# Attrition Resistant Iron-Based Fischer-Tropsch Catalysts

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## DISCLAIMER

# ABSTRACT

The Fischer-Tropsch (F-T) reaction provides a way of converting coal-derived synthesis gas ($CO+H_2$) to liquid fuels.  Since the reaction is highly exothermic, one of the major problems in control of the reaction is heat removal.  Recent work has shown that the use of slurry bubble column reactors (SBCRs) can largely solve this problem.  Iron-based (Fe) catalysts are preferred catalysts for F-T when using low $CO/H_2$ ratio synthesis gases derived from modern coal gasifiers.  This is because in addition to reasonable F-T activity, the FT catalysts also possess high water gas shift (WGS) activity.  However, a serious problem with the use of Fe catalysts in a SBCR is their tendency to undergo attrition.  This can cause fouling/plugging of downstream filters and equipment, making the separation of catalyst from the oil/wax product very difficult if not impossible, and results in a steady loss of catalyst from the reactor.

The objectives of this research are to develop a better understanding of the parameters affecting attrition resistance of Fe F-T catalysts suitable for use in SBCRs and to incorporate this understanding into the design of novel Fe catalysts having superior attrition resistance.  Catalyst preparations will be based on the use of spray drying and will be scalable using commercially available equipment.  The research will employ among other measurements, attrition testing and F-T synthesis, including long duration slurry reactor runs in order to ascertain the degree of success of the various preparations.  The goal is to develop an Fe catalyst which can be used in a SBCR having only an internal filter for separation of the catalyst from the liquid product, without sacrificing F-T activity and selectivity.

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## EXECUTIVE SUMMARY

A NIRO Mobile Minor Spray Dryer has been purchased and installed.  A standard bench-mark iron catalyst was obtained and a preliminary experiment was carried out using this catalyst. A preliminary iron catalyst was prepared by coprecipitation and then it was spray dried.  Catalyst preparation will be standardized in the next reporting period. An attrition test apparatus is being fabricated.

# INTRODUCTION

Fischer-Tropsch Synthesis (FTS) is a set of reactions by which CO and $H_2$ (syn gas) are converted into a wide variety of hydrocarbons. This synthesis provides the best means currently available for the conversion of coal into synthetic transportation fuels. While over the near to mid term this indirect coal liquefaction route is not likely to be competitive with cheap oil on a global basis, there are a number of commercial activities in this area. Improvements and innovation in FTS is strategically very important to the U.S. because of its vast coal reserves and because it represents the best way to make high quality liquid products from coal.

Since the gasification of coal gives syn gas relatively lean in hydrogen ($H_2/CO \approx 0.5$-$0.7$), the use of a catalyst which converts the oxygen of the CO to $CO_2$ rather than $H_2O$ is preferable. This is achieved by using catalysts which, in addition to being active for FTS, are also active for the WGS:

$$CO + H_2O \rightleftarrows CO_2 + H_2$$
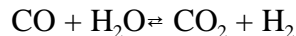
Fe is the preferred catalyst since it is one of the more active FTS catalysts, active for the WGS reaction, and relatively inexpensive.

Because FTS is so exothermic, one of the major problems in control of the reaction is heat removal. Recent work has concentrated on the use of slurry-phase reactors, especially SBCRs, which are able to be controlled more easily because of the liquid phase present. Such reactors have relatively simple designs and low initial costs while still permitting high catalyst and reactor productivity. Obviously, much recent work related to slurry-phase FTS based on coal-derived syn gas has focused on using Fe catalysts. Unfortunately, the use of Fe catalysts in SBCRs has presented a number of problems. Because of the difficulty in reducing highly dispersed Fe and its lower FTS activity than Co (which does not posses much WGS activity) or Ru (which is too expensive to use by itself), bulk Fe catalysts have had to be used in order to have sufficient active surface area per catalyst weight. The bulk Fe catalysts used in SBCRs have been usually prepared by precipitation, one of the typical methods of preparation of Fe catalysts for use in fixed bed reactors.

