THE DEVELOPMENT OF PRECIPITATED IRON CATALYSTS WITH IMPROVED STABILITY

by

H. Abrevaya and P. P. Shah

UOP
Des Plaines, Illinois

DOE Contract No: DE-AC22-87PC-79812

U.S. Department of Energy
Indirect Liquefaction Contractors Review Meeting

Pittsburgh, Pennsylvania
November 6-8, 1990

THE DEVELOPMENT OF PRECIPITATED IRON CATALYSTS WITH IMPROVED STABILITY

by

H. Abrevaya and P. P. Shah

UOP
Des Plaines, Illinois

INTRODUCTION

Precipitated iron catalysts are expected to be used in the next generation of slurry reactors for the large-scale production of transportation fuels from synthesis gas. These reactors may operate at higher temperatures and lower H_2:CO ratios relative to the Sasol Arge reactor. The feasibility of iron catalysts has been demonstrated under relatively mild Arge-type conditions but not under the more severe slurry conditions.

The goal of this program is to identify the chemical principles governing the deactivation of precipitated iron catalysts during Fischer-Tropsch synthesis and to use these chemical principles in the design of catalysts suitable for slurry reactors. The work done under the three tasks that have already been completed is described below:

- Under Task 1, the existing fixed-bed catalyst testing plant was upgraded so that it has the capability of testing slurry-bed and Berty reactors.
- Under Task 2, MSCG-4, a precipitated iron catalyst, was acquired from Mobil corporation and tested in the fixed-bed reactor.
- Under Task 3, an iron catalyst preparation plant was constructed.

This paper covers testing an iron catalyst under Task 4. A new precipitated iron catalyst was prepared and tested in the slurry autoclave reactor at various conditions. This catalyst did not noticeably deactivate during 1,250 hours of testing. The test was extended to include performance evaluations at different conversion levels ranging from 35 to 88% at 265 and 275°C. The conversion levels were varied by changing the feed rate. The catalytic performance at different

conversion intervals was then integrated to approximately predict performance in a bubble column reactor. The run was shut down at the end of 1,996 hours because of a 24-hour-power outage. When the power was back on, the run was restarted from room temperature. Catalytic performance during the first 300 hours after the restart-up was monitored. Overall product distributions are being tabulated as analytical laboratory data are obtained.

TARGET PERFORMANCE

The target performance for this program is to achieve 88% CO + H_2 conversion with less than 1% deactivation per day for 1 month. Methane + ethane selectivity was orginally targeted for no more than 7% at a space velocity of at least 2 normal liters/hour-gram iron (nL/h-gFe) using a synthesis gas with H_2:CO ratio 0.5-1.0 in a slurry reactor. This target performance has been revised to a more stringent methane + ethane + ethylene selectivity of no more than 7%.

EXPERIMENTAL

Catalyst Preparation Procedure

Metal was not used as a material of construction for any wetted section in the iron catalyst preparation plant to avoid catalyst contamination that may occur through the dissolution of metallic components in contact with acidic solutions. The iron-containing solution and the base solution were kept in two separate 15 gallon feed tanks. The weights of these solutions were continuously measured during precipitation. The feed solutions were pumped separately to a precipitation reactor. The precipitate slurry was then pumped to a centrifugal filter, where the catalyst was washed with a separate water feed stream. The precipitate that passed through the centrifugal filter was collected in a drum and allowed to settle. The solution was later decanted, and the concentrated slurry was pumped back to the centrifugal filter, resulting in a high collection efficiency. The catalyst was finally dried, calcined, and crushed to 140-400 mesh-size range before being impregnated with additional components. This procedure was followed by a final calcination and an in situ reduction in the Fischer-Tropsch synthesis reactor.

Catalyst Testing Procedure

For the test, 95 g of calcined iron catalyst was loaded into a 1 L autoclave along with 380 g of C_{32} n-paraffin wax at 130°C. After the wax melted, the autoclave was sealed and pressure tested with N_2 at 25 atm. After a successful pressure test, the pressure was lowered to 14 atm, the stirring was initiated at 1,100 rpm, and the catalyst temperature was raised to 280°C in 3 hours under nitrogen flow. A thermocouple inserted in a thermowell inside the slurry was used for temperature control. The temperature control point was 3 cm above the bottom of the autoclave. After 280°C was achieved, the N_2 feed was cut out and synthesis gas with an H_2:CO molar ratio of 0.7:1 was introduced at 1.6×10^{-1} nm^3/h. After a 12-hour pretreatment, in situ, new test conditions were established, and the test was continued.

