature, gas flow rate or H_2/CO feed ratio) were varied in both tests. The base-line conditions were repeated later during the test to determine the extent of catalyst deactivation. The (H_2+CO) conversion increased with time on stream from 24.8% at 40 h to 35.5% at 428 h in the test with the H_2 activated catalyst, whereas the CO activated catalyst deactivated significantly during the synthesis. In the latter case, the (H_2+CO) conversion at 437 h on stream was only 17.4%. During the first mass balance (40 h on stream) the hydrocarbon distributions were similar: 4.6 (CH_4), 25.0 (C_2-C_4), 22.7 (C_5-C_{11}), and 47.7% ($C_{12}+$) for H_2 reduced catalyst compared to 6.9 (CH_4), 22.3 (C_2-C_4), 20.4 (C_5-C_{11}), and 50.4% ($C_{12}+$) for CO reduced catalyst. This trend is different than that observed in fixed bed reactor tests, where CO activated catalyst produced significantly less methane and C_2-C_4 products than H_2 activated catalyst.

The two slurry reactor tests show that activation procedures have the same effect on catalyst activity and stability as that found in fixed bed reactor tests. However, the trends in catalyst selectivity were not the same. The differences in selectivity trends may be caused by the different catalyst compositions used in the slurry (100Fe/0.3Cu/0.5K) and fixed bed (100Fe/3Cu/0.2K) tests.

Catalyst Characterization Studies

The catalyst (100Fe/3Cu/0.2K) used for the activation studies in fixed bed reactors was characterized using temperature-programmed reduction (TPR), isothermal reduction and X-ray photoelectron spectroscopy (XPS). A brief description of procedures and summary of pertinent results is given below.

Temperature-programmed and isothermal reduction studies were performed using both 5% H_2/N_2 and 5% CO/He mixtures as reducing agents at atmospheric pressure. The consumption of H_2 or CO was measured by the change in thermal conductivity of the effluent gas stream. Catalyst sample weights of 10 to 15 mg and reductant flow rates of 12 cc/min were used in all experiments. A temperature program rate of $20^\circ C/min$ from room temperature to $800^\circ C$ was used in TPR experiments, or to $300^\circ C$ in isothermal reductions. The latter temperature was maintained for 12 h or 8 h in reductions with H_2 and CO , respectively.

TPR reduction studies of calcined samples (in air at $300^\circ C$ for 16 h) have revealed that reduction of Fe_2O_3 occurs in two steps (1) $Fe_2O_3 \rightarrow Fe_3O_4$, and (2) $Fe_3O_4 \rightarrow Fe$, and that

both steps of iron reduction occur more rapidly in CO than in H₂. The same behavior and trends were also observed under isothermal reductions. The times required for completion of iron reduction to the zero-valent state were found to be: 300 and 60 min, for H₂ and CO reductants, respectively.

These two techniques, TPR and isothermal reduction, can differentiate the reducibility of the bulk composition but do not provide information on the surface composition after reduction. XPS studies complement these reduction studies by providing information about the identity of the surface iron phases. XPS measurements were performed using a Hewlett-Packard Model 5950 A ESCA spectrometer, which was equipped with an Al K α X-ray source monochromator used at a 1250.0 eV accelerator potential setting. Samples were in the form of pressed disks, and were handled under a dry, O₂-free N₂ atmosphere during spectrometer loading to prevent surface reoxidation due to atmospheric H₂O and O₂.

XPS studies of the calcined catalyst sample after isothermal reduction with H₂ or CO at 300°C for 12 h have revealed the following. The surface of H₂ reduced catalyst consists of approximately 45% Fe₂O₃/Fe₃O₄ iron, and 55% of zero valent iron, which is in contrast with the result obtained from the isothermal reduction. This is probably due to reoxidation of surface iron by water, a byproduct of reduction in H₂. On the other hand, CO treatment leads to quantitative reduction of iron to the zero valent metallic state. This treatment also results in deposition of surface carbon.

The activation parameters (temperature, gas flow rate and duration) employed in characterization studies were not the same as those employed in the fixed bed catalytic studies, but they nevertheless provide useful information on the qualitative differences between H₂ and CO reductions.

