The Development of Precipitated Iron Catalysts with Improved Stability

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Executive Summary

Objective

The objective of this program was 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 performance targets are 88% $CO+H_2$ conversion with less than 1% deactivation per day for 1 month and a methane and ethane selectivity of no more than 7% (based on hydrocarbons and oxygenates only) at a space velocity of at least 2 normal liters per hour per gram iron (NL/hr/gFe) using a synthesis gas with a 0.5 to 1.0 H_2:CO ratio in a slurry reactor.

Tasks in the Program

The program was divided into five major tasks to be conducted over a three-year period:

- **Task 1**: Upgrade the existing fixed-bed pilot plant with slurry and Berty reactor testing capabilities.

- **Task 2**: Evaluate the performance of reference precipitated iron catalysts. Under secrecy agreements not to characterize the catalyst, Mobil Research and Development Corporation provided an iron catalyst (MCSG-4) to be used for reference performance. This catalyst was evaluated in the fixed-bed reactor. Also a fused-iron ammonia synthesis catalyst C-73-1-101 was tested.

- **Task 3**: Construct an iron (Fe) catalyst preparation plant and develop a baseline iron catalyst.

- **Task 4**: Elucidate the deactivation chemistry for iron catalysts.

- **Task 5**: Modify the chemistry of the catalyst to improve its stability.

Key Results

Draining of Liquid Products from Slurry Autoclave

Several procedures were used to drain liquid products made in the slurry autoclave reactor. Typically, a filter was attached at the end of a stainless steel tube. The tube passed through the

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autoclave head and formed the liquid (and sometimes gas) exit line for the reactor. A ceramic filter with a nominal pore diameter of 0.40 micron (μm) rapidly plugged with catalyst particles. This type of filter eventually disintegrated because of the pressure drop that developed between the inside and the outside of the filter. When filters with a larger pore size were used (5 or 17 μm nominal pore diameter) plugging did not occur, but a substantial amount of catalyst was lost.

Reference Iron Catalysts

A fused-iron ammonia synthesis catalyst C-73-1-101 cannot be fully activated with synthesis gas in situ at the relatively low temperatures that are typical of the Fischer-Tropsch process. The full reduction of Fe requires high temperatures. The observed difficulty in reduction is probably caused by the presence of a large amount of aluminum oxide (Al_2O_3) promoter in the fused-iron catalyst.

Assuming the Fe content in the Mobil MCSG-4 catalyst to be 60 to 65%, a space velocity that was five times lower was needed to achieve 80% conversion in the fixed-bed reactor relative to the space velocity reported by Mobil for the same catalyst in the slurry bubble-column reactor tests at similar temperature and pressure. The causes of this unexpectedly low activity are not currently understood but may be tentatively attributed to the specific catalyst-handling procedure used in this lab and to the differences in the activation treatments between the two tests.

Several iron-copper (Fe-Cu) catalysts were prepared in the laboratory at different pH levels by coprecipitating the nitrates of Fe and Cu with sodium carbonate (Na_2CO_3) solution. The precipitates were washed with water, dried, and then calcined. The catalysts were examined by scanning transmission electron microscopy (STEM), X-ray diffraction (XRD), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), temperature-programmed reduction (TPR), and nitrogen adsorption.

The findings of this work are:

- A pH of at least 2 is required to precipitate an iron nitrate solution by using sodium carbonate or ammonia solutions. A pH of at least 5 is required to precipitate a copper nitrate solution. However, in the presence of iron nitrate, copper precipitation occurs at lower pH's.

- An increase in calcination temperature decreases the surface area and pore volume of precipitated Fe-Cu catalysts. Therefore, the calcination temperature should be no higher than that required for forming ferric oxide (Fe_2O_3) from goethite (FeO(OH)).

- The amount of crystalline Fe_2O_3 in a precipitated Fe-Cu catalyst is maximized when calcination is conducted at the high-temperature maximum in the DSC

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curve. This result suggests that DSC experiments may be useful for determining the calcination temperature requirement for Fe-Cu catalysts.

- According to DSC measurements, the calcination temperature requirement for precipitated 100:1 Fe:Cu catalysts prepared from Na_2CO_3 increased from about 380°C to about 450°C as the pH of precipitation increased from 3.5 to 9.5.

