

Attrition Resistant Iron-Based Fischer Tropsch Catalysts

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ABSTRACT

The Fischer-Tropsch (F-T) reaction provides a way of converting coal-derived synthesis gas ($\text{CO}+\text{H}_2$) 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 F-T 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.

The effect of silica addition via coprecipitation and as a binder to a doubly promoted Fischer-Tropsch synthesis iron catalyst (100 Fe/5 Cu/4.2 K) was studied. The catalysts were prepared by coprecipitation, followed by binder addition and drying in a 1 m diameter, 2 m tall spray dryer. The binder silica content was varied from 0 to 20 wt %. A catalyst with 12 wt % binder silica was found to have the highest attrition resistance. F-T reaction studies over 100 hours in a fixed-bed reactor showed that this catalyst maintained around 95 % CO conversion with a methane selectivity of less than 7 wt % and a C_5^+ selectivity of greater than 73 wt %. The effect of adding precipitated silica from 0 to 20 parts by weight to this catalyst (containing 12 wt % binder silica) was also studied. Addition of precipitated silica was found to be detrimental to attrition resistance and resulted in increased methane and reduced wax formation.

An HPR series of proprietary catalysts was prepared to further improve the attrition resistance. Based on the experience gained, a proprietary HPR-43 catalyst has been successfully spray dried in 500 g quantity. This catalyst showed 95 % CO conversion over 125 h and had less than 4 % methane selectivity. Its attrition resistance was one of the highest among the catalyst tested.

Future activities will include testing of improved attrition-resistant iron Fischer-Tropsch catalysts (HPR-43) in a SBCR.

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EXECUTIVE SUMMARY

The objective of this project is 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.

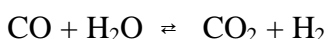
The accomplishments to date are as follows:

- A NIRO Mobile Minor Spray Drier (6' high x 3' diameter) has been purchased, installed, and commissioned.
- A high-temperature, high-pressure (HTHP) fixed-bed test apparatus with associated analytical equipment for F-T testing has been commissioned.
- A baseline Ruhrchemie iron catalyst was tested.
- Several iron catalysts were prepared by coprecipitation followed by spray drying. Spray drying parameters were optimized. These catalysts showed high conversion, high α (0.9), high stability, and reasonable attrition resistance.
- Attrition procedures for small quantities of catalyst were developed.
- An HPR-43 material was prepared as a larger 500 g batch to demonstrate scalability of the proprietary preparation technique.

INTRODUCTION

Fischer-Tropsch Synthesis (FTS) is a set of reactions by which CO and H₂ (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 (H₂/CO≈0.5-0.7), the use of a catalyst which converts the oxygen of the CO to CO₂ rather than H₂O is preferable. This is achieved by using catalysts which, in addition to being active for FTS, are also active for the WGS:



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 possess 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 (α) 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/cm³) to that of Fischer-Tropsch wax (about 0.68 g/cm³) 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

Task 1. Catalyst Preparation

An HPR series of proprietary catalyst was prepared to further improve attrition resistance. Based on the experience gained, a proprietary HPR-43 catalyst has been successfully spray dried in 500-g quantity.

Task 2 & 3. Catalyst Performance Evaluation and Catalyst Characterization

Catalyst Characterization

The attrition of catalysts was measured using a 3-hole air-jet attrition tester as well as with jet cup. The attrition properties of the catalysts are shown in Table 1. The following conclusions can be drawn from Table 1 (i) jet-cup and ASTM fluidized bed method agree (ii) HPR series of catalysts (HPR-39, 40, 41, 42, 43) have improved attrition resistance.

SEM micrographs of all the fresh catalyst (Figure 1-10) show that the catalyst particles are roughly spherical.

Fischer-Tropsch Activity Tests

The F-T activity of the HPR-43 catalysts was measured in a fixed-bed microreactor system at 250°C, 1.48 MPa, and 2.0 NL/g cat-h, at an H₂/CO ratio of 0.67. This catalyst showed 95 % CO conversion over 125 h of testing, with a methane selectivity of less than 4 wt % and a C₅⁺ selectivity of greater than 78 wt. The chain growth parameter (α) was 0.89.

Task 4. Slurry Reactor Testing

500 g of HPR-43 proprietary catalyst was supplied to RTI. RTI is currently negotiating with an industrial party for testing the catalyst in a pilot scale SBCR. The results of the SBCR will be submitted as a separate report before August, 1999. However this is contingent upon reaching a satisfactory agreement with the industrial party and resolution of intellectual property issues.

FUTURE WORK

Future activities will include testing of HPR-43 catalyst in a SBCR.