Two 0.5 μm filters (Mott Corporation, Farmington, CT) were placed at 6-5/8 in. from the bottom of the autoclave so that the liquid products could be drained periodically. During the first 420 hours, one of the filters was continuously back-flushed with 0.2 nL/h-gFe of N_2, and the other filter was used for draining the liquid products.

Although this procedure prevented the filter from plugging, it is more than likely that some catalyst was lost through the filter during the run period. The reported catalyst activities are based on the initial catalyst inventory.

Conversion and Selectivity Calculations

Argon was present in the synthesis gas feed at about 6% (by mole) and was used as an internal standard to determine conversions and the carbon atom selectivities of light hydrocarbons according to the following expressions:

$$\text{CO Conversion, \%} = \frac{(CO/Ar)_{feed} - (CO/Ar)_{product}}{(CO/Ar)_{feed}} \times 100$$

The CO + H_2 conversion was calculated in a similar manner:

$$C_n \text{ Selectivity, \%} = \frac{(C_n/Ar)_{product} \times n}{(CO/Ar)_{feed} - (CO/Ar)_{product}} \times \frac{100}{100 - CO_2 \text{ selectivity}} \times 100$$

where n is the number of carbon atoms in one molecule of hydrocarbon C_n. The calculation of selectivity of CO to CO_2 was done in the following manner:

$$CO_2 \text{ Selectivity, \%} = \frac{(CO_2/Ar)_{product}}{(CO/Ar)_{feed} - (CO/Ar)_{product}} \times 100$$

RESULTS AND DISCUSSION

The catalytic performance was stable at 83% CO + H_2 conversion between hours 452 and 1,250 at 275°C, 21 atm with a synthesis gas having a H_2 to CO ratio of 0.7 at a space velocity of 0.9 nL/h-gFe. The selectivities were 6.9% to methane, 2.5-3.0% to ethane, 5-6% to ethane + ethylene, 2.5-3.0% to ethanol, 48-55% to CO_2. The olefin to paraffin ratios were 5.5-6.0 at a carbon number of 3 and 4.0-4.5 at a carbon number of 4.

Effect of Conversion Level on Reaction Rate

Starting from 1,260 hours on-stream, the space velocity was gradually increased, typically every 48 hours, from 0.9 nL/h-gFe to 4.0 nL/h-gFe, by increasing the feed rate. At 1,510 hours on-stream, the temperature was lowered to 265°C, and the catalytic performance at different conversion levels was evaluated. At 1,640 hours on-stream, the space velocity was brought back to 1.2 nL/h-gFe and maintained there until 1,740 hours on-stream. These latter test conditions were identical to those between 280 and 420 hours on-stream. Further space velocity and temperature changes were made between 1,740 and 1,950 hours on-stream. The run was shutdown at 1,996 hours because of a power outage.

Catalyst performance after the shutdown is discussed in a later section.

The effect of reciprocal space velocity $(nL/h\text{-}gFe)^{-1}$ on the $CO + H_2$ conversion at 265°C and 275°C is illustrated in Figure 1. These data were later used to determine the effect of conversion level on reaction rate in Figure 2. Here, the reaction rate, is expressed as the product of space velocity amd $CO + H_2$ conversion. The results, which are summarized in Figure 2, indicate that the reaction rate is adversely affected by the conversion level at conversion levels greater than 50%. The decrease in reaction rate with an increase in conversion level is caused by the decrease in the partial pressure of the reactants, and possibly by the increase in the partial pressure of some of the reaction products. This effect, also, is likely to occur at lower conversions but to a lesser degree. However, insufficient data was available at low conversions to determine the relation of reaction rate with conversion at low conversions.

