

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.

Future activities will include testing of improved attrition-resistant iron Fischer-Tropsch catalyst both in fixed bed and SBCR reactors.

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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.

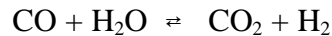
The accomplishments to date are as follows:

- 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.

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

Two types of silica-containing iron catalysts were prepared. The first series of catalysts contained binder silica but no precipitated silica and had a composition of 100 Fe/5 Cu/4.2 K (plus binder silica). These catalysts were prepared by coprecipitation followed by spray drying. Finally it was calcined at 300°C in a muffle furnace. The binder silica content was varied from 4 to 20 wt %. These catalysts are designated Fe-bSi(x), denoting that they contain x wt % binder silica.

The second series of catalysts contained both precipitated and binder silica. Four such catalysts were prepared containing 5, 10, 15 and 20 parts by weight (pbw) precipitated silica (yielding catalysts of the composition 100 Fe/5 Cu/4.2K/y SiO₂, where y is 5, 10, 15 or 20). To each of these catalysts, 12 wt % binder silica was added. The catalysts are designated Fe-pSi(y). These catalysts were spray dried and calcined in the same way as those above.

Task 2 & 3. Catalyst Performance Evaluation and Catalyst Characterization

Catalyst Characterization

Table 1 shows the BET surface areas of the fresh and reduced catalysts, the hydrogen uptake, and the attrition resistance of all the catalysts prepared. The BET surface area decreased as the catalyst was reduced, but decreased less after reduction as the silica content (either precipitated or binder) increased, as expected. The pore volume, bulk density, and average pore diameter of the Fe-pSi fresh catalysts is also shown in Table 1.

The hydrogen uptake generally decreased with silica content, though the effect of the precipitated silica is much less than the effect of the binder silica. The higher H₂ consumption by the Fe-bSi catalysts compared to the Fe-pSi catalysts indicates a greater extent of reduction for catalysts

containing binder silica only and no precipitated silica. XRD of all the fresh catalysts showed only Fe_2O_3 , while all the reduced catalysts showed only the $\chi\text{Fe}_{2.5}\text{C}$ and Fe_3O_4 phases.

The attrition resistance is perhaps the most interesting result. There is a minimum in the weight loss as a function of binder silica content, with the most attrition-resistant material being the Fe-bSi (12) catalyst, containing 12 wt % binder silica. For this reason, this material was used as the basis for preparing the Fe-pSi (y) series of catalysts with various levels of precipitated silica. The catalysts containing precipitated silica were less attrition-resistant than those containing only binder silica as seen Table 1.

Fischer-Tropsch Activity Tests

The F-T activity of the catalysts was measured in a fixed-bed microreactor system at 250°C, 1.48 MPa, and 2.0 NL/g cat-h, at an H_2/CO ratio of 0.67. The catalyst was reduced in-situ in CO at 0.1 MPa, 280°C, for 16 h. After 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 ($\text{H}_2/\text{CO} = 0.67$) was introduced at a gas space velocity of 2 NL/g cat-h. The reactor temperature was then increased gradually to 250 °C. The catalysts were then tested over a period of 100 h.

Table 2 shows the CO conversion and hydrocarbon selectivity for the various catalysts, along with data obtained on a Ruhrchemie catalyst for comparison. The CO conversions plot are shown in Figures 1 and 2. All catalysts tested were more active than the Ruhrchemie catalyst. The selectivity varied with the silica content. There was a beneficial effect of binder silica up to 8 to 12 wt% on selectivity (reduced methane, nearly constant C_{12}^+). As the binder silica content increased above 12 wt%, the C_1 , $\text{C}_2\text{-C}_4$, and $\text{C}_5\text{-C}_{11}$ selectivities increased, while the C_{12}^+ selectivity decreased. As the precipitated silica content increased (at 12 wt% binder silica), the selectivities of all the $\text{C}_1\text{-C}_{11}$ products increased. However, the $\text{C}_5\text{-C}_{11}$ selectivity for the catalysts containing precipitated silica was generally higher than the selectivity for those catalysts containing only binder silica. Finally, as shown in Table 2, the chain growth parameter (α) was as high as 0.9 for the most attrition resistant catalysts.

