Attrition Resistant Iron-Based Fischer-Tropsch Catalysts

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Principal Authors	K. Jothimurugesan James G. Goodwin,Jr. James J. Spivey Santosh K. Gangwal
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Name and Address of Submitting Organization:	Dr. K. Jothimurugesan Department of Chemical Engineering Hampton University Hampton, Virginia 23668
	Dr. James G. Goodwin, Jr.

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 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.

Two doubly promoted iron catalysts of standard Ruhrchemie composition were prepared by coprecipitation followed by spray drying (atomization). These catalysts had a particle size of 20 to 40 µm. One catalyst had no silica (HPR-23) while the other had a significant amount of silica (HPR-22). The catalyst with no silica (HPR-23) had much higher activity and selectivity. It gave 95% CO conversion at 1.48 MPa, $H_2/CO=0.67$, and 2 nL/(g of cat-h). Also, the selectivity to C_2^+ hydrocarbon was 95% and the α was around 0.9. The attrition resistance of HPR-23 was also significantly better than HPR-22. It appears that silica is detrimental to performance of a spray dried iron catalyst.

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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.

- Two iron catalysts were prepared by coprecipitation followed by spray drying. Spray drying parameters were optimized for an atomizer at the top of the chamber. These catalysts showed high conversion, high α (0.9), high stability, and reasonable attrition resistance.

During next year, we will attempt to prepare improved catalyst using a two-fluid nozzle spray configuration from the bottom of the chamber. This will help in increasing the particle size of the spray dried product to 50 to 70 µm from the current 20 to 40 µm.

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 ($H_2/CO \cong 0.5\text{-}0.7$), 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 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

Several parameters (e.g., slurry concentration, atomizer speed, feed flow rate, etc.,) were varied to get coarse particles in the spray drier. The best conditions provided the maximum particle size of about 45 µm. Under these conditions, the following iron catalysts were prepared.

Catalysts having a composition of $100Fe/5Cu/4.2K/25SiO_2$ (HPR-22) and 100Fe/5Cu/4.2K (HPR-23) by weight were prepared by precipitation technique. The iron catalysts were prepared by the precipitation of aqueous solution containing $Fe(NO_3)_3.9H_2O$, $Cu(NO_3)_2$ $2.5H_2O$, $Si(OC_2H_5)_4$ in a desired ratio by the addition of ammonium hydroxide. The resulting precipitate was then filtered and washed three times with deionized water. The potassium promoter was added as aqueous $KHCO_3$ solution to undried, reslurried Fe/Cu/Si coprecipitate. The final step was to spray dry the catalyst at 250°C in a Niro spray drier. An atomizer wheel at the top of spray chamber was used for spray drying. A number of spray drying parameters associated with spray drying were investigated (such as air pressure, temperature, slurry concentration etc.,). The catalyst was calcined at 300°C for 5 h in a muffle furnace.

Task 2. Catalyst Performance Evaluation

As can be seen from Figures 1 and 2, the iron catalysts showed high activity with a CO conversion of 86 % for HPR-22 and about 95 % for HPR-23. The run was stopped at 100 hours for HPR-23 mainly due to the plugging of the reactor and wax trap by wax. The activity and selectivity of the iron catalysts are summarized in Table 1.

Table 1. Catalyst Activity and Selectivity

Catalysts	Ruhrchemie	HPR-22				HPR-23
Time-on-stream, h	42.75	71.25	123	175	197	42.5
CO Conversion (%)	86	84.2	84.3	85.4	86	95.3
Hydrocarbon Selectivity (wt %)						
CH_4	8.3	9.8	10.8	11.6	11.8	5.5
C_2-C_4	21.3	22.9	22.3	22.6	22.4	21.0
C_5-C_{11}	14.3	14.9	14.9	16.7	14.7	14.3
C_{12}^+	56.1	52.4	52.0	49.1	51.0	59.2

The activity of HPR-22 is comparable with the standard Ruhrchemie catalysts. Particularly noteworthy is the low methane selectivity of HPR-23 at very high CO conversion, and also its high activity. It appears that removing the SiO_2 from the catalyst has a beneficial effect on activity and selectivity.

Representative carbon number product distributions for HPR-22 and HPR-23 are presented in Figure 3 and 4 in the form of Anderson-Schulz-Flory plots. The data fitted reasonably well. The chain growth parameters (alpha) values (based on C_{30} - C_{40}) are given Table 2. These are quite high alpha values.