Catalytic Performance after Return to Early Test Conditions

The $CO + H_2$ conversion between 1,640 and 1,740 hours on-stream was about 70%, which is 2% higher than that observed between 280 and 420 hours on-stream under the same test conditions. This result indicates that the catalyst did not deactivate during the first 1,740 hours on-stream. Between 1,640 and 1,740 hours, the selectivity to methane was about 4.5%, the selectivity to ethane was 1.5-2.0% and the selectivity to ethane + ethylene was 4.5%. These selectivities were 6.1%, 1.4%, and 5-6% during 280-420 hours on-stream. These results indicate that catalytic selectivity was improving with time on-stream. Also, the olefin to paraffin ratio and the water gas shift activity of the catalyst did not noticeably decrease.

Effect of Conversion Level on Catalytic Selectivity

The selectivities to methane and ethane + ethylene at 265°C as a function of conversion are summarized in Figure 3. Because selectivity improved with time on-stream, only data from the latter part of the run are illustrated in this figure. These data indicate a noticeable increase in selectivity to light ends at conversions greater than about 65%.

Predicting Catalytic Performance in a Slurry Bubble Column Reactor

Because the most likely candidate for a commercial-size slurry-phase reactor is a slurry bubble column reactor, an attempt was made to predict the performance of the new precipitated iron catalyst in a slurry bubble column reactor based on the slurry autoclave data obtained here. The following assumptions were made:

- The slurry bubble column reactor could be modelled as 11 slurry autoclave reactors-in-series operating at 0-8%, 8-16%, 16-24% ... 78-80%, 80-80% CO + H_2 conversions.
- The reaction rate and selectivity did not change below 35% conversion because data at 265°C were not available at less than 35% CO + H_2 conversion.
- At 275°C, reaction rate and selectivity at <50% conversion were equal to the rate and selectivity at 50% conversion.

The calculations made using these asumptions are summarized in Table 1.

These calculations indicate that the selectivity to methane + ethane + ethylene is estimated to be about 8.9% at 265°C and 11.8% at 275°C, in a slurry bubble column reactor. At 265°C, the selectivity to methane + ethane + ethylene is about 2% higher than the revised selectivity target. At 275°C, the $C_1 + C_2$ hydrocarbon selectivity was about 5% higher than the revised selectivity target.

The space velocity required to reach 88% CO + H_2 conversion was 1.1 nL/h-gFe at 265°C and 1.6 nL/h-gFe at 275°C. These results appear to indicate that the new precipitated iron catalyst may be short of the activity target by a factor of 1.8 at 265°C and by about 1.3 at 275°C. However, actual specific activities are likely to be closer to target because of unknown catalyst inventory loss across the filter during the run and also because the catalytic activities were probably underestimated at low conversions, as discussed previously.

Catalytic Performance after Restart-Up Following Cold Shutdown

The run was shutdown at 1996 hours on-stream because of a 24-hour power outage. The shutdown involved lowering the temperature to 125°C and maintaining a feed space velocity of 1.2 nL/h-gFe. At 125°C, the synthesis gas feed was cut out, the reactor was blocked at a pressure of 21 atm, and the stirring was stopped. The feed was cooled to room temperature. Twenty-four hours later, the reactor was first heated to 90°C, stirring was initiated at 1,100 rpm and, the feed was cut in at 1.2 nL/h-gFe to maintain a pressure of 21 atm. Then, the temperature was raised to 265°C, and the catalyst was maintained at these conditions for another 250 hours. These test conditions were the same ones that prevailed at 280-420 hours and 1,640-1,740 hours.

The product wax drained from the reactor daily through the 0.5 μm filter during the test period of 2,000-2,250 hours was initially black in color and gradually attained its typical brown color. The same phenomenon was also observed during the initial part of this run. These results indicate that the new precipitated iron catalyst is undergoing substantial attrition following a cold start-up and some of the catalyst was lost from the reactor during these periods. The determination of catalyst loss across the filter in this current run is now in progress.

A slight deactivation of about 0.5% per day was observed after the restart-up. This conversion loss was partly caused by catalyst loss across the filter. After the restart-up, methane selectivity did not increase noticeably. The H_2:CO ratio at the outlet was slightly less than earlier in the run. This result may be partly caused by the lower conversion level during this period rather than a loss of water gas shift activity of the catalyst. Because of problems associated with the analysis of CO_2 by gas chromatography (GC) making a definite conclusion about the status of water gas shift activity after the restart-up was not possible. Similarly, fluctuations in the propylene to propane ratios were too large to reach conclusions concerning the state of the olefin to paraffin ratios after the restart-up relative to their values before shutdown.