Improved Attrition Resistant Catalysts

Additional catalysts were prepared with improved attrition resistant. The properties these catalysts are given below.

Properties of iron-based catalysts

Catalyst Designation	Binder silica (wt %)	BET Surface area, m ² /g	Attrition loss (wt %)	
			1 h	5h
HPR-39	12	107.8	4.7	10.0
HPR-40	10	81.4	4.1	9.7
HPR-41	8	60.5	6.4	17.7
HPR-42	10	79.8	5.2	15.5
HPR-43	10	81.5	7.6	14.6

FUTURE WORK

Future activities will include testing of improved attrition-resistant iron Fischer-Tropsch catalyst both in fixed bed and SBCR reactors.

Table 1. Chemical and physical properties of iron-silica catalysts

Catalyst designation	Binder silica (wt%)	Precipitated silica (pbw)	BET surface area (m ² /g)		H ₂ TPR (mmol H ₂ / g cat)	Attrition loss ^b (wt%)		Pore Volume, mL/g	Bulk Density, g/mL	Pore Diameter, μm
			Fresh	Reduced ^a		1 h	5h			
Fe-bSi(4)	4	-0-	80.3	35.6	24.3	24.4	32.6	NA	NA	NA
Fe-bSi(8)	8	-0-	95.7	50.8	23.0	25.7	35.4	NA	NA	NA
Fe-bSi(12)	12	-0-	121	68.7	20.6	12.8	22.7	NA	NA	NA
Fe-bSi(16)	16	-0-	151	103	19.0	22.0	30.1	NA	NA	NA
Fe-bSi(20)	20	-0-	172	98.9	18.4	34.9	35.0	NA	NA	NA
Fe-pSi(5)	12	5	163	116	18.8	24.2	37.3	0.54	0.95	0.0310
Fe-pSi(10)	12	10	168	144	17.9	31.0	39.6	0.54	0.89	0.0165
Fe-pSi(15)	12	15	189	163	17.7	42.1	^c	0.62	0.95	0.0230
Fe-pSi(20)	12	20	218	181	17.6	39.1	^c	0.64	0.92	0.0175

^a Reduced in CO, 27 cc/g cat.min, 0.1 MPa, 280 °C, 16h.

^b Measured using ASTM-D-5757-95.

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

Table 2. Catalyst activity and selectivity

Catalyst	Ruhrchemie	Catalysts with binder silica					Catalysts with precipitated silica ^a			
		Fe-bSi					Fe-pSi			
		4	8	12	16	20	5	10	15	20
Time-on-stream (h)	42.7	52	42	65	90	67	68	66	66	66
CO conversion (%) ^b	86	94.3	94.1	94.3	95.5	94.5	95.5	94.4	90.1	88.2
Hydrocarbon selectivity (wt%)										
C ₁	8.3	7.4	6.8	6.8	9.9	9.6	8.8	10.2	10.2	9.5
C ₂ -C ₄	21.3	18.1	17.6	19.6	25.0	23.5	23.2	23.5	22.4	20.1
C ₅ -C ₁₁	14.3	12.7	13.0	12.8	17.3	17.6	22.0	26.5	30.5	32.8
C ₁₂ ⁺	56.1	61.8	62.5	60.8	47.8	49.3	46.0	39.8	36.9	37.7
Alpha (α)	NA	0.92	0.91	0.89	0.87	0.81	0.87	0.86	0.87	0.88