V.1.4. Discussion

CO Activations

The major findings from our catalytic tests conducted at 250°C, 1.48 MPa, 2 NI/g-cat.h, and H₂/CO=1, following activations with CO under different conditions, are: (1) The catalyst displayed high initial activity, which decreased with time on stream; (2) Catalyst stability and selectivity were affected by differences in the activation parameters (temperature, pressure and duration). Activation at atmospheric pressure (0.1 MPa) gave a more stable catalyst than that at 1.48 MPa, whereas the effects of activation temperature and duration on catalyst stability and selectivity could not be separated.

Pichler, as described by Storch et al. (1951, pp. 290-297) and Anderson (1956, pp. 176-180), used CO and syngas activations in studies with alkalized precipitated iron catalysts with and without Cu promoter. He studied the effects of activation (induction) pressure and temperature on catalyst activity and stability. The length of induction was 25 hours with a gas flow of 0.4 NI/gFe.h, and subsequent synthesis was conducted with $H_2/CO=2/3$ gas at 1.52 MPa, 235°C and 0.4 NI/gFe/h. He found that activation with CO was superior to that with $H_2/CO=2/3$ syngas, and that the optimum pretreatment conditions were 325°C and 0.01 MPa (absolute). Activation with CO at atmospheric pressure (0.1 MPa) was not greatly inferior in terms of catalyst activity and stability during the synthesis, whereas activation at 1.5 MPa (synthesis pressure) led to lower activity and rapid deactivation with time on steam. Characterization studies of activated catalysts, by acid decomposition and thermomagnetic methods, revealed that lower induction pressures result in higher carbide content (Hägg or χ -carbide) and lower concentrations of free carbon deposited on the catalyst. Activations at temperatures in the range 255-305°C led to catalyst deactivation, whereas catalyst activated at 325 and 345°C displayed high stability at gas contractions of 52-55% (high (H_2+CO) conversions) over 120 and 80 days of synthesis, respectively. Characterization studies revealed that the catalyst activated at high temperatures (325-345°C) was converted almost completely to Hägg carbide, whereas activations at lower temperatures resulted in formation of a mixture of hexagonal carbides, magnetite and free carbon. On the basis of these results, it was speculated that Hägg carbide is the active phase which resists chemical change during the synthesis. The loss of activity was believed to be related to progressive conversion of Hägg carbide to magnetite.

Zarochak and McDonald (1986, 1987) used CO activation at 280°C, 1.48 MPa, 1.3 NI/g-cat.h for 24 h in their studies with a precipitated 100Fe/1Cu/0.5K catalyst. As revealed by Mössbauer spectroscopy, the catalyst was essentially completely reduced/carbided to χ -carbide during 24 h CO activation. Following the in situ activation in a slurry reactor, the catalyst was tested at a gas space velocity of approximately 2.5 NI/g-cat.h, 260°C, 1.48 MPa using a synthesis gas with an H_2/CO feed ratio of 1 or 0.7. In the test with 1:1 syngas, CO conversion decreased slowly from 88.8% at 95 h to 80.4% at 359 h, whereas in the test with $H_2/CO=0.7$ syngas, catalyst deactivation was much higher. The CO conversion was about 80% at 100 h but only 25% at 260 h on stream. This shows that catalyst stability is not determined solely by the pretreatment, but also by process conditions (oxidizing/reducing environment) during

the synthesis.

On the basis of results from the literature and the present study it seems difficult to maintain a constant catalyst activity over a long period of time. Pichler was able to achieve high stability over a long period of time with CO pretreatments at 325 and 345°C and subatmospheric pressure. These conditions (high temperature and low pressure) are not suitable for in-situ activations in slurry reactors and thus were not employed initially in our study. We have also used Pichler's type of activation, pure CO at 0.1 MPa, 335°C, and 3 Ni/g-cat.h, in a study with another precipitated iron catalyst (100Fe/3Cu/0.5K). Subsequent synthesis was conducted at 1.48 MPa, 260°C, 2 Ni/g-cat.h and $H_2/CO=0.64$ in a fixed bed reactor, but the catalyst deactivated rather rapidly. Initial (H_2+CO) conversion was 74.2% but decreased to 50% after 70 hours at the process conditions (See Section VI.2.2).