Table 2. Alpha Values

Catalysts	Sample ID	Time-on-stream, h	ALPHA (α)

Attrition Testing

Work has begun on developing instrumentation and methodology for measuring catalyst attrition. A fluidized 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

Scanning Electron Microscopy (SEM)

The SEM micrograph was taken using a Cambridge Stereoscan 100. Figures 5 a and b show the SEM micrographs of fresh HPR-22 and HPR-23 catalysts. Figure 6 shows the SEM micrograph of reduced (CO reduction at 280°C for 16 h) HPR-22 and HPR-23 catalysts. The catalysts grains are roughly spherical and are approximately 20-40 µm in diameter.

BET Surface Area and Pore Size Distribution

The BET surface area of the catalysts were determined by N_2 physisorption using a Micromeritics Gemini 2360 system. The samples were degassed in a Micromeritics Flow Prep 060 at 120°C for 1 h prior to each measurement. The BET surface area and the pore volume of the HPR-22 and HPR-23 catalysts are shown in Table 3. The very low surface areas of used materials is due to wax in the pores.

Table 3. BET and Pore Volume Results

Catalysts	BET Surface Area, m^2/g	Pore Volume, mL/g	Average pore Diameter, Å	Bulk density, g/mL
HPR-22 (Fresh)	249	0.6663	180	0.6483
HPR-22 (Reduced)	96.7	NA	NA	NA

Temperature Programmed Reduction (TPR)

For determination of the reduction behavior and the reducibility of the catalysts, TPR experiments were carried out in Micromeritics 2705 system. A sample of close to 50 mg was dried and degassed under high purity Ar at 400°C for 1h followed by cooling to ambient temperature. Reduction was achieved under H_2/Ar gas mixture (volume ratio 5/95). Total gas flow was 40 cc/min and temperature program was from 25 to 900°C at a heating rate of 10°C/min. Hydrogen consumed by the catalyst was detected using a thermal conductivity detector (TCD) and recorded as a function of temperature.

As shown in Figure 7, the sharp peak at 320°C is due to the first step of iron reduction ($Fe_2O_3 \rightarrow Fe_3O_4$) while the smaller peak at approximately 240°C arises from the reduction of copper oxide ($CuO \rightarrow Cu$). The broad peak centered at 750°C is due to the reduction of Fe_3O_4 to metallic iron. A summary of the TPR characterization results for all the catalysts studied is given in Table 4. The higher H_2 consumption by HPR-23 indicates a greater extent of iron reduction.

Table 4. Results of TPR Measurements

Catalysts	TPR Measurements	
	Peak Max Temp, °C	H_2 Consumed µmol/g.cat
HPR-22	240, 320,750	16,114
HPR-23	240,320,750	24,386

X-Ray Diffraction (XRD)

X-ray powder diffraction patterns were obtained using a Phillips PW1800 x-ray unit using CuKα radiation. Analyses were conducted using a continuous scan mode at a scan rate of 0.05° 2θ per second. The results of the XRD analysis of the catalysts is shown Figures 8 and 9. The HPR-22 and HPR-23 “fresh” samples are identical and are composed of Fe_2O_3. The “reduced” (CO, 280°C, 16 h) samples are similar in that they both contain

CHN Analysis

Table 5 shows the results of carbon analysis used to determine the weight percent carbon as function of activation and reaction. The reduced and used HPR-23 have much more carbon than the corresponding HPR-22 samples. This result is consistent with reactor carbidization of HPR-23 as seen by XRD and the reactor wax formation by HPR-23 as seen by the F-T data.

Table 5. Carbon Content (wt %) of the Catalysts

Catalysts	Carbon Content, Wt %
HPR-22 (fresh)	0.38
HPR-22 (reduced)	7.23
HPR-22 (used)	14.67
HPR-23 (fresh)	1.37
HPR-23 (reduced)	12.59
HPR-23 (used)	31.71

Attrition Test

The attrition of the iron catalysts was tested using the ASTM-method in a 3-hole attrition tester. Table 6 shows the attrition of the iron catalysts. The ASTM test is a much more severe condition than would be experienced in a slurry bubble column reactor. HPR-23 seems to have better attrition resistance, that is reasonable for the initial attempts in the spray drier.