- The Na_2CO_3-derived Fe-Cu catalysts prepared at pH ≤ 6.5 had small amorphous particles. Catalysts prepared at pH ≥ 7.9 were increasingly crystalline and had with large hematite (α-Fe_2O_3) particles after drying at 110°C. These morphological differences remained through the calcination step. This result indicates that the pH of precipitation is the key variable for controlling the Fe-Cu particle size.

- The Na_2CO_3-derived 100:0.5 Fe:Cu catalyst prepared at a 6.5 pH had large goethite (α-FeO(OH)) particles. A 100:1 Fe:Cu catalyst and a 100:5 Fe:Cu catalyst prepared at the same pH had small amorphous particles. Because large goethite particles would develop into large hematite particle during calcination, the copper level may also be a key variable for controlling the Fe-Cu particle size.

- The formation of Fe_3O_4 from Fe_2O_3 occurred at lower temperatures with Na_2CO_3-derived 100:5 Fe:Cu and 100:1 Fe:Cu catalysts relative to 100:0.5 Fe:Cu catalyst prepared at a 6.1 to 6.5 pH. T..is result indicates that Cu enhances the reduction of Fe_2O_3 to Fe_3O_4.

- The formation of Fe_3O_4 from Fe_2O_3 occurred at a higher temperature, while formation of metallic iron from Fe_3O_4 occurred at a lower temperature after K_2CO_3 impregnation of Na_2CO_3 - derived catalysts prepared at pH=6.1-6.5. This result indicates that although potassium may inhibit the reduction of Fe_2O_3 to Fe_3O_4, it may enhance the reduction of Fe_3O_4 to metallic iron.

- The NH_4OH-derived 100:1 Fe:Cu catalyst precipitated at a pH of 9.5 had small amorphous particles. The Na_2CO_3-derived catalyst prepared at the same pH had large hematite particles after 110°C drying. However, after 450°C calcination, the average particle sizes were similar for both catalysts. This result indicates that the use of NH_4OH relative to Na_2CO_3 does not provide obvious advantage.

- The complete reduction of precipitated Fe-Cu catalysts requires temperatures in excess of 800°C. Because reduction temperatures no higher than 300°C can lead to very active catalysts, the reduction of Fe-Cu catalyst surface must be occurring at much lower temperatures than those required for bulk reduction.

Iron Catalyst Performance in Fixed-Bed Reactor

A precipitated iron catalyst prepared in the laboratory was evaluated in an extended 800-hour test in a fixed-bed reactor. The objective was to determine the catalyst stability at high conversion.

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The results indicate that the activity of the experimental iron catalyst 5709-91 was not very stable in the fixed-bed reactor under the selected operating conditions: the deactivation rate was about 0.8% conversion/day. These operating conditions are more severe than those typically used in a slurry reactor for which this iron catalyst is intended. Specifically, the fixed-bed catalyst temperature reached as high as 295°C (compared with 255 to 280°C for slurry reactors), which may have enhanced the deactivation rate. Also, at the inlet of the catalyst bed where little water exists, the $H_2:CO$ ratio may have reached a value much lower than the feed ratio (0.7) because of the essential absence of the water gas shift reaction.

Iron Catalyst Preparation Plant

A new pilot plant was constructed for the large-scale synthesis of iron catalysts. In this plant, approximately 250 grams per hour (g/hr) of iron and copper is precipitated on a continuous basis. This plant is not currently set up for unattended operation. Accordingly, the precipitation time has typically been limited to an 8-hour operation. Filtering and washing steps, which follow precipitation, are also performed in the plant. However, these two steps were not performed on a continuous basis because of equipment limitations. The subsequent steps of drying, grinding, calcination, impregnation, and calcination were performed in the laboratory.

The findings from lab-prepared Fe-Cu-K catalysts were applied to the preparation of larger scale catalyst synthesis in the newly constructed preparation Plant 752. A total of 16 runs were conducted in Plant 752. The catalyst prepared in Run 16 (6616-18) was evaluated in a

long-term stability test in a slurry autoclave reactor (Run 19, Plant 700B). Specific preparation conditions used for this catalyst, as well as its properties and batch size, are described in Table 1.

Iron Catalyst Performance in a Slurry Reactor

The activation procedure for the new iron catalyst 6616-18 involved 12 hours of $CO+H_2$ treatment at 2 NL/hr/gFe), 280°C and 15 atmosphere (atm). The new iron catalyst (from Run 16, Plant 752) is predicted to perform slightly below the performance targets for slurry bubble-column operation. Stability targets appear to be achievable. This catalyst did not noticeably deactivate during 1,740 hours on-stream. Compared to the selectivity target, an excess of 2% C_1+C_2 was formed at 265°C. A continuous stirred tank reactor (CSTR) model was used to predict activity in a slurry bubble-column reactor. 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. At the end of the 2,250-hour run, (Run 19, Plant 700B), 30% of catalyst was lost through wax withdrawals.