In addition to the observed strong effect on catalyst stability, the activation parameters also influence the product selectivity. The activation temperature and duration largely determine the initial state of the catalyst, including bulk phases, surface oxidation states of iron and promoters, carbon deposited, and crystallite size. Although, the catalyst composition (bulk and surface) varies during the synthesis, it is clear that its initial state has a marked influence on the product selectivity. Detailed characterization studies of catalysts after activation and during the synthesis are necessary to try to explain differences in product selectivities arising from the use of different activation parameters.

H₂ Activations

Four different activations with H₂ as reducing agent were employed in the present study, and their effect on catalyst activity, stability, and selectivity during the synthesis may be summarized as follows: (1) Catalyst activity was either constant or gradually increased with time on stream (up to 120 hours) for all four reductions; (2) Activity was higher when the catalyst was reduced at lower temperature and/or when a shorter duration was employed. The latter effect was particularly evident for the two activations conducted at 280°C; (3) The hydrocarbon product distributions were similar for all four activations, whereas the olefin content was lower and olefin isomerization was higher for activations conducted at 250°C.

Pichler found that hydrogen reduction at high temperature (about 360°C) is not effective in producing an active catalyst. Pennline et al. reported that activation with H₂ at 275°C and 1.48 MPa yielded an inactive catalyst (precipitated Fe/Mn catalyst). Scheuermann (Anderson, 1956, pp.180-181) found that reduction in H₂ at lower temperatures (180-220°C) gives better

activity than does reduction at 300°C. All these results, including the ones obtained in our study, point to the fact that reductions in H₂ at lower temperature result in improved activity. This can be explained by the fact that water vapor generated by reduction of iron in H₂ enhances the rate of sintering, and this results in the formation of large crystallites and loss of active sites for the synthesis reaction. At higher activation temperature, the water is released more rapidly during the reduction and its partial pressure is higher than that occurring during the reduction at lower temperatures. Both of these effects, higher temperature and higher H₂O concentration, would contribute to a larger degree of sintering and thus decrease catalyst activity. Similarly, longer duration will have a detrimental effect on catalyst activity due to a loss of active surface sites. Dry (1981, p. 179) states that high linear velocities of hydrogen are needed to obtain higher surface areas after the reduction, as this will result in rapid removal of water vapor. It should be noted, however, that after reduction to metallic iron is complete, continued treatment in H₂ should not produce additional hydrothermal effects, such as water-induced sintering, since byproduct water is no longer being generated. This is in contrast to the case for activation in CO, where deposition of surface carbon or formation of carbides continues to occur, even after iron reduction is complete.

If the loss of activity is primarily caused by sintering, this can explain the fact that different reduction procedures did not have a significant effect on hydrocarbon selectivity. In other words, different pretreatments led to different numbers of active sites, which affects activity, but there is no change in the nature of the sites and thus no effect on product selectivity. Differences in olefin selectivity (lower olefin content and higher isomerization activity for activations at 250°C in comparison to those conducted at 280°C) are at least partly caused by differences in conversions, as explained earlier (higher conversions favor secondary reactions).

In the absence of catalyst characterization following the reduction and after the synthesis, it is difficult to explain why the catalyst displayed a constant or gradually increasing activity during 120 hours of synthesis. A possible explanation was given by Dry (1981, p. 181) who reported that the activity of the partly reduced Fe-Cu-SiO₂-K₂O catalyst increases somewhat during several days of synthesis due to further reduction/carbiding which results in continued creation of active sites.

Effect of the Reducing Gas

Three different gases were employed for catalyst activation in the present study: CO (6 activations), H₂ (4 activations) and syngas with H₂/CO=0.68 (1 activation). Catalyst activity,

stability, and selectivity during the synthesis were strongly affected by the nature of the reducing gas. The major findings from catalytic tests are: (1) Catalyst activated in CO or syngas had initially higher activity than the catalyst activated in H₂, but the activity of the former decreased with time on stream, whereas the activity of the latter remained constant or gradually increased with time on stream; (2) CO and syngas activations favor the production of higher molecular weight products in comparison to H₂ activations; (3) Water-gas-shift activity was higher with H₂ activations than with CO activations.