Product Distributions

The approximate product distributions based on the total amount of hydrocarbons and oxygenates recovered during 300-324 hours and 660-684 hours on-stream at 265°C and 68% CO + H_2 conversion and at 275°C and 83% CO + H_2 conversion, respectively, are summarized in Tables 2 and 3. These product distributions are still approximate chiefly because the determination of oxygenates by GC has not yet been completed.

The results indicate that with increases in temperature and conversion, the selectivity to light ends and to gasoline range increases and the selectivity to middle distillates and to wax decreases. The hydrocarbon products are 45-47% liquid fuels. The LPG and gasoline fractions are olefinic. Linear α-olefins make up 83% of the LPG hydrocarbons. The linear α-olefin content is 43% in the gasoline-range hydrocarbons. Forty-one percent of the hydrocarbons in the gasoline range have not yet been identified but are most likely to be internal olefins.

CONCLUSIONS

950 The new precipitated iron catalyst is predicted to perform reasonably close to performance targets in slurry bubble column operation. Stability targets appear to be achievable. Compared to the revised selectivity target, an excess of 2% $C_1 + C_2$ was formed at 265°C. Based on the initial catalyst inventory in the autoclave, the catalyst seems to be short of the activity target by a factor of 1.8 at 265°C and 1.3 at 275°C. However, actual specific activities are likely to be closer to target because of catalyst inventory loss across the filter during the run and because catalytic activities were underestimated at low conversions.

A NEW UOP FISCHER-TROPSCH CONTRACT

The U.S. Department of Energy's Pittsburgh Energy Technology Center has recently awarded UOP a new contract to continue work on the development of iron Fischer-Tropsch catalysts. The contract was awarded in September 1990 for work to be performed over a period of three years.

The objective of the new contract is technology development for the production of active, stable, and selective iron Fischer-Tropsch catalysts for use in slurry-phase synthesis reactors. The key tasks of the contract are catalyst development, both precipitated iron as well as various other novel iron phases; catalyst testing; catalyst-aging studies; and preliminary design and cost-estimate of a catalyst synthesis facility.

ACKNOWLEDGMENT

The work under the current Fischer-Tropsch contracts at UOP is being sponsored by the U.S. Department of Energy's Pittsburgh Energy Technology Center.

Table 1

Performance of Precipitated Iron Catalyst
in 11 Autoclave Reactors in Series at 21 ATM, 0.7 H_2: CO Feed
(wt-%)

	265°C	275°C	Target
Cl	4.3	5.8	--
C_2 (Ethane + Ethylene)	4.6	6.0	--
$C_1 + C_2$	8.9	11.8	7
Sv, nL/h-gFe	1.1	1.6	≥2

Table 2

Approximate Product Distribution (Wt-%) at 68% Conversion, 265°C, 300-324 Hours

	N-Paraffin	α-Olefin	Alcohol	Aldehyde	Unidentified	Total
C_1	5.5	--	--	--	--	5.5%
C_2	0.9	5.0	2.9	0.2	--	9.0%
C_3-C_4	3.0	11.7	2.0	1.5	--	18.2%
C_5-C_{11}	3.8	8.9	2.9	1.1	7.3	24.0%
C_{12}-C_{18}	-3.0	-6.0	0	0	-4.0	13%
C_{19}-C_{25}	--	--	--	--	9.9	9.9%
C_{26}+	--	--	--	--	20.4	20.4%
	16.2	31.6	7.8	2.8	41.6	100.0

Table 3

Approximate Product Distribution (Wt-%) at 83% Conversion, 275°C, 660-684 Hours

	N-Parafin	α-Olefin	Alcohol	Aldehyde	Unidentified	Total
C_1	6.2	--	--	--	--	6.2%
C_2	2.4	4.1	4.6	0.3	--	11.4%
C_3-C_4	3.3	16.5	2.6	1.0	--	23.4%
C_5-C_{11}	4.0	11.1	2.1	0.8	10.6	28.6%
C_{12}-C_{18}	-3.0	-6.3	0	0	-1.9	11.2%
C_{19}-C_{25}	--	--	--	--	4.7	4.7%
C_{26}+	--	--	--	--	14.5	14.5%
	18.9	38.0	9.3	2.1	31.7	100.0

