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TITLE: Development and Process Evaluation of Improved Fischer-Tropsch Slurry Catalysts

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OBJECTIVE: To develop a consistent technical data base for a variety of iron-based Fischer-Tropsch catalysts. This data base will allow comparisons of the performance between the new catalysts tested as well as with state-of-the-art catalyst compositions.

TECHNICAL APPROACH: Improved activity will be developed by investigating the role of promoters, binders/supports, and activation procedures on catalysts activity, selectivity, and stability. The best catalysts will be tested further to determine their long term stability and selectivity over a range of process conditions.

SIGNIFICANT ACCOMPLISHMENTS: Six catalysts with nominal compositions of 100 Fe/5 Cu/4.2 K with 0 to 100 parts SiO_2 or Al_2O_3 as a binder/support have been prepared and tested. The high potassium level favored high activity and selectivity towards high molecular weight products. Higher support levels decreased activity, but improved catalyst stability. Long term stability runs using selected unsupported, supported (8 and 24 parts SiO_2), and commercial (Ruhrchemie LP 33/81) catalysts were made in fixed bed or slurry reactors. Catalyst containing 24 parts SiO_2 was very stable and had good activity and selectivity. This catalyst was more active and stable than Ruhrchemie catalyst, with similar selectivity. A study of activation/reduction conditions (CO, H_2, and H_2/CO = 0.68 reductants, 250-310°C, 8 and 24 h duration, ambient and 1.48 MPa pressure) for unsupported, precipitated catalyst has been completed. CO reduced catalyst had higher initial activity and was more selective towards higher molecular weight products than H_2 reduced catalyst, although the activity of H_2 reduced catalyst was more stable. Two slurry runs were made to confirm results found in fixed bed studies of activation procedures. H_2 or CO reduced catalysts in slurry were found to behave similarly to those in fixed bed reactors.

PUBLICATIONS

Bukur, D. B., Lang, X., Rossin, J. A., Zimmerman, W. H., Rosynek, M. P., and Li, C., "Activation Studies with a Precipitated Iron Fischer-Tropsch Catalyst," *submitted to Ind. Eng. Chem. Res.* (1988).

Zimmerman, W. H., and Bukur, D. B., "On the Use of Approximate Velocity Profiles for Modeling Bubble Column Slurry Reactors," *submitted to Chem. Eng. Sci.* (1988).

Zimmerman, W. H., Rossin, J. A., and Bukur, D. B., "Effect of Particle Size on the Activity of a Fused Iron Fischer-Tropsch Catalyst," *submitted to Ind. Eng. Chem. Res.* (1988).

INTRODUCTION

The objective of this contract is to develop a consistent technical data base on the use of iron-based catalysts for the Fischer-Tropsch synthesis. This data base will allow the unambiguous comparison of the new catalysts developed during this project to each other and with the state-of-the-art catalyst compositions. A systematic study of the role of promoters, binders/supports, and activation procedures on the activity and selectivity of iron-based catalysts may lead to development of improved catalyst compositions. The most improved catalysts, based on activity and selectivity, will be more thoroughly tested in slurry reactors in order to investigate activity and selectivity behavior over a wide range of process conditions, evaluate catalyst stability, and obtain estimates of kinetic parameters.

PROMOTER EFFECT RESEARCH

The most common promoters for iron catalysts are copper and potassium. It is generally thought that copper serves only to promote the reduction of iron during activation, thus allowing lower activation temperatures and consequently, giving less sintering, greater surface areas, and increased activity. Potassium, on the other hand, acts as both structural and chemical promoter, and it affects the catalyst activity as well as the selectivity. Higher potassium concentrations give heavier products (increased hard wax selectivity) and more olefins in the hydrocarbon products. A systematic study of promoter concentrations on catalyst performance and properties will be conducted by varying the Cu and K levels independently. A pure precipitated iron catalyst, containing neither Cu nor K, provides an unpromoted comparison case. Several Fe/Cu (1 and 3 g of Cu per 100 g of Fe) and Fe/K (0.05-1.0 g of K per 100 g Fe) catalysts were synthesized to study the effect of individual promoters. Finally, eight Fe/Cu/K precipitated catalysts were prepared and tested in a fixed bed reactor. The status of this task is summarized in Figure 1. Sixteen fixed bed reactor tests have been completed and four additional tests are planned. Results from catalytic tests

454

with eight different catalyst compositions were reported at the last year's meeting (Bukur *et al*, 1987). Results from recently completed tests and from the new tests will be discussed at the next Contractors' Review Meeting.

SLURRY REACTOR KINETIC AND PROCESS EVALUATION STUDIES

Reliable kinetic data for slurry phase Fischer-Tropsch synthesis are needed for comparisons of catalyst performance, rational reactor design, and preliminary economic evaluations. The kinetic parameters for the rate of syngas disappearance and the water-gas-shift reaction have been determined from three tests in slurry reactors. The objectives and the status of the slurry reactor kinetic studies are listed in Figure 2.

In four out of eight slurry reactor runs a relatively rapid catalyst deactivation was observed. The loss in activity was accelerated by withdrawal of accumulated wax (slurry) from the reactor and by frequent changes in process conditions. Development of efficient procedures for wax withdrawal and/or separation of catalyst from the wax is essential for demonstrating viability of the slurry phase Fischer-Tropsch technology. The overall objectives and status of the slurry reactor kinetic studies are listed in Figure 2.

ACTIVATION/REDUCTION STUDIES

The activation/reduction procedure followed can have a significant effect on catalyst activity, selectivity, and stability. Eleven different sets of reduction conditions were tested in fixed bed reactors to evaluate the influence of the reduction parameters (reductant type, temperature, and duration) on subsequent catalyst performance. All activations were conducted at a space velocity of 4.5 Nl/g-Fe$\cdot h$ and atmospheric pressure, except in test A-3517 where the activation was conducted at 1.48 MPa (200 psig). A precipitated, unsupported 100 Fe/3 Cu/0.2 K (3 parts Cu and 0.2 parts K per 100 parts Fe, by weight) catalyst was used in all tests, which was first calcined in air at 300°C for 5 h, crushed and sized to 30/60 mesh, and diluted 1:8 by volume with glass

beads of the same mesh size range. The catalysts were tested at a fixed set of operating conditions (250°C, 1.48 MPa, 2 Nl/g-cat·h, (H_2/CO) = 1) for up to 120 h on stream, during which time two mass balances were made at approximately 40 and 90 h on stream. Conversions were measured regularly throughout the entire run. Test identifications and conditions are shown in Table 1.

Results from tests following activations with CO and H_2 at atmospheric pressure were described at the last Contractors' Meeting (Bukur et al., 1987). These tests have shown that the CO activation at 280°C for 24 h gave the best results in terms of catalyst activity, stability, and selectivity.

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 high pressure. The activation pressure did not have a strong effect on hydrocarbon product selectivity.