In the early studies at Ruhrchemie (Anderson, 1956 pp.181-182) it was found that the catalyst pretreatment in syngas (H₂/CO=1.3) yields less methane and more high molecular weight products in comparison to the H₂ reduction. The same trend was observed in studies conducted at the U. S. Bureau of Mines with a precipitated catalyst having a composition 100Fe/10Cu/0.5K₂CO₃ (Anderson, 1984 pp.56-58). Activations with either syngas (H₂/CO=2) or pure CO resulted in similar hydrocarbon product distributions and produced less gaseous hydrocarbons and more higher molecular products than did the H₂ reduced catalyst. Thus the trends observed in our study concerning the effect of the reducing gas on catalyst selectivity and activity are in agreement with results from the literature. The reasons for the observed differences in selectivity resulting from the use of different reductants are not well understood. It appears that different activations lead to formation of different active sites and/or ensembles of sites on the catalyst surface.

In order to explain the observed differences in the catalyst activity for the FT and WGS reaction, some speculation concerning the nature of bulk phases of the catalyst after activation and during the synthesis is required. It will be assumed that H₂ activations lead to formation of magnetite and metallic iron, whereas CO activations lead to formation of iron carbides and magnetite. The relative fractions of these phases are a function of activation temperature and duration. During the synthesis, metallic iron is converted rapidly to iron carbides, which in turn may be partially oxidized to magnetite (Anderson, 1956; Dry, 1981). The used catalyst consists of a mixture of iron carbides and magnetite.

Our results show that CO activated catalyst has higher initial activity than H₂ reduced catalyst, which may indicate that iron carbides are more active for the synthesis than is magnetite and/or α -Fe. This is in agreement with results obtained at the U. S. Bureau of Mines (Anderson, 1984, p. 47) with a fused iron catalyst, where it was found that the catalysts converted to Hägg carbide are initially more active than H₂ reduced (either partially or com-

pletely) catalysts. A possible explanation for the observed activity trends may be given in terms of the competition model of Niemantsverdriet and van der Kraan (1981). In this model, the surface carbon (carbide or active carbon) obtained by CO dissociation is the intermediate for FT synthesis. This surface species can participate in three reactions: (1) formation of bulk carbides; (2) hydrocarbon synthesis (by combining with surface hydrogen atoms); and (3) formation of inactive carbon (deactivation). Thus, during the synthesis with a partially carbided catalyst (CO activations), more of the surface carbon is available for FT synthesis, whereas with H₂ reduced catalysts some of the surface carbon is consumed to form the bulk carbides. Therefore, the rate of FT synthesis will be initially lower with H₂ reduced catalysts. The CO reduced catalysts lose activity more rapidly from the blocking of active sites by inactive carbon and possibly also by high molecular weight hydrocarbons (recall that CO activated catalyst produced much more C₁₂— products than H₂ activated catalyst).

The higher WGS activity of H₂ activated catalysts, in comparison to carbided catalysts, was also observed in several previous studies with iron catalysts (Kölbel and Engelhardt, 1949; Anderson, 1984 (p. 45); Schultz et al., 1955). It was inferred that carbides are less active for the WGS than are reduced iron or magnetite. However, in a recent study by Satterfield et al. (1986b), with a fused iron catalyst, the WGS activity could not be correlated with a bulk concentration of magnetite.

Detailed catalyst characterization studies after activation and during the synthesis are needed to help explain catalytic results and provide a basis for development of improved catalysts.

V.1.5. Related Studies

In this section we present additional results which illustrate effects of activation parameters and reactor type on catalyst activity and hydrocarbon selectivities. These results were obtained from runs which were not specifically designed to study effects of activation parameters in a systematic way, as it was done in the previous section, but are included here since they extend the existing data base and provide some general trends.