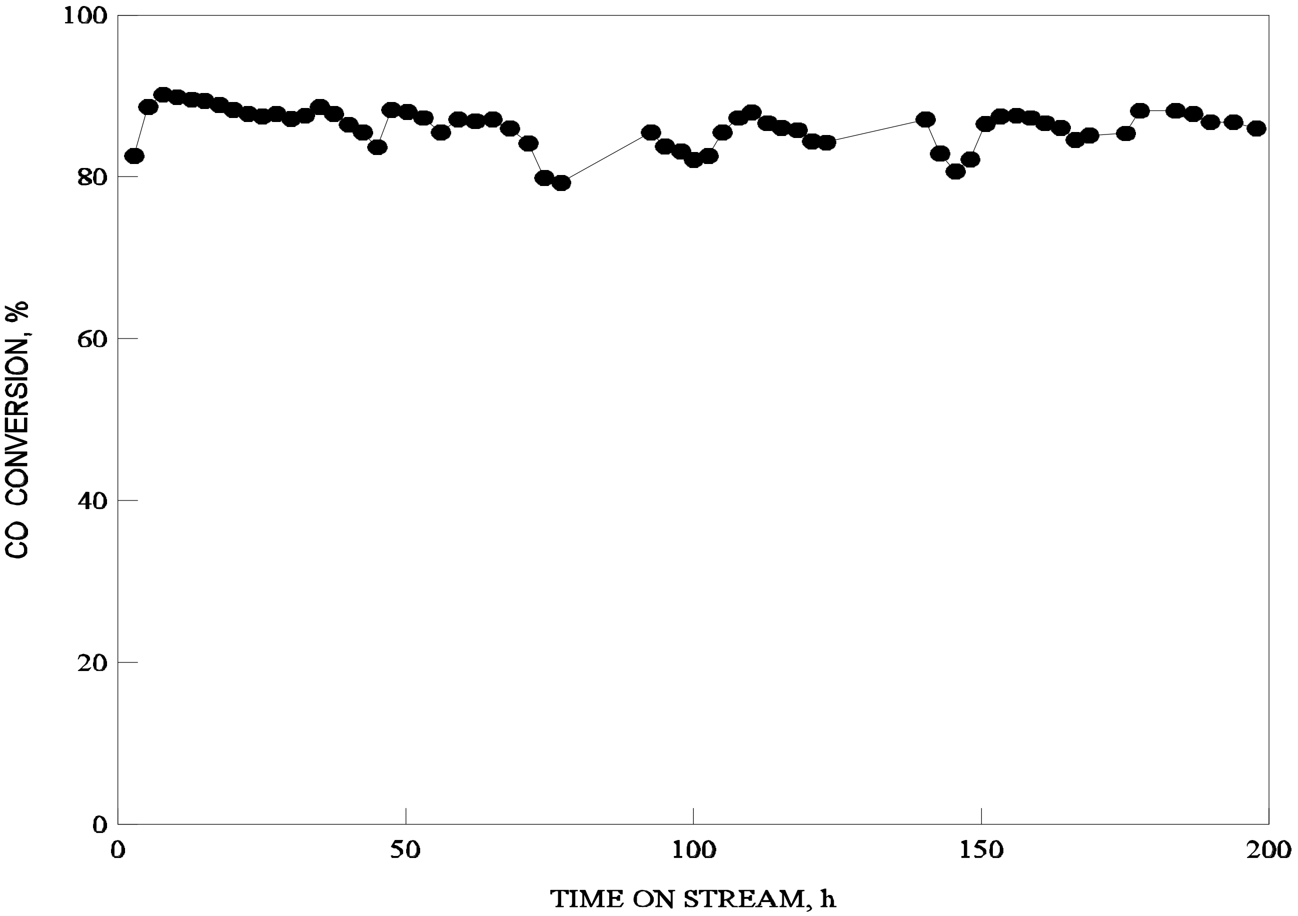
Table 6. Attrition Test of Iron Catalysts

Catalysts	3-hole attrition loss (wt %)	
	1 hour	5 hour
HPR-22	20	Plugged due to attrition
HPR-23	15	35

detrimental to performance of a spray dried iron catalyst.