^a These catalysts also contain 12 wt% binder silica

^b Measured at 250^BC, 1.48 MPa, 2 NL/g cat-h, H₂/CO = 0.67

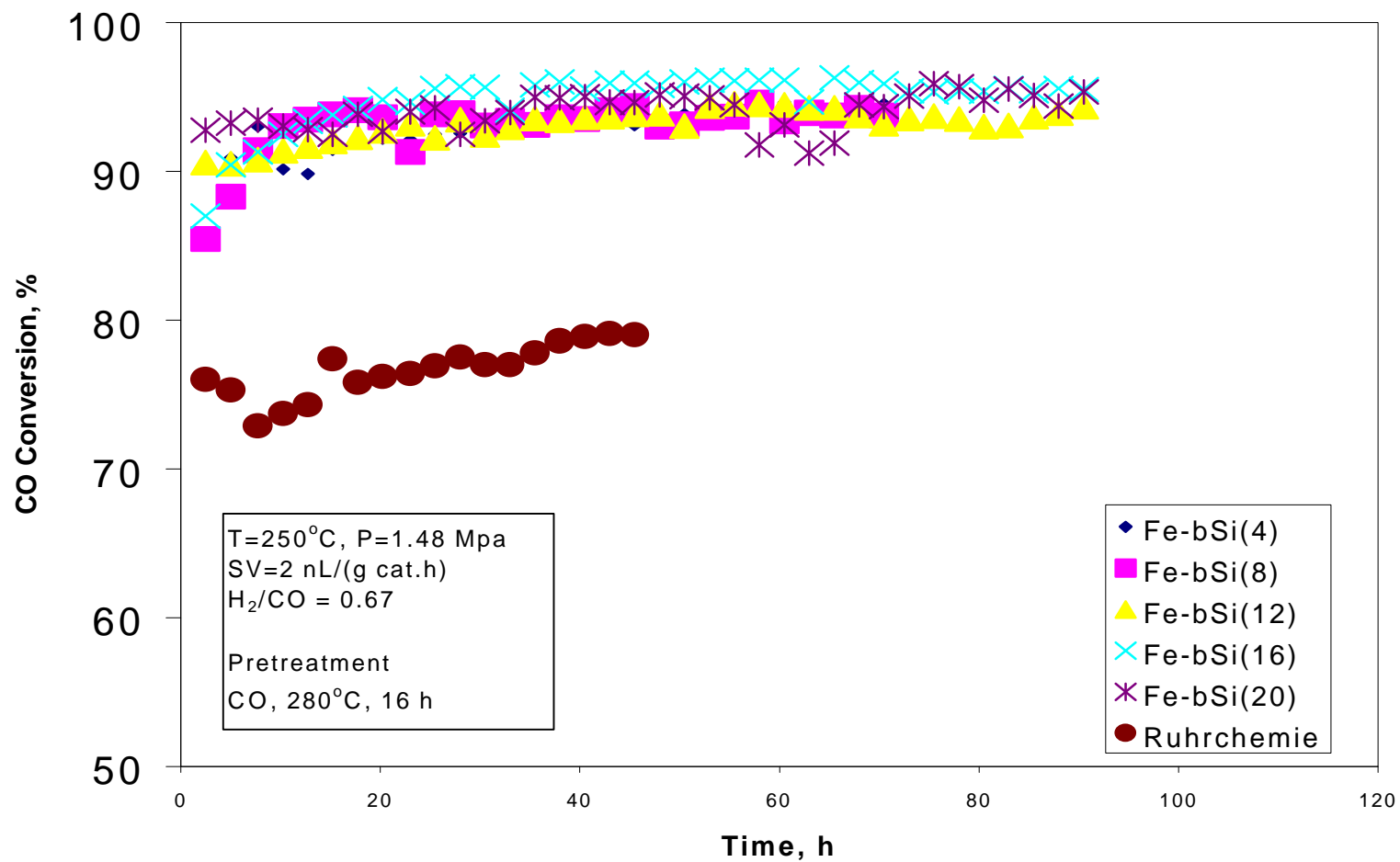


Figure 1. Variation of carbon monoxide conversion with time (binder silica)