One test (B-3377) was conducted using a CO rich synthesis gas (H_2/CO = 0.68), at 280°C for 24 h, for activation. Results from this test are shown together with results obtained from catalytic tests following H_2 and CO activations in Figures 3 and 4.

The activities of the catalyst activated with CO, H_2 and syngas (H_2/CO = 0.68) at atmospheric pressure and 280°C for 24 h are compared in Figure 3. The CO activated catalyst was more active and stable than the catalyst activated with the CO rich syngas, whereas the H_2 reduced catalyst showed high stability but a very low activity, about 30% (H_2 + CO) conversion throughout the run. The change in activity with time on stream for the H_2 reduced catalyst 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.

A comparison of the effect of reductant (gas) type on catalyst selectivity is given in Figure 4 for the same four tests shown in Figure 3. The weight percent hydrocarbon distribution obtained in tests following the CO and syngas activations were similar, with some minor shifting of products between the C_5 - C_{11} and C_{12} + product ranges. The catalyst reduced with H_2 favored the formation of methane and C_2 - C_4 products, with correspondingly lower weight percents of the higher molecular weight products (C_5+). The (1 + 2) -olefins/n-paraffin ratios were higher for the catalyst activated with synthesis gas, compared to the catalyst activated with either H_2 or CO, particularly the CO activated catalyst. These ratios are somewhat enhanced by the low conversions obtained in tests with the synthesis gas or H_2 (280°C, 24 h) activated catalyst, which may be seen by comparing olefin selectivities from tests A-2967 and A-3237 at approximately equal (H_2 + CO) conversions. In this case the olefin selectivity of the H_2 activated catalyst is only slightly greater than that of the CO activated catalyst.

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.

The products of Fischer-Tropsch synthesis often 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 or more 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. 5, for the data from test A-3077, balance 2. The two-α model of Huff and Satterfield was found to accurately represent these data:

$$x_n = \beta(1-\alpha_I) \alpha_I^{n-1} + (1-\beta) (1-\alpha_{II}) \alpha_{II}^{n-1} \tag{1}$$

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_I and α_{II} 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).

Slurry Bed Reactor Tests - Activation Studies

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 H_2 for 24 h (test SB-0458) or in CO for 16 h (test SA-0468) both at 280°C, 0.79 MPa and $3Nl/g$-cat·h. These two activations correspond to the worst and nearly the best set of conditions, respectively, based on our fixed bed reactor tests. Following activation, the catalyst was tested at 250°C, 1.48 MPa, $2Nl/g$-cat·h and $H_2/CO = 1.0$ (the same process conditions used in the fixed bed reactor tests). The (H_2+CO) conversions at about 40 h on stream were 24.8 and 74.8% for the H_2 and CO reduced catalysts, respectively. These conversions are similar to those obtained in fixed bed tests when similar activation procedures were employed (Table 2). 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

458

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 (Table 2). 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 (see Table 2).

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.

During the process variable studies in the test SB-0458, the catalyst was tested under conditions similar to that employed in Mobil's study in a bubble column slurry reactor (Kuo et al., 1985). Comparison of catalyst performance between our catalyst and Mobil's catalyst I-B in high wax mode of operation is shown in Table 3. Hydrocarbon product selectivities of the two catalyst are very similar, but the activity of our catalyst was lower. However, the activity of our catalysts can be significantly improved by using a lower activation temperature and/or shorter duration. Whether this might have some adverse effect on catalyst stability and selectivity would need to be determined. In any case, the performance of this catalyst, in terms of stability and selectivity, was comparable to that of the best catalyst developed by Mobil.

Major conclusions from activation/reduction studies are summarized in Figure 6.

BINDER/SUPPORT RESEARCH

Supported catalyst systems with high support-to-metal ratios have not been overly effective in yielding good Fischer-Tropsch synthesis performance. In the slurry phase process, supported catalysts reduce the bulk concentration of metal and thus may hinder mass transfer of gas to liquid as solids loadings are increased to maintain metal concentrations. On the other hand, supported systems may actually increase the concentration of active metal sites by maintaining higher metal

dispersions. The nature of the support is also important, since acidic sites on the support can render basic promoters like potassium ineffective, preventing interaction between promoter and metal. Previous work at SASOL (Dry, 1981) in fixed bed reactors, examined the effects of promoters and supports on the performance of Ruhrchemie-type precipitated Fe catalysts. In one set of experiments, a series of Fe/Cu/K_2O precipitates was prepared using Cr_2O_3, MgO, Al_2O_3 or ZnO in place of the silica. None of these catalysts was as active as the standard SiO_2-containing material. An unsupported composition was also less active. Compositions containing both SiO_2 and a second support material also showed lower performance. Of all the supports, small amounts of added Al_2O_3 resulted in the lowest wax selectivity without excessive deactivation. This concept could be used to control selectivity to some extent.

A brief examination of promoted iron catalysts containing silica or alumina as binder/support has been made in our laboratory. Compositions of catalysts tested and current status of this research are shown in Figure 7. Selected results from tests in fixed and slurry bed reactors will be briefly described.

Initial screening tests

In this type of tests a catalyst was evaluated at different process conditions (temperature, space velocity or pressure) using synthesis feed gas with H_2:CO molar ratio of about 1 to obtain information on its activity and selectivity. These tests lasted between 140 and 200 hours. The unsupported precipitated catalyst with composition 100Fe/5Cu/4.2K was used as a base case. The effect of silica and alumina concentrations on catalytic performance was studied with catalysts containing 8-100 g of SiO_2 per 100 g of Fe or 8 and 25 g of Al_2O_3 per 100 g of Fe, respectively, while keeping the promoter concentrations constant. A comparison of activities of the SiO_2 and Al_2O_3 containing catalysts, the Ruhrchemie LP 33/81 catalyst and an unsupported 100Fe/5Cu/4.2K catalyst is shown in Figure 8 for tests conducted at 235°C and 1.48 MPa.

Catalyst activity, as measured by (H_2+CO) conversion, decreases as the binder concentration increases. The 8 parts SiO_2 and the unsupported catalysts had the highest activities, and on a per Fe basis, gave essentially the same (H_2+CO) conversions. The 8 parts Al_2O_3 catalyst also had high activity. The similarity in conversions for the unsupported and 8 parts supported catalysts show that the high activity is not due to surface areas alone. The very high potassium concentrations are responsible for the increase in catalyst activity over previous unsupported catalyst tests. While the BET surface areas of the SiO_2-containing catalysts increase from 94, 148, and 250 m^2/g at 8, 25, and 100 parts SiO_2/100 parts Fe, the (H_2+CO) conversions decrease at all conditions tested. The unsupported catalyst has a BET surface area of 38 m^2/g. The increased BET surface areas are caused by the addition of high surface area binder and do not necessarily reflect a large increased active metal surface area in the presence of a binder. Our measurements by H_2 temperature programmed desorption showed that the fractional metal exposures of CO reduced, silica-containing catalysts are the same as for unsupported with the same promoter concentrations, (~2.3%), thus crystallite size is constant. When alumina is added to the catalyst, the exposure roughly doubles. Egiebor and Cooper (1985) measured the BET surface areas of both fresh and used silica supported catalysts, with compositions of 100 Fe/4.2 Cu/6.7 K with 21, 50, and 73 parts SiO_2. Prior to use, these catalysts had surface areas of 151, 252, and 275 m^2/g, respectively. The authors attributed the decrease in surface areas to carbon deposition on the catalyst during synthesis. Wax accumulation in catalyst pores may also contribute to low used catalyst surface areas. The high surface areas of fresh catalyst may not be representative of the actual area of the activated catalyst. The high surface area catalysts have smaller pore diameters increasing intraparticle diffusional limitations. Also, the catalysts with high binder concentrations show stronger resistance to reduction and may not be fully activated.