V.1.6. Additional Tests with the 100Fe / 3Cu / 0.2K Catalyst

The activity and stability of this catalyst as a function of time on stream during runs FB-0029 and SA-3657 (Promoter Effect Research - Sections V.2.1 and V.2.3, respectively) and SB-2878 (Process Evaluation Research - Section VI.4.2) is shown in Figure V.1-10. Hydrogen reduced catalyst had high activity and excellent stability during the fixed bed test, but it

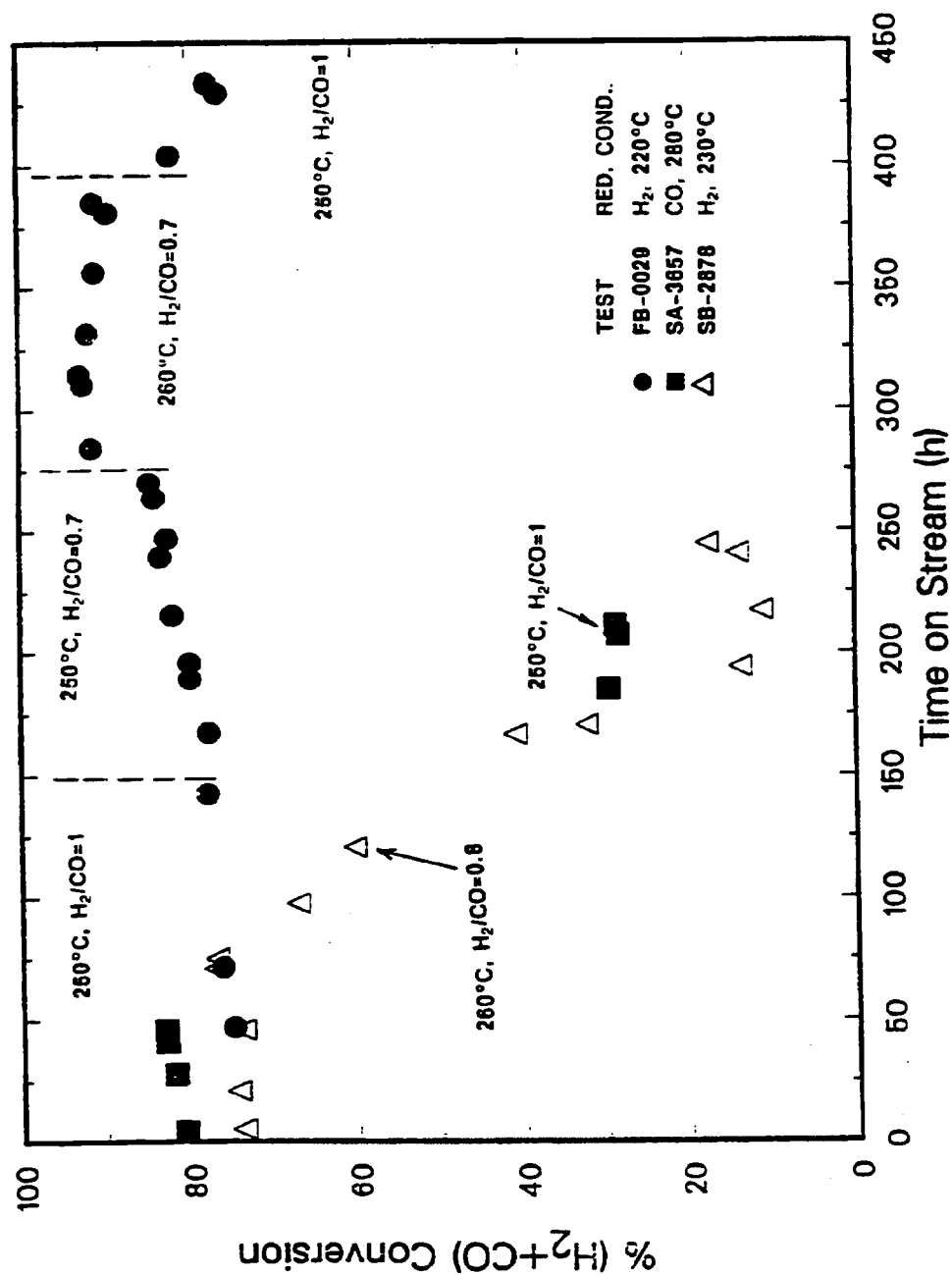


Figure V.1-10. Effect of activation conditions on activity and stability of the 100 Fe/3 Cu/0.2 K catalyst

deactivated rather rapidly in a slurry bed reactor test. The catalyst activated with CO had higher initial activity than the H₂ reduced catalyst, but it also deactivated rapidly (between 50 and 170 hours the catalyst was tested at different process conditions: SV=4 NI/g-cat.h at 250°C, or SV=2 NI/g-cat.h at 235°C).