The problems encountered in using precipitated iron catalysts are mainly due to two major characteristics: (a) their low density and (b) their attrition properties. Since SBCRs are used to produce high alpha ($\alpha$) FTS products, there is a need to easily and inexpensively separate the catalyst from the liquid products. The apparent density of typical precipitated Fe catalysts is estimated to be very close (near 0.7 $g/cm^3$) to that of Fischer-Tropsch wax (about 0.68 $g/cm^3$) at reaction conditions. While this is beneficial in keeping the catalyst slurried, catalyst separation from the products can be extremely difficult since the catalyst does not settle well. Although internal/external filtration systems can be incorporated with slurry reactors, plugging of the filters by Fe catalyst particles is encountered. This is due to the low attrition resistance of the Fe catalyst and the significant breakage of the Fe particles.

The objectives of this research are to develop a better understanding of the parameters affecting attrition resistance of Fe F-T catalysts suitable for use in SBCRs and to incorporate this

understanding into the design of novel Fe catalysts having superior attrition resistance. The goal is to develop an Fe catalyst which can be used in a SBCR having only an internal filter for separation of the catalyst from the liquid product, without sacrificing F-T activity and selectivity.

## RESULTS AND DISCUSSIONS

The project consists of four major experimental tasks (Tasks 1-4) addressing the contract objectives described above. They are:

Task 1: Catalyst Preparation
Task 2: Catalyst Performance Evaluation
Task 3: Catalyst Characterization
Task 4: Slurry Reactor Testing

A NIRO Mobile Minor Spray Dryer has been purchased and installed. We received this spray on November 7, 1996. It is ideal for spray drying small amounts of feed liquids, solutions or light slurries. The unit is completely assembled within a sturdy framework. The drying chamber is 800 mm in diameter, 600 mm cylindrical height and conical based. The cone angle is 60°. All internal surfaces that contact the product are stainless steel AISI 360. The floor area occupied by the unit is given by the following dryer dimensions:

Length      1.8 m
Width       0.925 m
Height      2.200 m
The total weight is 280 kg.

## Task 1.  Catalyst Preparation

80 grams of (Sample ID: Ruhrchemie-52119) 1/8" pellet Fe catalyst was received from Federal Energy Technology Center. The composition of the catalyst is $100Fe/5Cu/4.2K/25\ SiO_2$. It was then crushed to 70-μm particle size prior to testing.

A 60 g batch of Iron catalyst having the composition $100Fe/5Cu/4.2K/25\ SiO_2$ was prepared by the coprecipitation method. The constant pH precipitation technique was used to prepare the Fe/Cu catalysts precursor. The catalyst precursor was continuously precipitated at room temperature from a flowing aqueous solution containing iron and copper nitrates at the desired Fe/Cu ratio, using aqueous ammonium carbonate solution. The precipitate was filtered by vacuum filter. Impregnation with $SiO_2$ (structural promoter) and potassium (chemical promoter) was accomplished by addition of an appropriate amount of dilute $K_2SiO_3$, $KHCO_3$ solutions to undried, reslurried Fe/Cu coprecipitate. Finally the slurry was spray dried at 250°C. The spray dried catalyst was calcined at 300°C for 5h. The analysis of the catalyst particle size distribution is given Table 1.

Table 1.  Particle Size Distribution of the Iron Catalysts (Sample ID: HPR-2)

| Sieve Designation, Micron | Weight of the Catalyst,g | Percentage Distribution |
|---|---|---|
| 297 | 22.1 | 36.1 |
| 210 | 10.8 | 17.7 |
| 149 | 4.59 | 7.5 |
| 125 | 1.92 | 3.1 |
| 105 | 1.93 | 3.2 |
| 88 | 1.92 | 3.1 |
| 63 | 3.83 | 6.3 |
| 53 | 2.28 | 3.7 |
| less than 53 | 11.8 | 19.3 |
| Total | 61.17 | 100.0 |

One major difficulty during the spray drying we faced was that due the large feed rate and or/dilute slurry concentration the powder already in the chamber absorbed moisture and stuck to the chamber wall. A detailed study will be carried out using the following parameters: (I) slurry concentration (ii) atomizer speed (iii) temperature of the spray dryer (iv) feed rate and (v) outlet air temperature.