No work was done under these tasks because the new iron catalyst developed in this program was very stable.

Contract Objective

The objective of this program was 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 performance targets are 88% CO+H$_2$ conversion with less than 1% deactivation/day for 1 month and a methane and ethane selectivity of no more than 7% (based on hydrocarbons and oxygenates only) at a space velocity of at least 2 NL/hr/gFe using a synthesis gas with 0.5:1.0 H$_2$:CO ratio in a slurry reactor.

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 (Table 1A). The feasibility of using iron catalysts has been demonstrated under relatively mild .

Arge-type conditions but not under more severe slurry conditions. Possibly, an 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. Originally, the program was divided into five major tasks to be conducted over a three-year period. Following is a description of these tasks:

- Task 1: Upgrade the existing fixed-bed pilot plant with slurry and Berty reactor testing capabilities. The major technical challenge in this task was expected to be the separation of catalyst fines (smaller than 5 to 10 μm) from the wax product in the slurry reactor.

- Task 2: Evaluate the performance of reference precipitated iron catalysts. Under this task, Mobil Research and Development Corporation provided an iron catalyst to be used for reference performance under secrecy agreements not to characterize the catalyst. This catalyst was evaluated in the fixed-bed reactor. Also a fused-iron ammonia synthesis catalyst was tested under this task.

- Task 3: Construct an iron catalyst preparation plant and develop a baseline iron catalyst. The major technical challenge in this task was expected to be the preparation of a superior precipitated iron catalyst. Major emphasis was given in this program to the design and construction of catalyst preparation equipment

and to the development of a catalyst-preparation procedure that would result in superior catalysts.

- Task 4: Elucidate the deactivation chemistry for iron catalysts. The major technical challenge in this task was expected to be the identification of the form of carbon that leads to deactivation.

- Task 5: Modify the catalysts chemistry to improve its stability. The plan was to evaluate several approaches to suppress coking reactions on iron catalysts.

Conversion and Selectivity Calculations

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

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

The $CO+H_2$ conversion was calculated in a similar manner. The calculation for the carbon atom selectivities is:

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$$CO_2 \ Selectivity, \ \% = \cfrac{\left(\cfrac{CO_2}{Ar}\right)_{product}}{\left(\cfrac{CO}{Ar}\right)_{feed} - \left(\cfrac{CO}{Ar}\right)_{product}}$$

$$C_n \ Selectivity, \ \% = \cfrac{\left(\cfrac{C_n}{Ar}\right)_{product}}{\left(\cfrac{CO}{Ar}\right)_{feed} - \left(\cfrac{CO}{Ar}\right)_{product}} \times 100 \times \left(\cfrac{100}{100 - CO_2 \ selectivity}\right)$$

In the latter formula, the n is the number of carbon atoms in one molecule of hydrocarbon (C_n). The selectivities of the light hydrocarbon and oxygenates carbon atom have been normalized to

100% by backing out carbon monoxide (CO) converted to carbon dioxide (CO_2).

Results and Discussion

Task 1. Upgrade of the Existing Pilot Plants

The existing fixed-bed pilot plant was upgraded with slurry-reactor testing capability. For the fixed-bed pilot plant (Figure 1) a premixed blend of CO, hydrogen (H_2), and argon (Ar) contained in an aluminum cylinder is compressed to about 3,000 pounds per square inch (psig) and then flows through a capillary restriction, where flow is controlled by regulating the pressure drop across the restriction. The feed gas then passes through a fixed bed of γ-Al_2O_3 particles at about 208°C, where iron carbonyl contaminant decomposes. The feed then flows downflow through a 7/8-inch ID glass-lined fixed-bed reactor situated in an electric furnace. The existing plant also has H_2-addition capability at the inlet of the reactor. The flow out of the reactor passes through a series of product collectors and is then metered by a wet test meter. The first collector, which is 100 cc in volume, is at 130°C. The reactor pressure is controlled by a back-pressure regulator past the first separator. The second product collector, which is also 100 cc, operates at 0°C and 50 psig. The third product collector operates at -78°C and 0 psig.