Selected results from these tests and from some of the fixed bed reactor tests of this catalyst that were described in the previous section, are shown in Table V.1-5. Results show that catalyst activity decreases as the activation temperature increases, which is related to the enhanced catalyst sintering in the presence of H₂O as discussed in section V.1.4 of this report. Catalyst reduced with H₂ at 220°C had the same activity as that obtained when CO activation at 280°C was employed (the optimal activation procedure for this catalyst). However, the H₂ reduced catalyst produced significantly more CH₄ and light hydrocarbons than the CO activated catalyst. Hydrocarbon selectivities of H₂ reduced catalysts show the following trend: The light gas fraction (C₂-C₄) increases, whereas C₁₂- fraction decreases as the reduction temperature increases. Methane yield of the catalyst reduced with H₂ at 220°C was higher than that obtained in tests where higher reduction temperatures (250 and 280°C) were employed. It is interesting to note that catalysts from two different batches were employed in these tests. Tests FB-0029 and SB-2878 were conducted with catalyst from a new batch, whereas all other tests were conducted using catalyst from the first batch.

Results from two slurry bed reactor tests with the 100Fe/3Cu/0.2K catalyst are also included in Table V.1-5 to illustrate effect of reactor type on activity and hydrocarbon product selectivity. The slurry bed operation gave better selectivity (less CH₄ and C₂-C₄ hydrocarbons) in comparison to fixed bed reactor tests, with both H₂ (Runs FB-0029 vs SB-2878) and CO (Runs FA-2967 vs SA-3657) activated catalysts, whereas the catalyst activity and stability were better in fixed bed reactor tests. During the run SA-3657, initial selectivity at 44h on stream, was inferior to that obtained in the fixed bed run FA-2967, however it improved with time on stream (see Table V.2-7, Section V.2.3) even though the catalyst had partially deactivated. Hydrocarbon distribution at 91h on stream (SV=4 NI/g-cat.h) had less methane and C₂-C₄ hydrocarbons, in comparison to the run FA-2967 in a fixed bed reactor.

V.1.7. Activation Studies with the 100Fe / 3Cu / 0.5K Catalyst

This catalyst was evaluated in several runs : FB-3368 (Promoter Effect Research - Section V.2.2), FB-2438, FA-2518 and SB-2168 (Process Evaluation Research - Sections VI.2.1 and VI.4.1) using different activation procedures. Figure V.1-11 shows catalyst activity as a

Table V 1-5. Effect of reduction procedure on catalyst activity and selectivity (100Fe/3Cm/0.2K)^a

Run Designation	FD-0029	FD-3087	FD-2957	FA-2967	SA-3057	SA-3057	SB-2878 ^b	FD-0029 ^b
Reduction Conditions	H ₂ , 8h 220°C	H ₂ , 8h 250°C	H ₂ , 8h 280°C	CO, 24h 280°C	CO, 8h 280°C	CO, 8h 280°C	H ₂ , 8h 230°C	H ₂ 220°C
Time on Stream (h)	72	73	75	73	44	91	70	380
Temperature, H ₂ /CO	250, 1	250, 1	250, 1	250, 1	250, 1	250, 1	280, 0.7	280, 0.7
CO Conversion (%)	89.3	81.1	61.2	88.0	93.9	47.6	85.3	96.2
H ₂ +CO Conversion (%)	70.0	65.2	48.0	70.2	83.0	40.7	77.2	89.7
r _{H₂} /r _{CO}	.47	.49	.54	.41	.45	.36	.49	.40
HC Selectivities (wt.%)								
C ₂ H ₄	10.7	14.2	14.0	7.1	9.3	4.6	10.4	13.4
C ₂ -C ₄	32.5	30.9	45.2	25.8	35.9	22.3	24.1	32.2
C ₅ -C ₁₁	37.0	39.4	30.9	22.7	39.0	28.0	39.3	42.2
C ₁₂ +	13.8	6.5	3.9	44.4	15.8	45.1	26.3	12.2
Olefin Selectivity (wt.%) ^c								
C ₂ -C ₄	52	65	75	69	51	75	54	61
C ₅ -C ₁₁	58	58	63	56	55	74	56	64