Figure 1

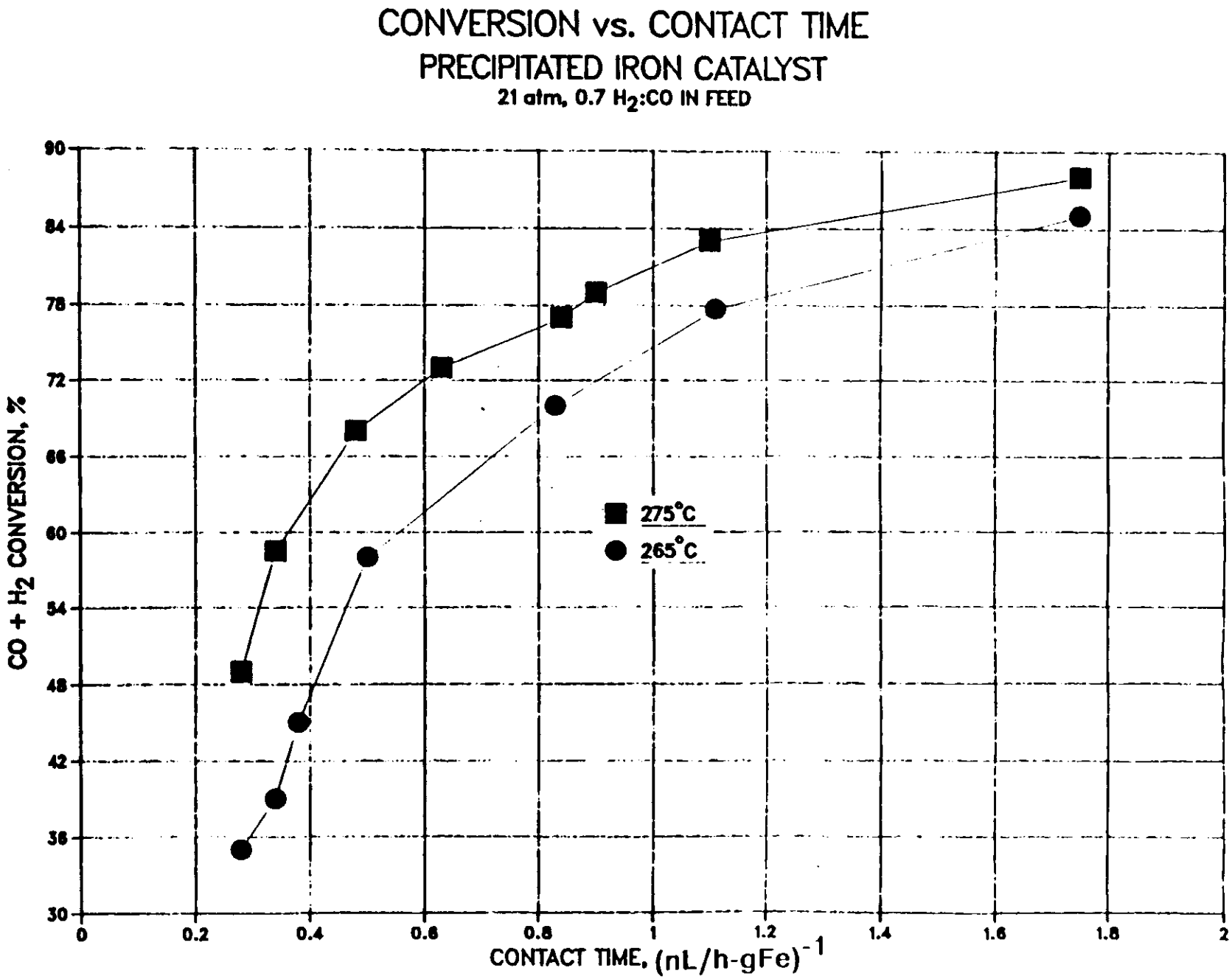

CONVERSION vs. CONTACT TIME
PRECIPITATED IRON CATALYST
21 atm, 0.7 H2:CO IN FEED
CO + H2 CONVERSION, %
CONTACT TIME, (nL/h-gFe)-1
275°C
265°C
90
84
78
72
66
60
54
48
42
36
30
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
1.8
2