The first on-line gas chromatograph samples the flow out of the reactor, just past the back-pressure regulator, and analyzes paraffins, olefins, aldehydes, and alcohols in the C_1-C_{30} carbon number range. The second on-line gas chromatograph samples the flow just past the second product collector and analyzes CO, H_2, CO_2, Ar, paraffins, and olefins in the C_1-C_4 carbon number range.

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The slurry-reactor system (Figure 2) is essentially independent of the fixed-bed reactor system, except for sharing the same on-line gas chromatographs. Therefore, the integrated pilot plant provides the capability of running a fixed-bed experiment parallel with a slurry-bed experiment. The on-line gas chromatographs then need to be shifted between the two experiments every other hour.

The slurry reactor has an independent feed system that is similar to that of the existing fixed-bed reactor system. The product-collecting system for the slurry reactor is similar to that for the fixed-bed reactor except for the size of the collectors, which are larger: 1,000 cubic centimeter (cc) for the first collector and 300 cc for the second collector. Also, these collectors have drainage capability during the experiment.

The slurry reactor is a 1-liter stirred autoclave placed in a two-zone electric furnace. The reaction products are removed from the slurry autoclave through a filter located inside the reactor vessel. This internal filtration allows product removal but keeps all the catalyst at reaction conditions. The filter is connected to a hollow shaft brought into the top of the autoclave. Later in the program, researchers determined that Berty reactor testing was not necessary to meet the objectives of the program.

Task 2. Performance of Reference Catalysts

Under Task 2, the fused iron ammonia synthesis catalyst C-73-1-101 (from United Catalysts Inc.) was tested. A sample of this catalyst was externally reduced with H_2 at 450°C and previously tested as a reference catalyst under Contract DE-AC22-84PC70023, "The Development of a Selective Ruthenium Fischer-Tropsch Catalyst."[1] The objective was to determine whether the fused iron catalyst, which is originally in the oxide form, can be activated with synthesis gas in situ at the relatively low temperatures that are used for Fischer-Tropsch processing.

Two runs, fixed-bed Runs 48 and 49, were conducted. Catalyst identification, nature of diluents, catalyst and diluent weights, catalyst and diluent mesh size ranges, and catalyst and diluent bed lengths are summarized in Tables 2 and 3. For all of these tests, the catalyst was first heated under nitrogen (N_2) flow at 1 atm to 100°C, and then synthesis gas was introduced. The reactor was pressured from 9 to 11 atm with synthesis gas, and the catalyst was heated to 280°C under a synthesis gas flow. The test conditions were changed several times during these runs. Catalyst inlet temperatures (2 inches before the catalyst bed) and maximum temperatures, inlet and outlet pressures, feed compositions, feed rates, and space velocities at different hours on-stream are also summarized in Tables 2 and 3.

Catalyst C-73-1-101 showed only 9% CO conversion at 280°C, 11 atm, and 3:0 NL/hr/gFe with 0.7:1 H_2:CO synthesis gas in fixed-bed Run 48. The test was repeated in

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fixed-bed Run 49, and the performance obtained at various hours on-stream is summarized in Table 3. The low activity of the catalyst under conditions of fixed-bed Run 48 was confirmed. High conversion required the use of high pressure (35 atm) and low space velocity (0.54 NL/hr/gFe). Under these conditions, the $CO+H_2$ conversion was 69%, and the methane and CO_2 selectivities were 3.2 and 40%, respectively. A comparison of the fused iron catalyst activated in situ to the earlier results with the externally reduced fused iron catalyst show 6 to 7 times lower activity with the current results.[1]

These results suggest that fused iron catalyst C-73-1-101 cannot be fully activated with synthesis gas in situ at the relatively low temperatures that are typical of Fischer-Tropsch process. Full reduction of iron requires high temperatures. The observed difficulty in reduction is probably caused by the presence of a large amount of Al_2O_3 promoter in the fused iron catalyst.

Iron Catalyst from Mobil

The iron catalyst by Mobil, MCSG-4, was tested in the fixed-bed pilot plant to establish reference performance. This catalyst was previously tested by Mobil in a slurry bubble-column reactor. In the Mobil test, after a 12-hour activation at 280°C, 11 atm, and 2.0 NL/hr/gFe feed rate with 0.7:1 H_2:CO feed, the catalyst showed 80% $CO+H_2$ conversion at 2.4 NL/hr/gFe, 257°C, and 14 atm with a synthesis gas having a H_2:CO ratio of 0.7.[2] The methane and ethane

selectivity typically increased during the tests. In Run 13, the increase in methane and ethane selectivity was from 2.5 to 4.5%.

