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TITLE: THE DEVELOPMENT OF PRECIPITATED IRON CATALYSTS  
WITH IMPROVED STABILITY  
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OBJECTIVE: The objective of this program is to develop a precipitated iron Fischer-Tropsch catalyst with improved stability, suitable for slurry reactors.

TECHNICAL APPROACH:

- (1) Upgrade the existing fixed-bed pilot plant with slurry and Bertly reactor testing capabilities.
- (2) Establish the stability of a state-of-the-art reference precipitated iron catalyst.
- (3) Construct a pilot plant for preparing precipitated iron catalysts.
- (4) Develop a baseline precipitated iron catalyst.
- (5) Elucidate the deactivation chemistry for iron catalysts.
- (6) Modify the catalyst chemistry to improve its stability.

SIGNIFICANT ACCOMPLISHMENTS:

- (1) Design work for upgrading the existing fixed-bed pilot plant with slurry and Bertly reactor testing capabilities has been completed.
- (2) A reference precipitated iron catalyst was acquired from Mobil Corporation.
- (3) A pilot plant for preparing precipitated iron catalysts was constructed.
- (4) Precipitated pH and calcination temperature requirements for the baseline iron catalysts were examined.

## INTRODUCTION

Precipitated iron catalysts are expected to be used in next generation slurry reactors for large scale production of transportation fuels from synthesis gas. These reactors are expected to 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 more severe slurry conditions. It is expected that a major improvement in catalytic stability will be needed to make iron catalysts suitable for slurry operation.

This program is aimed at identifying the chemical principles governing the deactivation of precipitated iron catalysts during Fischer-Tropsch synthesis and to use these chemical principles in the design of more stable catalysts.

The program has been divided into five major tasks to be conducted over a two-year period. These tasks are described below:

- Task 1: Upgrade the existing fixed-bed pilot plant with slurry and Bertly reactor testing capabilities.
- Task 2: Establish the stability of a state-of-the-art reference precipitated iron catalyst.
- Task 3: Construct an iron catalyst preparation plant and develop a baseline iron catalyst.
- Task 4: Elucidate the deactivation chemistry for iron catalysts.
- Task 5: Modify the catalyst chemistry to improve its stability.

So far, work has been done under Tasks 1 and 3 as described in this paper.

## EXPERIMENTAL

### Catalyst Preparation Procedure

The schematic diagram for the iron catalyst preparation plant is shown in Figure 1. Metal was not used as a material of construction for any wetted section in order to avoid catalyst contamination that may occur through dissolution of metallic components in contact with acidic solutions. The iron-copper solution and the base solution are in two separate 15-gallon feed-tanks. The weights of these solutions are continuously measured during the experiment. The feed solutions are pumped separately to a precipitation reactor. The precipitate slurry then flows to a 55-gallon tank which contains a large amount of water. This water acts as a quenching medium for the precipitation reactions. The precipitate slurry then is pumped to a centrifugal filter where the catalyst is washed with a separate water feed stream. The catalyst is finally dried, calcined and impregnated with potassium carbonate, followed by a final calcination prior to in situ reduction in the Fischer-Tropsch synthesis reactor.

Several iron-copper catalysts were made in the laboratory, with smaller equipment using a similar procedure. These catalysts were characterized by various techniques.

### Catalyst Testing Procedure

An experimental iron catalyst was crushed to 170-200 mesh size range, mixed with 60-200 mesh  $\gamma$ -alumina powder and loaded into a 7/8" inner diameter glass-lined fixed-bed reactor. The catalyst weight and volume were 6.28 g and -9 cc, respectively. The alumina diluant weighed 21 g and had an approximate volume of 120 cc. After a pressure test with  $N_2$  at room temperature and 500 psig, the catalyst temperature was raised to 110°C under  $1.42 \times 10^{-2} \text{ Nm}^3/\text{hr } N_2$  at 1 atm, in about 2 hours and maintained under these conditions for 3 hours. Then,  $N_2$  flow was cut out, synthesis gas with 0.7 $H_2$ :1CO molar ratio was introduced at  $8.54 \times 10^{-3} \text{ Nm}^3/\text{hr}$  and the pressure was raised to 11 atm with synthesis gas. The catalyst inlet temperature was then raised to 270°C in 10 hours for in situ reduction. At 270°C a CO+ $H_2$  conversion of about 85% was achieved by increasing the feed rate to  $1.07 \times 10^{-2} \text{ Nm}^3/\text{hr}$ . The inlet temperature was maintained at 270°C for 12 hours. Under these conditions the maximum temperature in the catalyst bed varied between 300-310°C. The pressure at the reactor outlet was then raised to 15 atm, the inlet temperature was lowered to 257°C and then to 244°C, and the feed rate adjusted to  $6.26 \times 10^{-3} \text{ Nm}^3/\text{hr}$  to achieve a CO+ $H_2$  conversion of about 85% at 78 hours on stream. No further condition change was made during the rest of the run which lasted 800 hours.

### Conversion and Selectivity Calculations

Argon was present in the synthesis gas feed at about 6% (by mole) level and used as an internal standard to determine conversions and light hydrocarbon selectivities according to the following expressions.

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

The CO+ $H_2$  conversion was calculated in a similar manner.

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

where n is the number of carbon atoms in one molecule of hydrocarbon  $C_n$ . The calculation of selectivity of CO to  $CO_2$  is similar to the calculation of selectivity to methane for which  $n = 1$ .

### RESULTS AND DISCUSSION

Characterization of several iron-copper-potassium catalysts prepared in the laboratory indicated that the iron particle size could be successfully controlled with the catalyst preparation procedure that was utilized.

One of these experimental catalysts was tested in the fixed bed reactor for 800 hours, according to the procedure described in the Experimental Section. The catalyst inlet temperature was 244°C, while the maximum temperature in the catalyst bed varied mostly between 270 and 290°C. The CO+H<sub>2</sub> conversion remained mostly between 85 and 90% during the test with no sign of deactivation. At this conversion level, the H<sub>2</sub>:CO ratio increased across the catalyst bed from 0.7 at the inlet to between 1 and 2 at the outlet. The methane + ethane selectivity was about 5.5% which is less than that reported for the Sasol Arge process (8.2%) [1]. Since the experimental Fe-Cu-K catalyst was stable, it appears that the potassium level in this catalyst could be increased in order to lower methane + ethane selectivity without a serious stability penalty.

#### FUTURE PLAN

A new Fe-Cu-K catalyst with the objective of achieving lower methane + ethane selectivity will be prepared to finalize the development of the baseline catalyst. This catalyst will be certified by comparing it with Mobil's MCG-4 reference Fe-Cu-K catalyst. After certification, the baseline catalyst will be tested in the slurry reactor to determine catalyst needs. Fixed-bed, slurry and Bertly reactors will finally be considered for screening improved catalysts.

#### REFERENCES

1. B. Jager, W. Holtkamp, H. Gaensslen, Opportunities for Low Temperature Fischer-Tropsch Processing, International Coal Conversion Conference, South Africa, August 16-20, 1982.

# IRON CATALYST PREPARATION PILOT PLANT

FIGURE 1