Table 1. Comparison of jet cup test and ASTM fluidized bed test results

Catalyst	Binder Silica (wt%)	Precipitated Silica (pbw)	Fluidized Bed Attrition Loss ^(a) (wt%)		Jet Cup Fines wt% ^(b)
			1 h	5h	
HPR-27	4	0	24.4	32.6	26.59
HPR-28	8	0	25.7	35.4	21.76
HPR-30	12	0	12.8	22.7	8.51
HPR-31	16	0	22.0	30.1	18.21
HPR-32	20	0	34.9	35.0	51.60
HPR-33	12	5	24.2	37.3	26.60
HPR-34	12	10	31.0	39.6	33.92
HPR-35	12	15	42.1	NA ^(c)	39.64
HPR-36	12	20	39.1	NA ^(c)	41.28
HPR-39 ^d	-	-	4.7	10.0	NA
HPR-40 ^d	-	-	4.1	9.7	NA
HPR-41 ^d	-	-	6.4	17.7	NA
HPR-42 ^d	-	-	5.2	15.5	NA
HPR-43 ^d	-	-	7.6	14.6	4.77
Co035	-	-	-	-	31.07

(a) Fluidized bed attrition loss: measured using ASTM-D-5757-95.

(b) Jet cup fines wt%: measured using proposed ASTM jet cup test (1 hr).

(c) Attrition was severe enough to plug the tester; wt% loss was >40 wt%.

(d) Proprietary

Figure 1 (HPR-27)

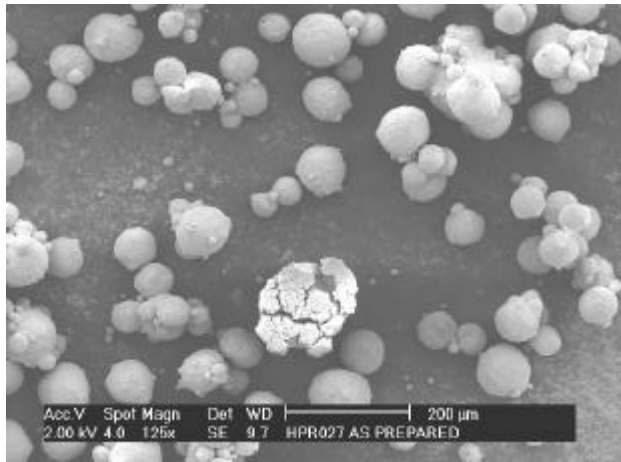


Figure 2 (HPR-28)

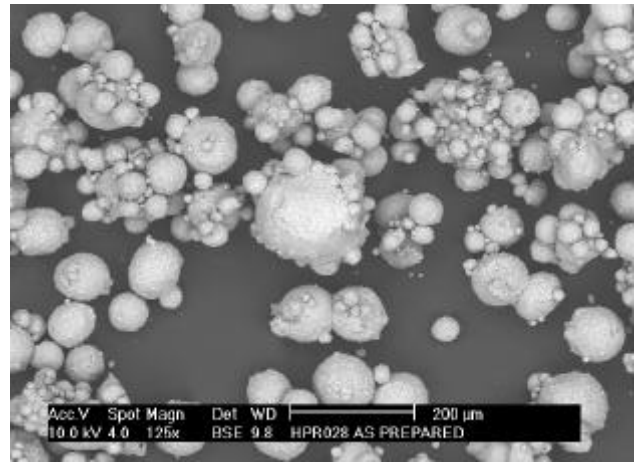


Figure 3 (HPR-30)

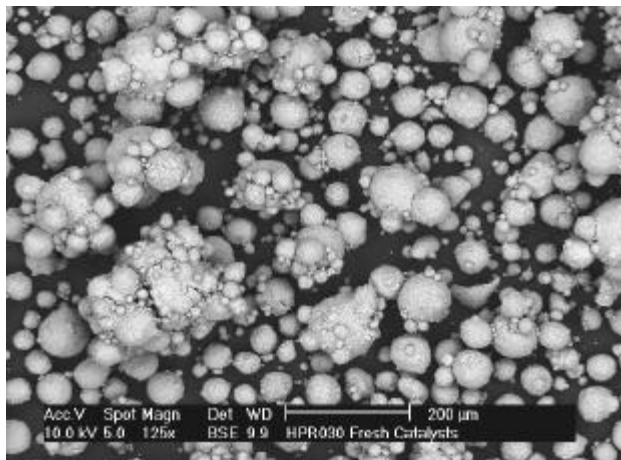


Figure 4 (HPR-31)

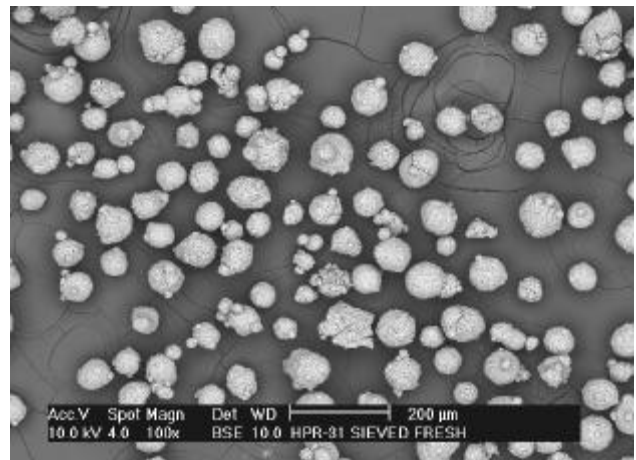


Figure 5 (HPR-32)