**Task 2. Catalyst Performance Evaluation**

Fixed-Bed FTS

In order to establish a base line, the bench-mark Ruhrchemie (Sample ID:Ruhrchemie-52119) catalysts was tested for its catalyst activity and selectivity in the 1-cm -i.d. stainless steel down flow, fixed bed reactor.  The feed gas was a premixed (Air Products and Chemicals, inc.) mixture of CO and $H_2$ ($H_2$/CO=0.67) containing 5% Ar which served as an internal standard for product analysis.  All the reactant gases were of high purity (99.9%) and were further purified by passing them through a Matheson Model 6411 oxygen absorbing purifier.  This purifier is a high-efficiency purification device which removes trace contaminants of both oxygen and water vapor.  The flow rate of the feed gas was automatically controlled by a mass flow controller.  The feed was preheated before entering the reactor.  The product distributions were recorded with time-on-stream under the fixed operating conditions. The reactor temperature was controlled to $\pm 1^{\circ}C$. The product was  analyzed by an on-line HP 5890 series II plus gas chromatograph, with advanced ChemStation control and capabilities.  The HP 3365 Series II Chemstation offered automatic flow and split ratio of GC pneumatics.  Three valves were used in the system: six-port gas sampling, ten-port gas sampling with back-flush to vent, and a six-port column isolation valve. The system was configured for an extended analysis of hydrocarbons.  The hydrocarbons $C_1$-$C_{28}$ and the oxygenates were analyzed using  HP-1 100m, 0.25mm, $0.5\mu$m Capillary column and detected by FID.  The wax analysis was performed only on selected samples.  The CO, $CO_2$, and Ar were separated by a 2. 6 ft x 1/8 in Haysep Q  Column and 3. 15 ft x 1/8 in Molecular Sieve 13x columns and detected by TCD.  The calibration was carried out using various calibration mixtures and pure compounds obtained from Supelco and HP.

About 1.0 g Ruhechemie catalyst was diluted 1:2 by volume with glass beads of the same size (Supelco, catalog No: 5-9200) prior to loading into the reactor. The catalyst was reduced with carbon monoxide at 280°C, ambient pressure, and a flow rate of 30 cc/min for 16 h. Following reduction the reactor temperature was lowered to 50°C. The system was then pressurized to 1.48 MPa, the carbon monoxide flow was cut off, and synthesis gas ($H_2/CO = 0.67$) was introduced at a gas space velocity of 2L(NTP)/(h.g of cat). (Space velocity is defined as normal liter per gram of catalyst per hour). The reactor temperature was then increased gradually to 250°C. This is referred to as the conditioning period. After achieving the desired process conditions of 250°C, 1.48 MPa, 2.0 Nl/g-cat/h and $H_2/CO = 0.67$, the catalyst was tested over a period of 75 h.

The CO conversion is plotted in Figure 1. The CO conversion is defined as follows:

$$FractionalConversion = \frac{[CO/Ar]_{feed} - [CO/Ar]_{run}}{[CO/Ar]_{feed}}$$

As can be seen from Figure 1, the catalyst showed high activity with a CO conversion as high as 93% and leveling off at about 86% over 70 hours on stream.

Attrition Testing

Work has begun on developing instrumentation and methodology for measuring catalyst attrition. A fludized bed system and a stirred beaker system has been set up and tested using crushed alumina. It is of interest to develop a system which permits testing as little as 5 g of catalyst. In addition, considerations are being given to developing separate means to measure catalyst particle abrasion, fracture due to collision, and fracture due to reaction.

**Task 3. Catalyst Characterization**

The techniques listed below will be used to characterize the fresh, pretreated and used catalysts. 1).Total surface area measurement will be based on the standard BET method. 2) Hg-porosimetry will be used for pore volume and pore size distributions. 3) X-ray Diffraction (XRD) will be used to determine the bulk phases of the catalysts. 4) CO chemisorption on the reduced iron catalysts will be used to measure the available active Fe surface area. 5) Particle size distribution will be determined using a Coulter counter. 6) The shape of the particles will be determined by optical microscopy. 7) Scanning electron microscopy with EDX will be used for the surface morphology and spatial variations of elemental distributions. 8) The reducibility of the catalysts will be examined by TPR 9) Elemental analysis will be carried out using atomic absorption (AA) spectrometry.

**CONCLUSION**

A standard iron catalyst was obtained and preliminary experiment was carried out. Iron catalyst was prepared by coprecipitation techniques and then it was spray dried. The effect of various parameters on catalyst preparation such as (I) slurry concentration (ii) atomizer speed (iii) temperature of the spray dryer (iv) feed rate and (v) outlet air temperature will be investigated.