The increase in silica concentration improves catalyst stability as can be seen from Table 4. In this table values of (H_2+CO) conversion obtained at the baseline conditions in the early part of

the test (40-49h) and near the end of the test (143-169h on stream) are listed. Between these two periods of time the process conditions were varied. Catalysts containing 25 and 100 parts of SiO_2 (per 100 parts of Fe) had a rather small loss in activity, whereas the catalysts with 8 parts or less of a binder (SiO_2 or Al_2O_3) had a more significant loss in activity. Alumina containing catalysts were less stable than the corresponding silica containing catalysts. Hydrocarbon selectivity of the catalyst with 8 parts SiO_2/100 parts of Fe was better than (low methane and C_2-C_4 hydrocarbons) or comparable to the selectivities of all other supported catalysts, Ruhrchemie LP33/81, and unsupported 100 Fe/5Cu/4.2 K catalyst. This catalyst is also one of the most active of all the catalysts tested in our laboratory and in comparison to the state-of-the-art catalysts from literature (Table 5). There were no significant trends in hydrocarbon selectivity with binder concentration.

Long term stability tests

Two of the three silica containing catalysts synthesized at TAMU (8 and 24 parts of SiO_2) and the Ruhrchemie catalyst were evaluated at a fixed set of process conditions over relatively long periods of time on stream (250-480 hours) to determine their activity and selectivity maintenance, and the rate of deactivation. Activity and stability comparison is shown in Figure 9, whereas the hydrocarbon selectivities are shown in Table 6.

Initial activity of catalyst containing 8 parts of SiO_2 was much higher than that of the other two catalysts, but after 120 hours on stream it declined rapidly with time on stream. Catalyst containing 24 parts of SiO_2 was remarkably stable over 480 hours on stream. Its activity declined by 5.6% only over a 400 hour period and was about 20% higher than that of the commercial Ruhrchemie catalyst. As can be seen from Table 6, hydrocarbon product distributions obtained in tests with the Ruhrchemie catalyst, and with the catalyst containing 24 parts of SiO_2 are very similar with either H_2/CO = 1.0 or H_2/CO = 0.67 synthesis gas feed ratios. Catalyst containing 8 parts of SiO_2 produced less light hydrocarbons but its stability needs to be improved.

The Ruhrchemie and the catalyst containing 24 parts of SiO_2 were also tested in a stirred tank slurry reactor and these results are shown in Figures 10, 11 and Table 6. Their activities were about 20% lower than those obtained in the fixed bed reactor, but hydrocarbon product distributions in the two reactor systems were similar. Catalyst stability was very good in both cases, and both hydrocarbon and olefin selectivities of the two catalysts were similar. A slight shift towards lighter hydrocarbons with time on stream was observed in tests with both catalysts (Fig. 11). Major conclusions from binder/support research studies are summarized in Figure 12.

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Egiebor, N. O., and W. C. Cooper, "Fischer-Tropsch Synthesis on a Precipitated Iron Catalyst: Influence of Silica Support on Product Selectivities," *Can. J. Chem. Eng.*, 63, 81-85 (1985).

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Figure 1. Promoter effect research

- Fe – Pure precipitated iron (base case)

- Fe/Cu (100 : 1 and 3 / weight basis) – 2 catalysts

- Fe/K (100 : 0.05 – 1.0) – 4 catalysts

- Fe/Cu/K (100 : 0.3 – 3.0 : 0.05 – 0.8) – 8 catalysts

    STATUS: 16 fixed bed reactor tests completed,
    additional four are planned.

Figure 2. Kinetic and process evaluation studies

These studies will provide:

- Information on the effect of process conditions on syngas conversion and product selectivity

- An assessment of the effect of process conditions on catalyst stability and deactivation

- Data for input into a slurry bubble column reactor model

- Information for economic assessments

- An unambiguous comparison of the new catalysts developed both with each other and with standard compositions

- Kinetic parameters for the rate of syngas consumption and the water-gas shift reaction

STATUS:

- 8 slurry bed reactor tests completed

- Substantial loss in activity observed in 4 tests

- Wax withdrawal accelerates deactivation

- Kinetic parameters estimated for 3 catalysts

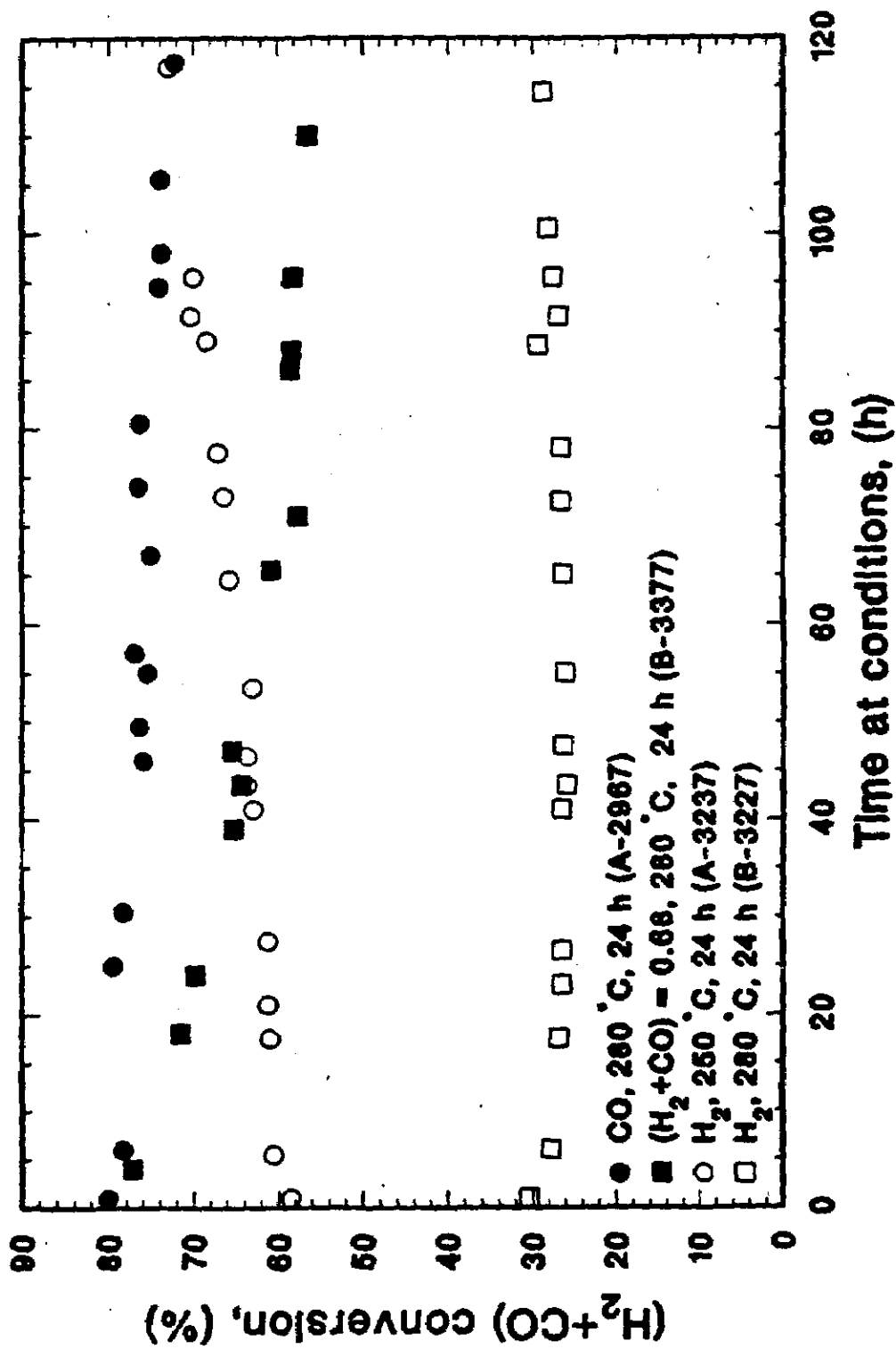- No additional experimental work is planned