^aAll tests were made at 200 psig and SV = 2 ml/g-cat.h

^bCatalyst from the second batch was used in these runs

^c100% Olefin/(Olefin+Paraffin)

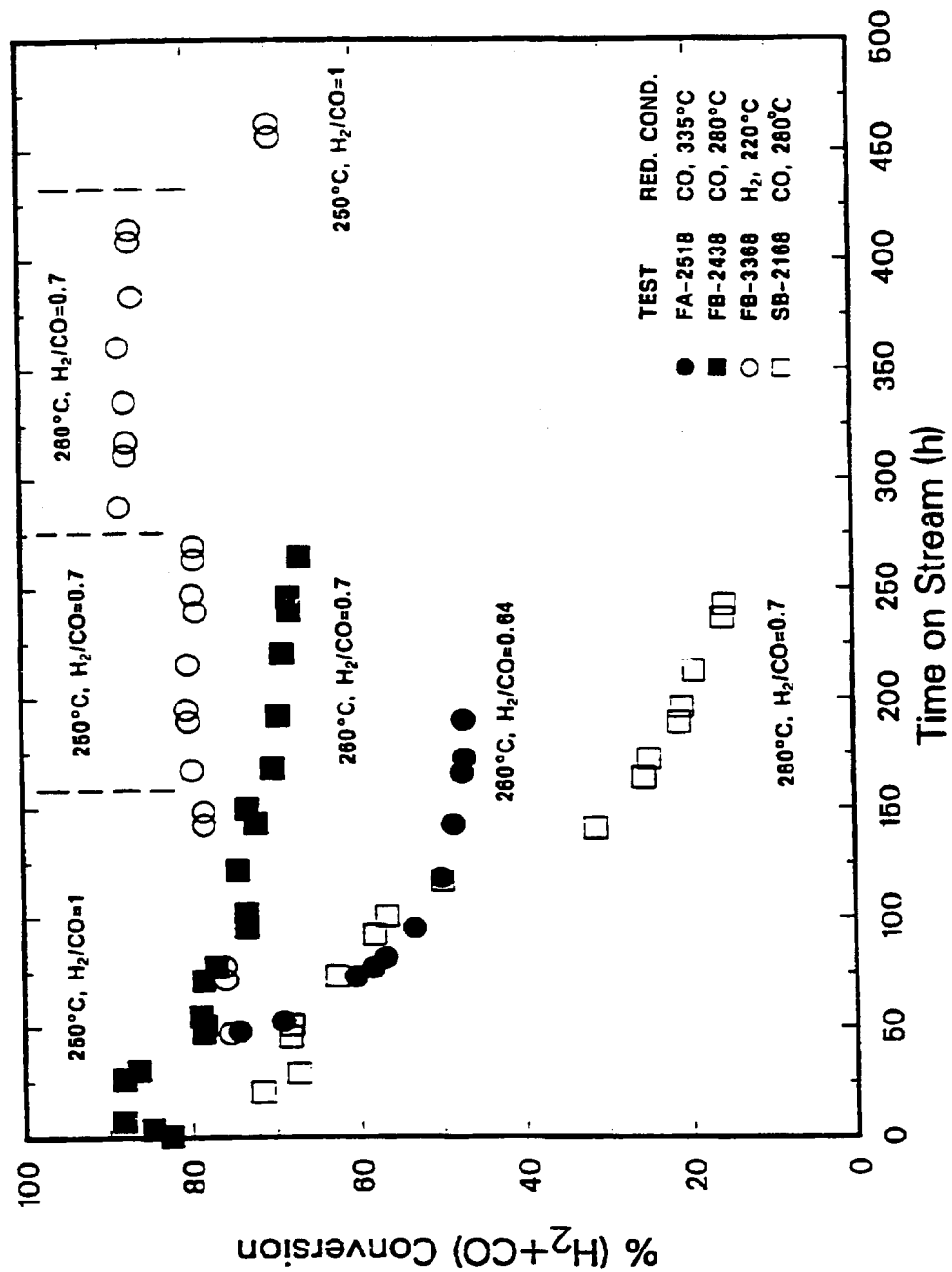


Figure V.1-11. Effect of activation conditions on activity and stability of the 100 Fe/3 Cu/0.5 K catalyst

function of time on stream. The reduction with H_2 at $220^\circ C$ gave high activity and excellent stability over a long period of time, whereas the CO activated catalyst had high initial activity but it deactivated with time on stream. The rate of deactivation is a function of activation temperature and duration. In the slurry bed reactor test (Run SB-2168) the catalyst was accidentally exposed to a mixture of CO and helium at $260^\circ C$ for about 27h following the CO activation at $280^\circ C$ for 12h, which might have accelerated its deactivation. The catalyst activated with CO at $335^\circ C$ for 24h (optimal Pichler's activation discussed in Section V.1.4) also deactivated rather rapidly during synthesis.