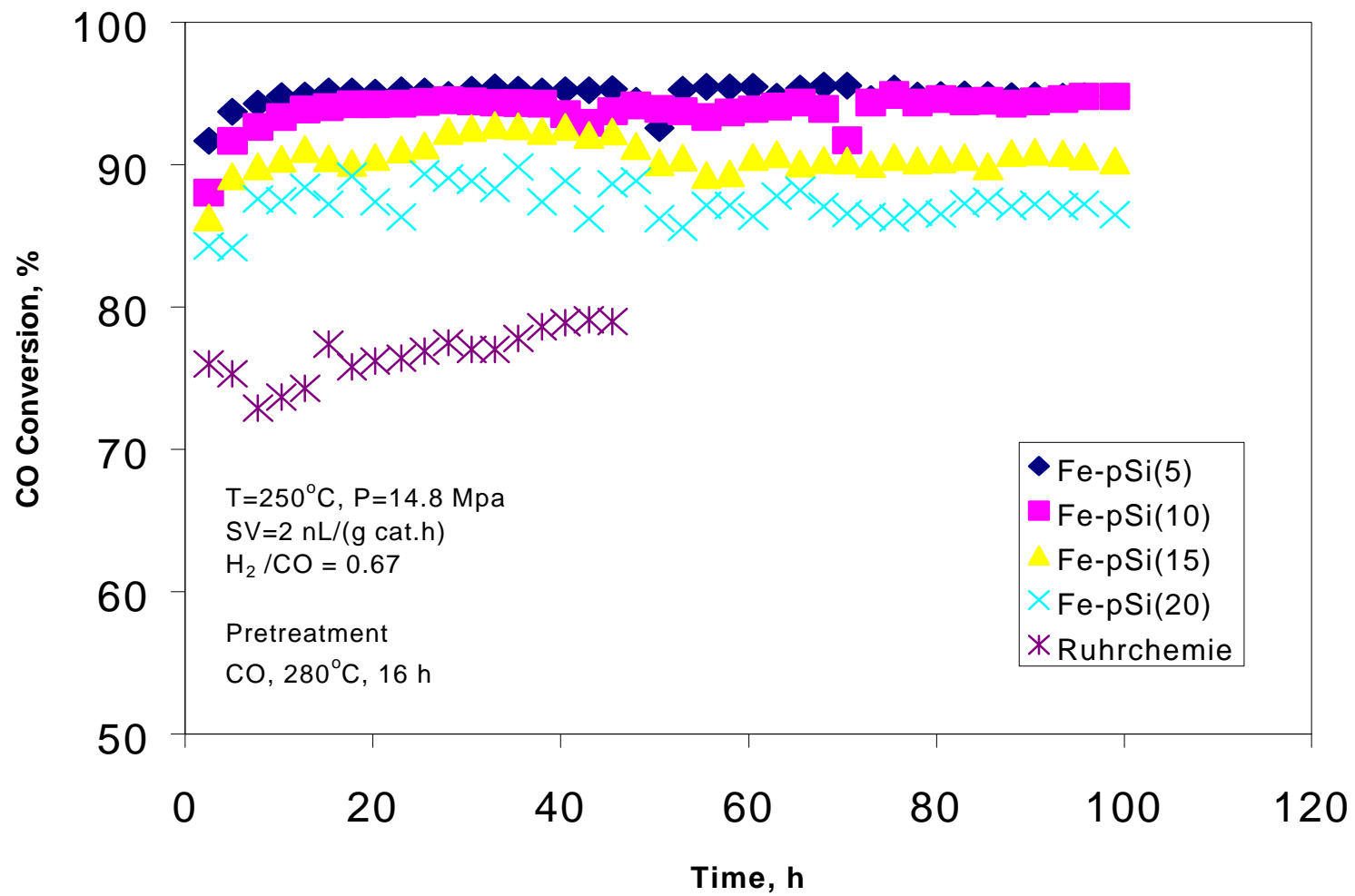


Figure 2. Variation of carbon monoxide conversion with time (precipitated silica)