Figure 2

EFFECT OF CONVERSION LEVEL ON REACTION RATE WITH PRECIPITATED IRON CATALYST

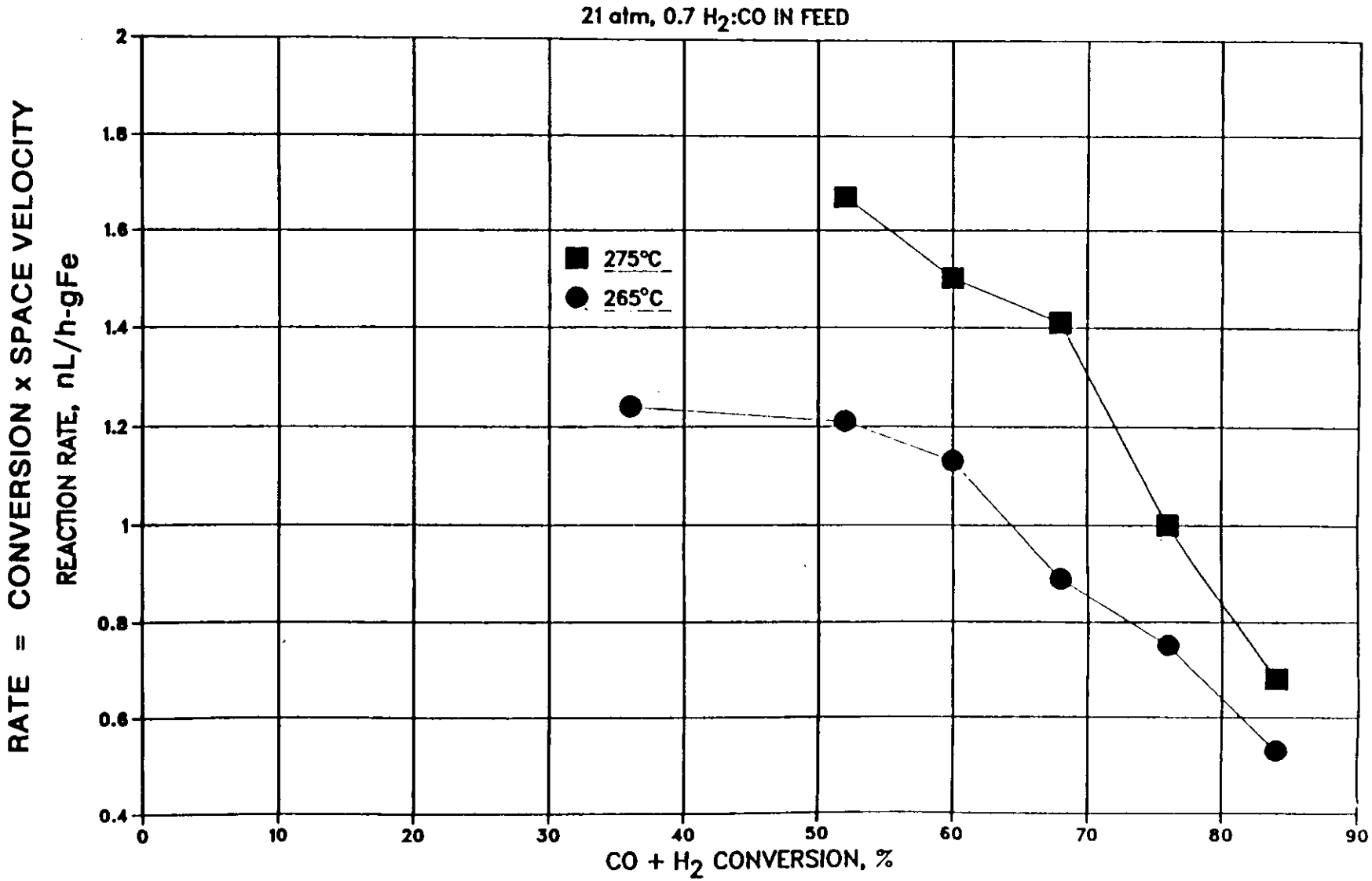
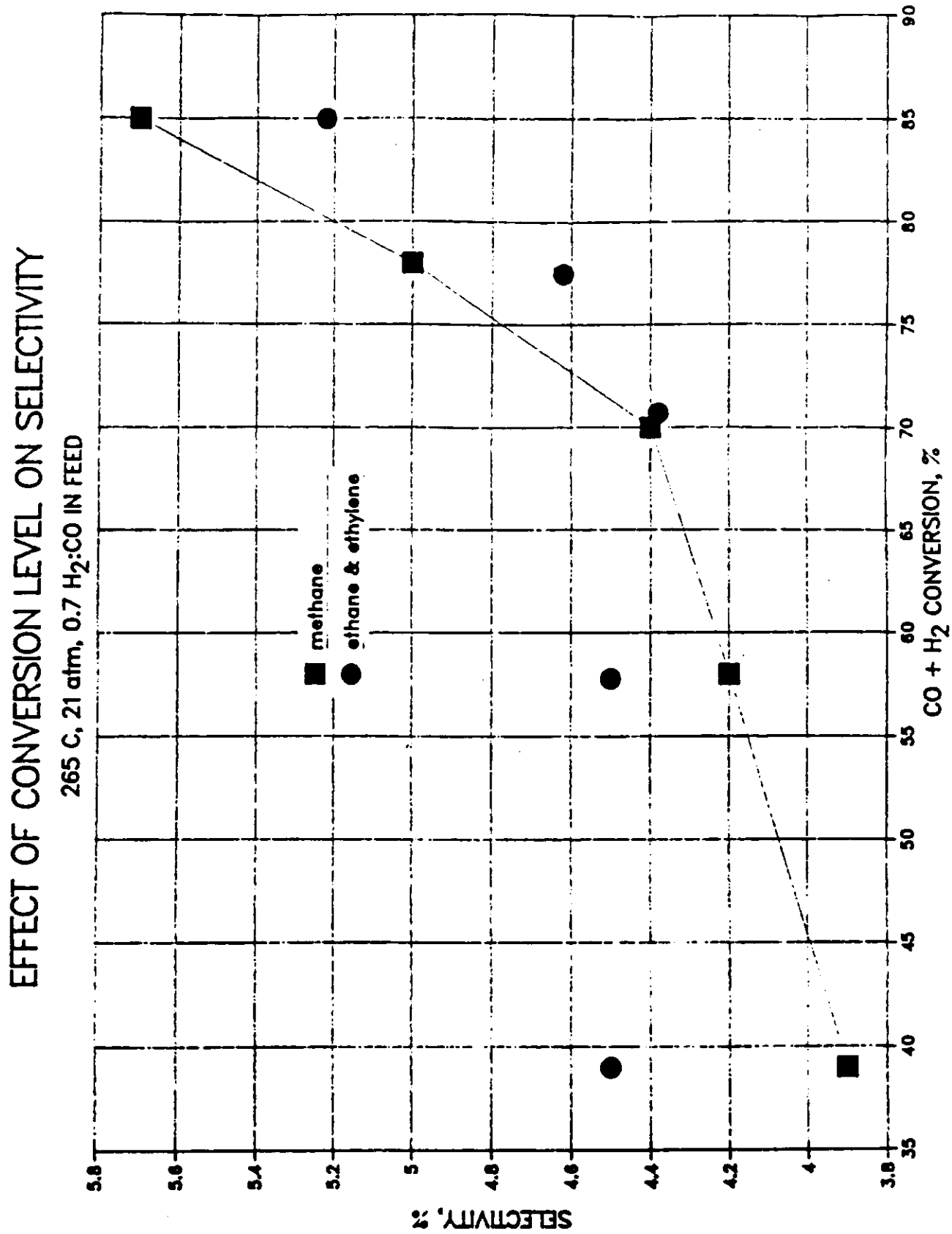


Figure 3


EFFECT OF CONVERSION LEVEL ON SELECTIVITY
265 C, 21 atm, 0.7 H_2:CO IN FEED
methane
ethane & ethylene
SELECTIVITY, %
$CO + H_2$ CONVERSION, %
5.8
5.6
5.4
5.2
5
4.8
4.6
4.4
4.2
4
3.8
90
85
80
75
70
65
60
55
50
45
40
35