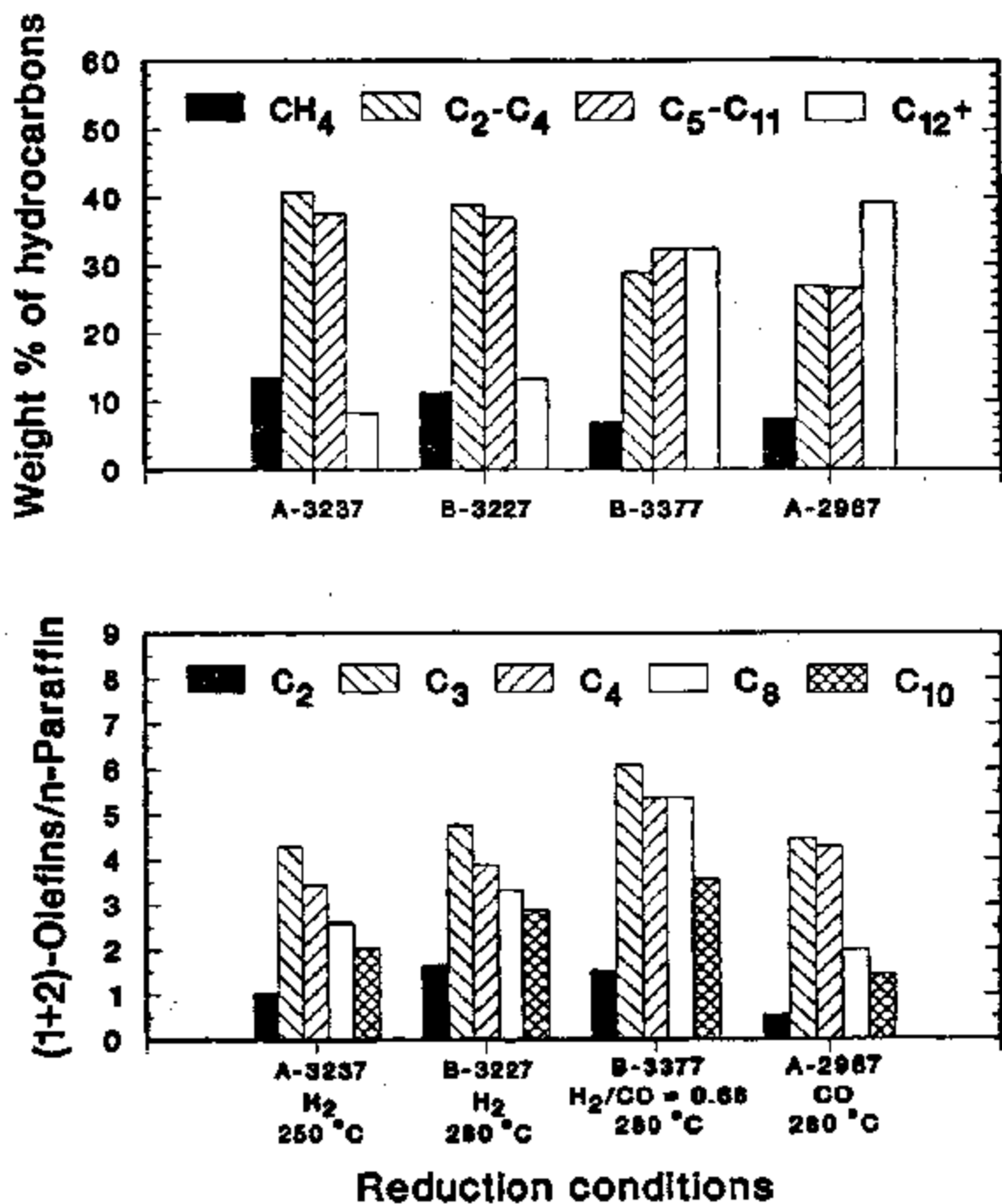Figure 3. Comparison of activity and stability for selected activation procedures