**FUTURE WORK**

        The future activity will include, development and testing of attrition-resistant iron Fischer-Tropsch catalyst using the spray drier.
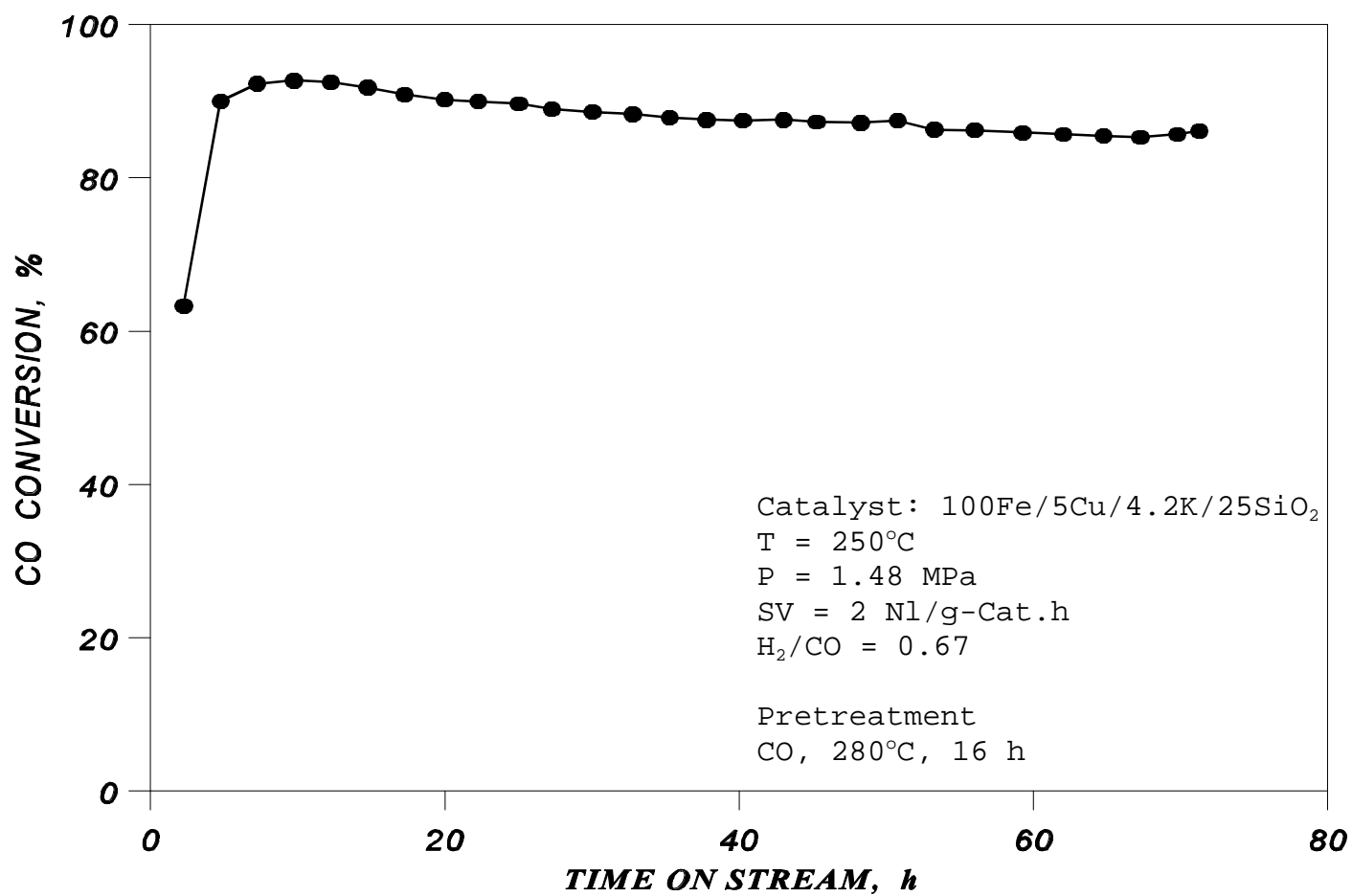
Figure 1.  Variation of Carbon Monoxide Conversion with Time-on-Stream (Ruhrchemie Catalyst)