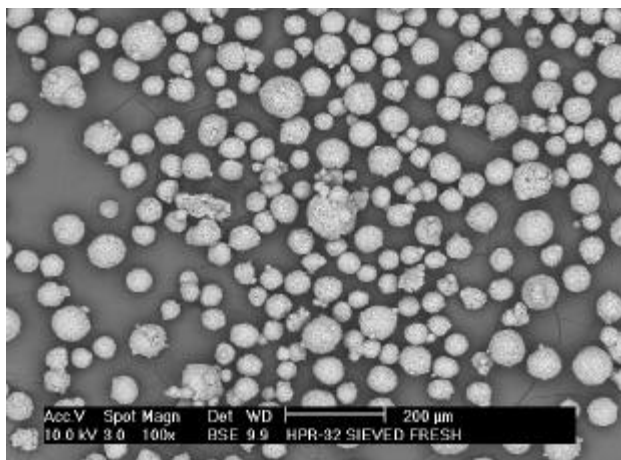


Figure 6 (HPR-33)

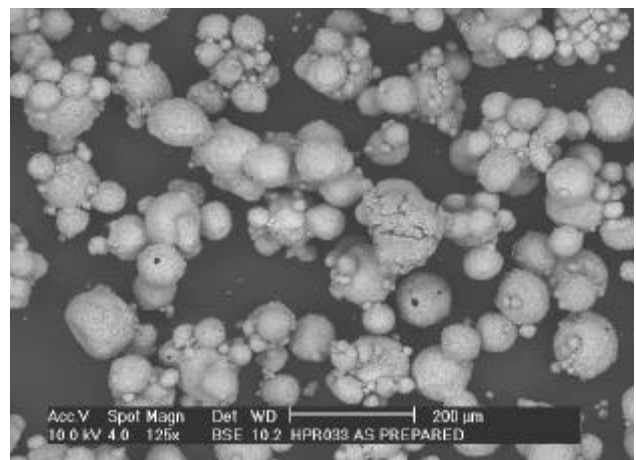


Figure 7 (HPR-34)

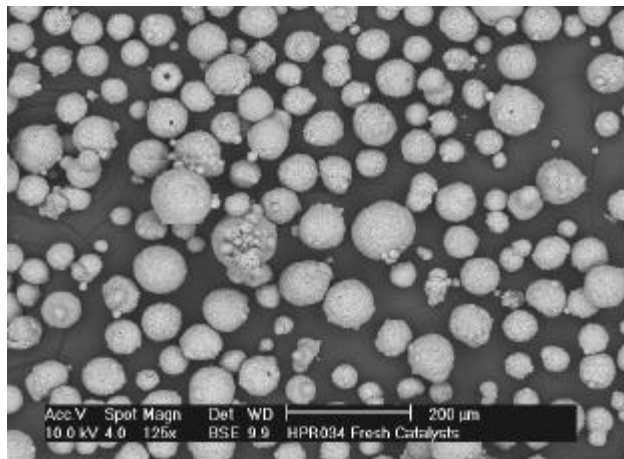


Figure 8 (HPR-35)

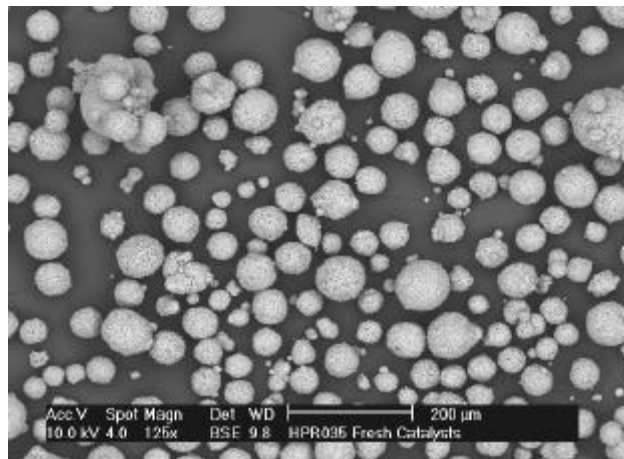


Figure 9 (HPR-36)

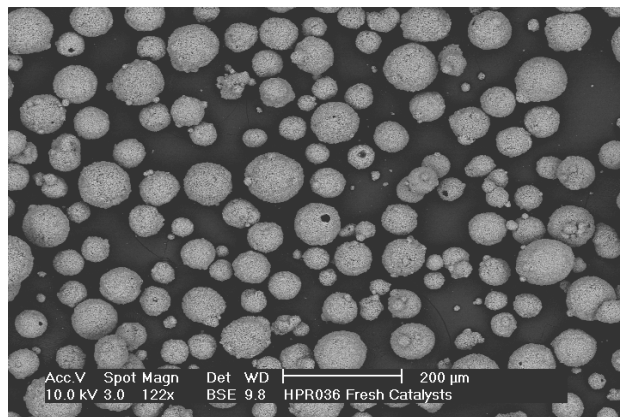


Figure 10 (HPR-43)