Figure 4. Comparison of hydrocarbon distribution and olefin selectivity for selected activation procedures
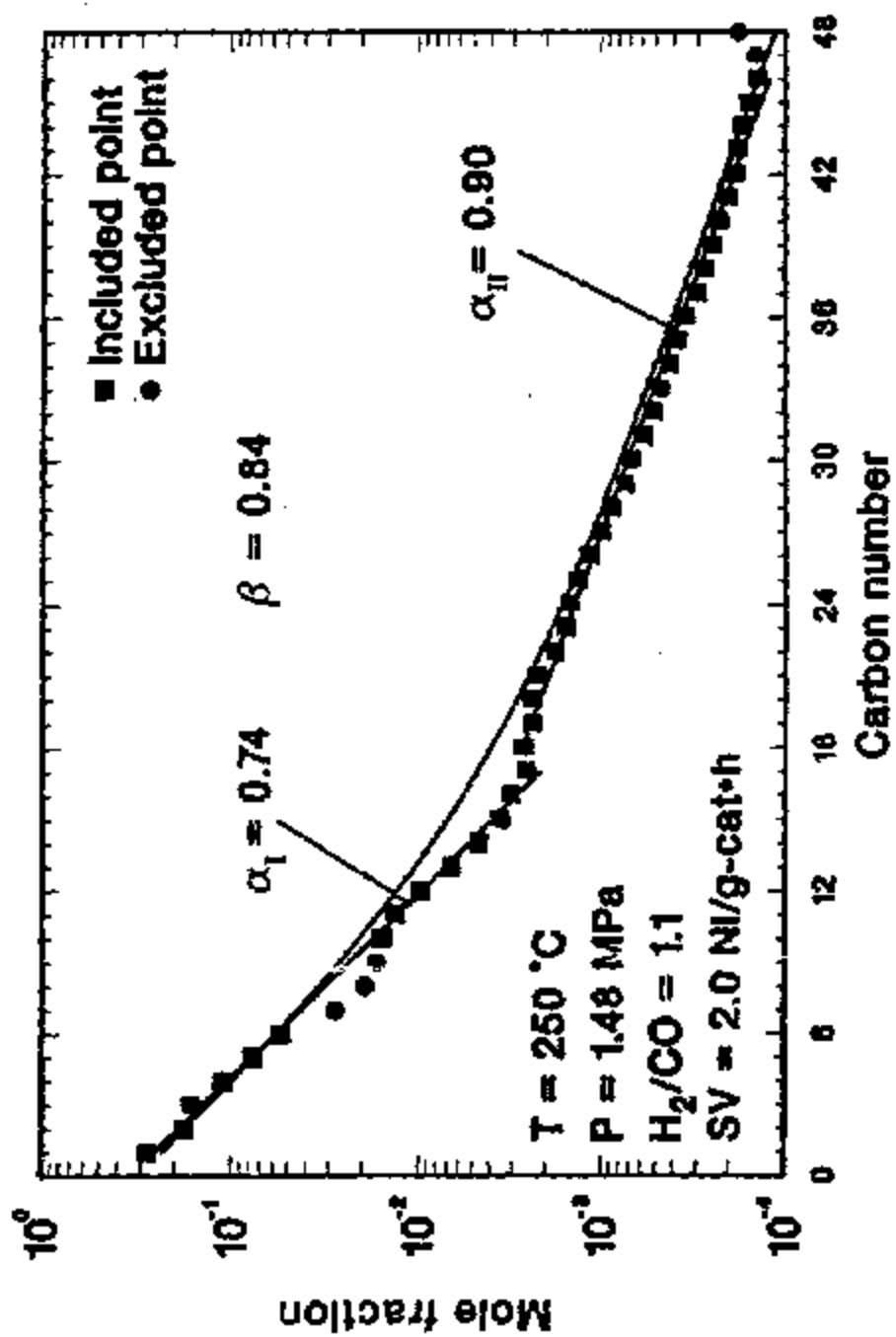
Figure 5. Anderson–Schulz–Flory plot for the products obtained in test A–3077 at 92 h on stream

Figure 6. Activation/reduction research conclusions

- Activation parameters (temperature, duration, pressure and the nature of reducing gas) have a strong effect on catalyst activity, selectivity and stability for the Fischer–Tropsch synthesis reaction.

- 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 (fixed bed and slurry reactor tests with two different catalysts).

- The CO activated catalyst produced less methane and other light hydrocarbons than the H_2 activated catalyst (fixed bed tests with 100Fe/3Cu/0.2K catalyst).

- Hydrocarbon selectivities in a stirred tank slurry reactor test with the 100Fe/0.3Cu/0.5K catalyst, were similar regardless of the reducing gas employed (H_2 or CO). (Reactor type or catalyst composition effect?)

- Detailed characterization studies are needed to help explain the observed differences in results following different activation procedures.

- H_2 reduced 100Fe/0.3Cu/0.5K catalyst displayed no loss in activity in a slurry reactor over 460h with variable process conditions. Its hydrocarbon selectivity was very similar to Mobil's I–B catalyst in a high wax mode of operation.

Figure 7. Binder/support research

<u>Catalysts</u>

- 100Fe/5Cu/4.2K – BASE CASE

<u>Silica containing</u>

- 100Fe/5Cu/4.2K/8SiO$_2$

- 100Fe/5Cu/4.2K/24SiO$_2$

- 100Fe/5Cu/4.2K/100SiO$_2$

- Ruhrchemie LP 33/81 (100Fe/4.3Cu/4.2K/25SiO$_2$)

<u>Alumina containing</u>

- 100Fe/5Cu/4.2K/8Al$_2$O$_3$

- 100Fe/5Cu/4.2K/20Al$_2$O$_3$

<u>STATUS</u>:

- 10 initial screening fixed bed reactor tests completed

- Long term stability tests: 3 in FBR, 2 in STSR

- No additional tests are planned

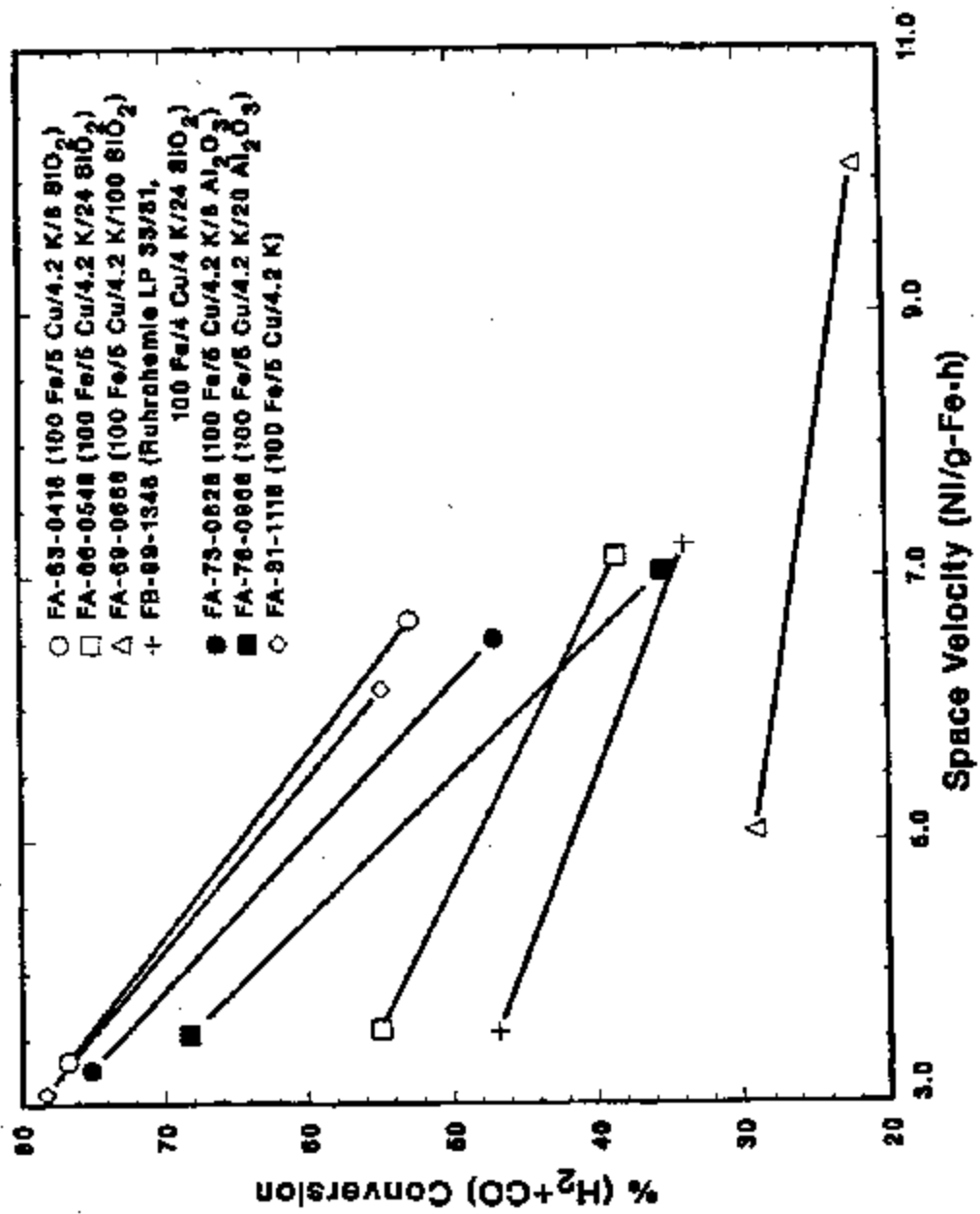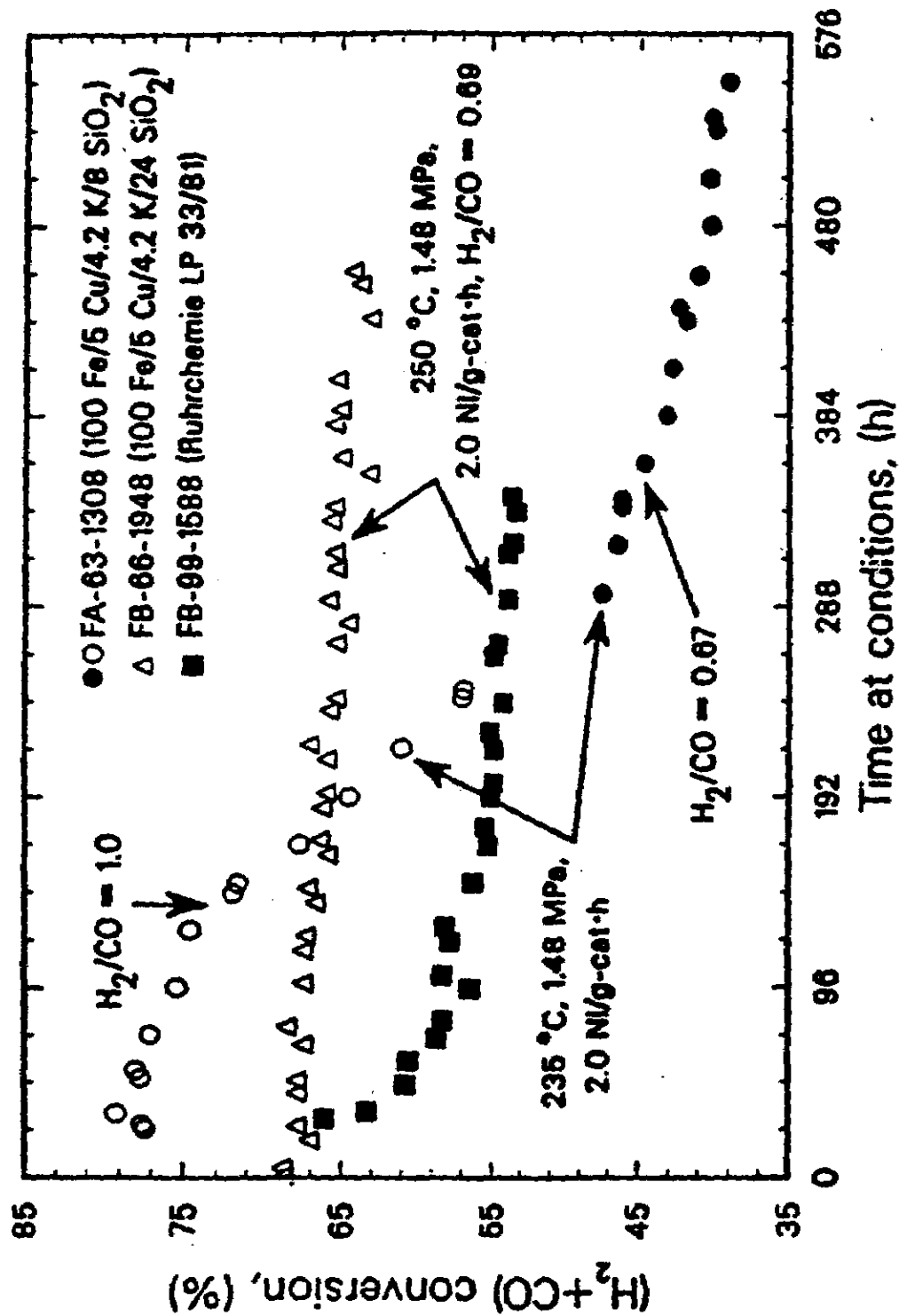Figure 8. Comparison of catalyst activity (235°C, 1.48MPa, $H_2/CO = 1.0$)