Hydrocarbon selectivities obtained during these four tests are shown in Table V.1-6. Similar trends were observed as in tests with the 100Fe/3Cu/0.2K catalyst, i.e., (1) H_2 reduced catalyst favored production of lower molecular weight products (FB-3368 vs. FB-2438) and (2) less methane and gaseous hydrocarbons were produced in a slurry reactor than in a fixed bed reactor (SB-2168 vs. FB-2438).

Pichler's activation procedure (FA-2518) produced more methane than the H_2 reduced catalyst, but the total fraction of gaseous hydrocarbons (C_1-C_4) was lower with the CO activated catalyst.

V.1.8. Summary

On the basis of tests with several precipitated catalysts (100 Fe/3 Cu/0.2 K or 0.5 K and 100 Fe/0.3 Cu/0.5 K) the following observations regarding effects of activation parameters and/or reactor type (slurry vs. fixed bed reactor) on catalyst activity and selectivity during Fischer-Tropsch synthesis can be made.

- (1) Activation parameters (temperature, duration, pressure and the nature of reducing gas) have strong influence on catalyst activity, selectivity and stability for the Fischer-Tropsch synthesis reaction.
- (2) Catalysts activated with CO were initially more active than catalysts activated with H_2 , however the activity of CO activated catalysts declined with time while the activity of H_2 activated catalysts increased or remained constant. The activity of the H_2 reduced catalysts can be improved by using lower reduction temperatures.
- (3) The CO activated catalysts produced less methane and other gaseous hydrocarbons than H_2 reduced catalysts in fixed bed reactor studies.
- (4) Slurry bed operation gives better selectivity (less methane and gaseous hydrocarbons) than the fixed bed under the same process conditions. Also, the effect of reducing gas (H_2

Table V.1-6. Effect of reduction procedure on catalyst activity and selectivity (100Fe/3Cu/.5K)^a

Run Designation	FB-3368	FB-2438	FA-2518	SH-2168
Reduction Conditions	H ₂ , 8h 220°C	CO, 12h 280°C	CO, 24h 335°C	CO, 12h 280°C
Time on Stream (h)	350	143	77	46
Temperature, H ₂ /CO	260, 0.7	260, 0.7	260, 0.65	260, 0.7
CO Conversion (%)	92.3	76.5	57.6	72.7
H ₂ +CO Conversion (%)	87.0	72.1	57.5	68.3
<i>t_{CO2}/t_{CO}</i>	.49	.40	.49	.49
HC Selectivities (wt.%)				
CH ₄	0.0	7.2	9.9	3.8
C ₂ -C ₄	30.80	27.0	26.4	15.1
C ₅ -C ₁₁	40.0	37.2	27.8	20.3
C ₁₂ +	20.2	28.6	35.9	60.7
Olefin Selectivity (wt.%) ^b				
C ₂ -C ₄	77	72	77	80
C ₅ -C ₁₁	70	76	72	82

^aall tests were made at 200 psig and SV=2 NL/g-cath

^b100*Olefin/(Olefin+Paraffin)

vs. CO) on product selectivity seems to be less pronounced in slurry bed reactors, but additional tests are needed to confirm these trends. Activity maintenance is more difficult to achieve in slurry bed reactors due to problems associated with wax removal. Hydrocarbon selectivities in a stirred tank reactor test with the 100Fe/0.3Cu/0.5K catalyst, were similar regardless of the reducing gas employed (H_2 or CO).

- (5) The CO and syngas activations produce catalysts with high activity and good selectivity. However, these catalysts do not have good stability and their performance deteriorates with time on stream.
- (6) Detailed catalyst characterization studies are needed to help explain the observed differences in results following different activation procedures.