The MCSG-4 catalyst was shipped to UOP after being slurried in an organic medium. The approximate weight was 500 grams. Two attempts were made to make the catalyst suitable for fixed-bed pilot plant testing. First, the catalyst was washed with n-hexane and then dried at 110°C before being tested in the pilot plant in fixed-bed Run 52. In the second attempt, the washed and dried catalyst was calcined with air at 380°C in an attempt to burn residual organics and then tested in fixed-bed Run 53.

Fixed-Bed Run 52

During the first 5 hours of Run 52, the MCSG-4 catalyst was heated from 110 to 250°C, under 0.7:1 H_2:CO synthesis gas and a space velocity of 1.7 NL/hr/g catalyst. During the following 35 hours, the catalyst inlet temperature was gradually increased to 280°C and was maintained there for another 11 hours. At 280°C inlet temperature, the maximum observable temperature in the catalyst bed was 294°C. The catalyst bed outlet pressure was 9 atm throughout the 51-hour activation treatment. The CO+H_2 conversion reached a level of about 81% by the end of the activation treatment. This level is equivalent to the conversion level reported for the same catalyst in the slurry bubble-column reactor at the end of a 12-hour activation treatment.[2]

After 51 hours, the catalyst inlet temperature was lowered to 257°C, and the catalyst outlet pressure was increased to 13 atm, which caused the conversion to decrease to about 40%. Under these conditions, the maximum temperature in the catalyst bed was no more than 260°C. Between 59 and 90 hours on-stream, the space velocity was lowered from 1.7 to 0.37 NL/hr/gFe catalyst, which increased the conversion to 79%. No further condition change was made after 90 hours. The conversion gradually decreased to 70% by 156 hours on-stream.

The catalytic activity observed with MCSG-4 catalyst at 257°C inlet temperature and 13 atm in the fixed-bed reactor was much lower than that reported for the same catalyst in the slurry bubble-column reactor, as is apparent from the space velocity differences between the two tests. The MSCG-4 catalyst was retested in Run 53 to verify the low activity observed in Run 52.

Fixed-Bed Run 53

The activation treatment in fixed-bed Run 53 was similar but not identical to that used in Run 52 (Tables 4 and 5). However, larger amounts of catalyst and diluent were used in fixed-bed Run 53, and so the pressure drop was slightly higher. At a 9 atm catalyst bed outlet pressure, the inlet pressure was about 13 atm. The $CO + H_2$ conversion gradually increased to 40% during the first 41 hours, and the catalyst inlet temperature was increased to 270°C (Figure 3). During the same period, the CO_2 selectivity gradually increased to about 25%, and the methane selectivity increased to 3.3% (Figures 4 and 5). Between 41 and 51 hours on-stream, when the

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catalyst bed inlet temperature was increased to 280°C, the maximum observable temperature in the catalyst bed increased to 314°C. Under these conditions, the conversion increased to 82%, and the CO_2 and methane selectivities increased to 46% and 6.6%, respectively.

Following 51 hours of activation, the catalyst inlet temperature was lowered to 257°C, and the catalyst outlet pressure was increased to 13 atm, which lowered the conversion to about 40%. The space velocity was then gradually lowered to 0.28 NL/hr/gFe catalyst to achieve about 80% conversion. The maximum observable catalyst temperature was 263°C. Under these conditions, the CO_2 and methane selectivities lined out at about 45 and 3.2%, respectively, and the H_2:CO usage ratio was 0.63 (Figures 4-6). The $CO+H_2$ conversion gradually decreased to about 73% by the end of 265 hours on-stream.

The propylene to propane ratio reached a maximum level of about 10 during the early part of the run at about 14% $CO+H_2$ conversion and then gradually decreased with an increase in conversion level. The propylene to propane ratio remained mostly between 1.3 and 1.5 during the later part of the run at 70 to 75% conversion and a H_2:CO outlet ratio of about 0.85 (Figures 7 and 8).

Assuming the iron content in the MCSG-4 catalyst to be 60 to 65%, a space velocity that was five times lower was needed to achieve 80% conversion in the fixed-bed reactor relative to the space velocity reported by Mobil for the same catalyst in the slurry bubble-column reactor tests at similar temperature and pressure. The causes of this unexpectedly low activity are not

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