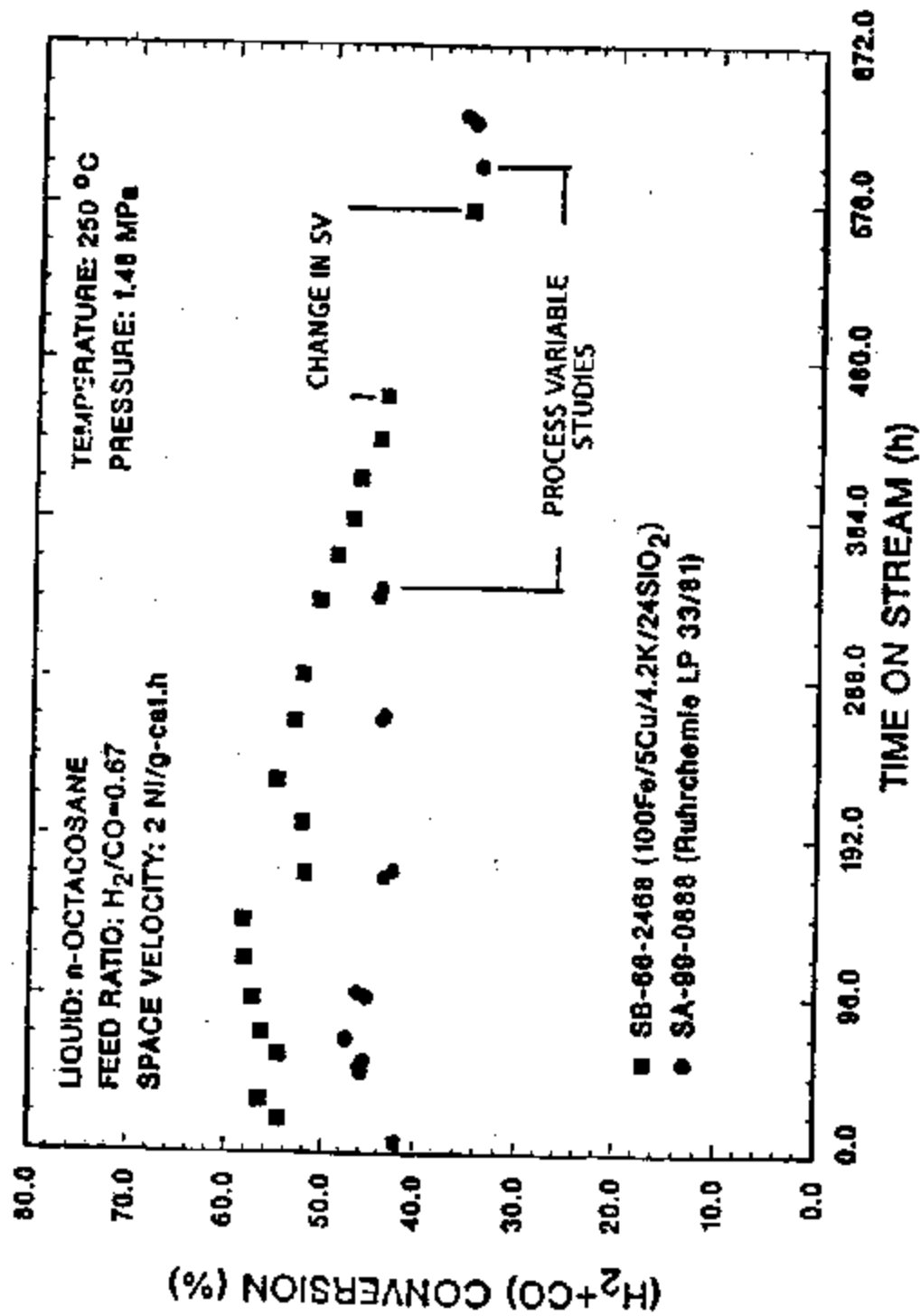Figure 9. Comparison of activity and stability of iron/silica catalysts (Fixed bed tests)

Figure 10. Comparison of catalyst activity and stability (Slurry-bed reactor tests)
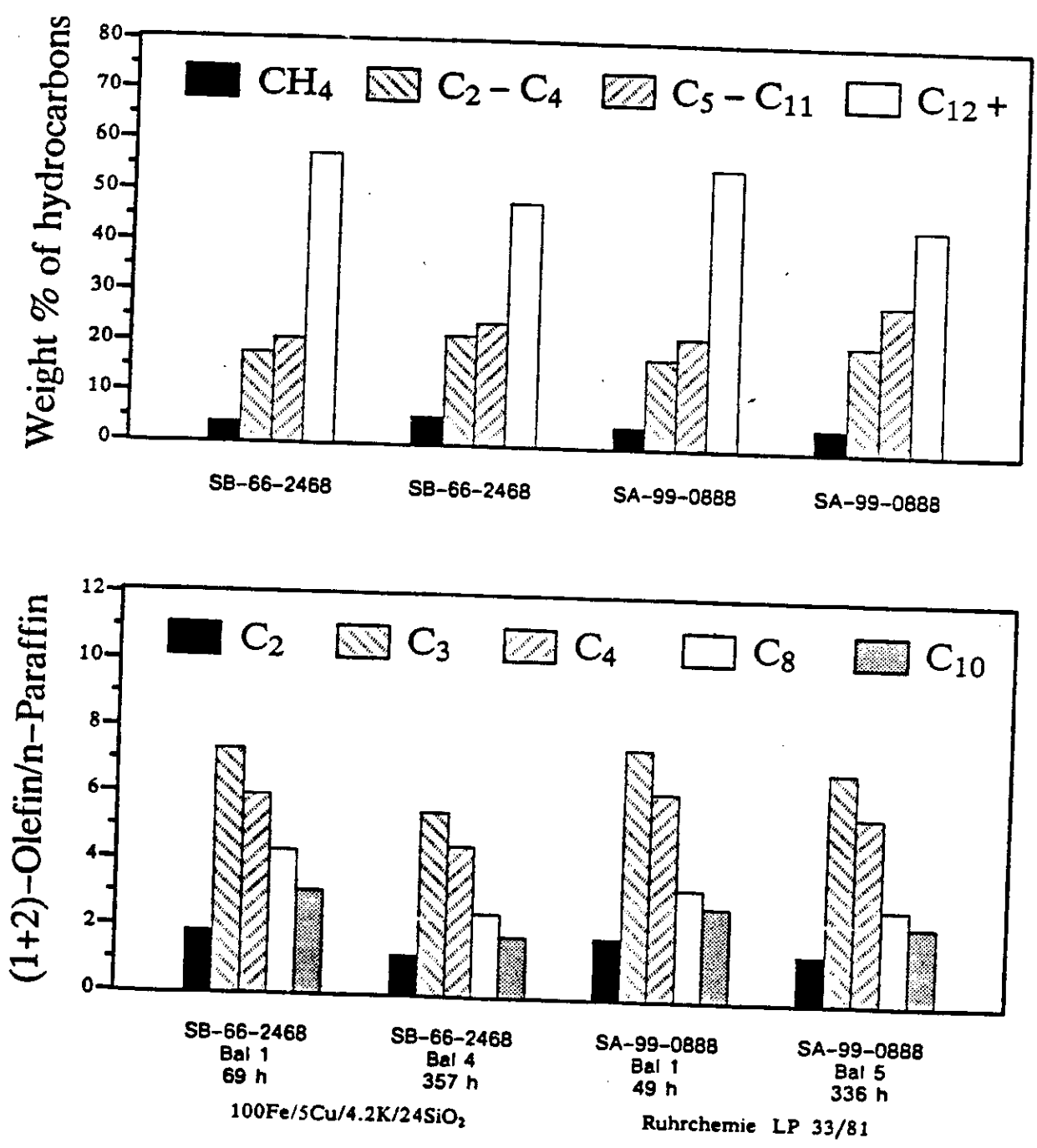
Figure 11. Comparison of selectivity of 100Fe/5Cu/4.2K/24SiO$_2$ and Ruhrchemie LP 33/81 catalysts (250 °C, 1.48 MPa; 2 Nl/g-cat.h, H$_2$/CO =0.67)

Figure 12. Binder/support research conclusions

- Activity of silica (or alumina) containing catalysts decreases with the increasing concentration of binder.

- The addition of binder improves catalyst's stability (lower rate of deactivation).

- There is no simple correlation between the hydrocarbon product distribution and the concentration of binder (8 – 100 g of SiO_2 per 100 g of Fe).

- Catalyst with composition $100Fe/5Cu/4.2K/8SiO_2$ had displayed high activity and excellent hydrocarbon selectivity (low CH_4 and high C_5^+ content), but its stability needs to be improved.

- Catalyst with composition $100Fe/5Cu/4.2K/24SiO_2$ had displayed about 20% higher activity than the Ruhrchemie LP 33/81 catalyst. Both catalysts had excellent stability and their product distributions were similar.

- Activities of these two catalysts were about 20% lower in a STSR than in a FBR, but hydrocarbon selectivities were similar (no effect of reactor type on hydrocarbon product distribution).

Table 1. Activation conditions and test designations

TEST	T ($^{\circ}$C)	P (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

Table 2. Activation studies – comparative catalyst performance

Catalyst	Fixed Bed 100Fe/3Cu/0.2K		Stirred tank slurry reactor 100Fe/0.3Cu/0.5K	
Run Designation	FB-3227	FA-2967	SB-0458	SA-0468
Reductant	H_2	CO	H_2	CO
Time on stream,h	71	73	45	41
CO + H_2-conv. (%)	26.0	76.2	24.8	74.8
Hydrocarbon Distribution				
C_1	10.7	7.1	4.6	6.9
$C_2- C_4$	39.3	25.8	25.0	22.3
$C_5- C_{11}$	39.6	22.7	22.7	20.4
C_{12}^+	10.4	44.4	47.7	50.4

Reduction conditions: 280°C, 24h (16h for SA-0468)
Process conditions: 250°C, 1.48 MPa, 2 Nl/g-cat.h, H_2/CO=1.0

Table 3. Comparative catalyst performance

Catalyst Reduction	TAMU – STSR 100Fe/.3Cu/0.5K H_2, 280°C, 24h		MOBIL – BCSR Fe/Cu/K_2O H_2/CO=0.7, 280°C, 12h
Run Designation	SB–0458	SB–0458	CT 256–13
Temperature, °C	265	265	258
Pressure, atm	15	15	15
SV, Nl/g–Fe.h	3.1	1.6	2.4
H_2:CO ratio	0.70	0.72	0.67
CO + H_2 conv. (%)	51.2	70.8	82.2
Hydrocarbon Distribution			
C_1	3.3	3.2	2.7
C_2– C_4	13.4	11.4	11.1
C_5– C_{11}	21.0	20.4	18.1
C_{12}^+	62.3	65.0	68.1

STSR – Stirred tank slurry reactor
BCSR – Bubble column slurry reactor

Table 4. Stability comparison – before and after process variables studies

Catalyst	TOS (h)	% Conv. ($H_2 + CO$)	TOS (h)	% Conv. ($H_2 + CO$)
100Fe/5Cu/4.2K	48	78.3	148	47.2
100Fe/5Cu/4.2K/8SiO$_2$	49	76.7	169	44.8
100Fe/5Cu/4.2K/25SiO$_2$	40	55.0	145*	48.1*
100Fe/5Cu/4.2K/100SiO$_2$	41	29.1	143	25.7
100Fe/5Cu/4.2K/8Al$_2$O$_3$	48	75.1	144	42.9
100Fe/5Cu/4.2K/20Al$_2$O$_3$	48	68.3	144	31.5

Process conditions: 235 °C, 1.48 or *3 MPa, 2 or *4 Nl/g–cat.h, H_2/CO = 1.0

Table 5. Activity and selectivity of the 100Fe/5Cu/4.2K/8SiO$_2$ catalyst
(Test FA – 0418, H$_2$/CO = 1.10)

TOS (h)	49	72	96	121	145	169
Temperature, °C	235	235	250	220	235	235
Pressure, MPa	1.48	1.48	1.48	1.48	3.00	1.48
SV, Nl/g–cat.h	2.00	4.01	4.01	2.00	4.01	2.00
STY*	0.069	0.094	0.116	0.055	0.076	0.040
CO + H$_2$ conv. (%)	76.7	52.8	65.1	62.1	42.7	44.8
Hydrocarbon Distribution						
C$_1$	3.5	3.2	3.7	2.8	2.8	3.4
C$_2$– C$_4$	16.4	16.9	16.0	16.0	17.5	18.8
C$_5$– C$_{11}$	20.1	20.3	12.4	15.4	16.7	16.5
C$_{12}^+$	60.0	59.6	67.9	65.8	63.0	61.3

* Space Time Yield (STY) = mols (H$_2$ + CO)/g – cat.h

481

Table 6. Activity and selectivity comparison of SiO$_2$ containing catalysts during long term stability tests in fixed and slurry bed reactors

Catalyst/ Reactor Type	Process Conditions				TOS (h)	% Conv. (CO+H$_2$)	STY[a]	Yield (g-HC/Nm^3)	Weight % of Hydrocarbons			
	Pressure (atm)	Temp (°C)	SV (Nl/g-Fe.h)	H$_2$/CO feed					CH$_4$	C$_2$-C$_4$	C$_5$-C$_{11}$	C$_{12}$+
Ruhrchemie LP 33/81 fixed bed	15	250	3.6	0.69	71	56.6	.052	191	5.5	22.7	18.6	53.1
	"	"	"	"	360	53.2	.046	212	5.4	21.7	20.0	52.9
Ruhrchemie LP 33/81 slurry	"	"	"	0.67	94	46.1	.041	182	4.9	20.9	19.5	55.0
	"	"	"	"	336	44.1	.040	212	6.1	22.3	22.8	49.7
100 Fe/5 Cu/4.2 K/24 SiO$_2$ fixed bed	"	"	"	0.69	71	67.9	.061	183	6.7	21.9	21.5	50.9
	"	"	"	"	350	65.5	.050	184	8.2	24.5	24.1	45.2
100 Fe/5 Cu/4.2 K/24 SiO$_2$ slurry	"	"	"	0.69	69	56.1	.050	203	3.9	17.9	20.7	57.5
	"	"	"	"	357	49.3	.044	205	5.5	21.8	24.4	48.3
Ruhrchemie LP 33/81 fixed bed	"	"	"	0.98	526	56.0	.050	189	8.5	29.6	25.3	36.6
	"	"	"	"	623	53.5	.050	197	7.9	27.7	23.2	41.2
100 Fe/5 Cu/4.2 K/24 SiO$_2$ fixed bed	"	"	"	1.03	644	60.6	.054	182	8.0	29.3	24.9	27.8
	"	"	"	"	716	60.6	.054	178	8.0	29.0	24.8	38.2
100 Fe/5 Cu/4.2 K/8 SiO$_2$ fixed bed	"	275	3.2	1.03	48	77.9	.069	188	4.2	17.2	21.4	64.6
	"	"	"	"	240	58.9	.051	195	4.9	16.6	18.8	60.6

[a] STY in moles (H$_2$+CO) converted/g-cat.h

482