FUTURE WORK

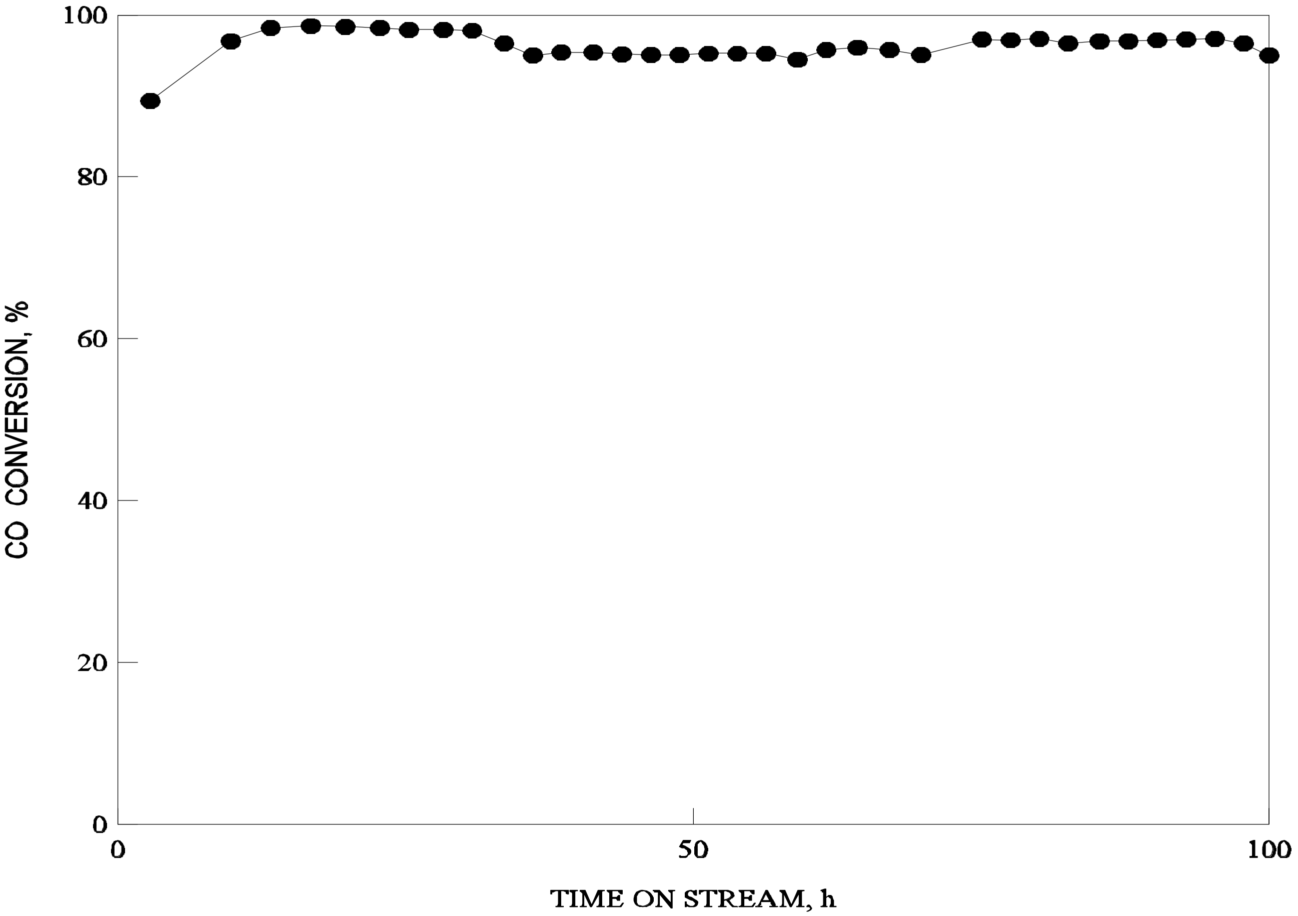
Future activities will include, preparation and testing of attrition-resistant iron Fischer-Tropsch catalyst using a two-fluid nozzle spray drier to increase the particle size to 50 to 70 µm. Activity will also include the development of an attrition procedure for small quantities of catalyst.


CO CONVERSION, %
100
80
60
40
20
0
0
50
100
150
200
TIME ON STREAM, h

Catalysts:HPR-22 (100Fe/5Cu/4.2K/25SiO_2)
T=250^{o}C
P=1.48 MPa
SV=2 nL/(g of cat-h)
H_2/CO=0.67

Pretreatment
CO, 280^{o}C, 16 h

Figure 1. Variation of Carbon Monoxide Conversion with Time-on-Stream (HPR-22)


CO CONVERSION, %
100
80
60
40
20
0
0
50
100
TIME ON STREAM, h

Catalysts:HPR-23 (100Fe/5Cu/4.2K)
T=250ºC
P=1.48 MPa
SV=2 nL/(g of cat-h)
H_2/CO=0.67

Pretreatment
CO, 280ºC, 16 h

Figure 2. Variation of Carbon Monoxide Conversion with Time-on-Stream (HPR-23)

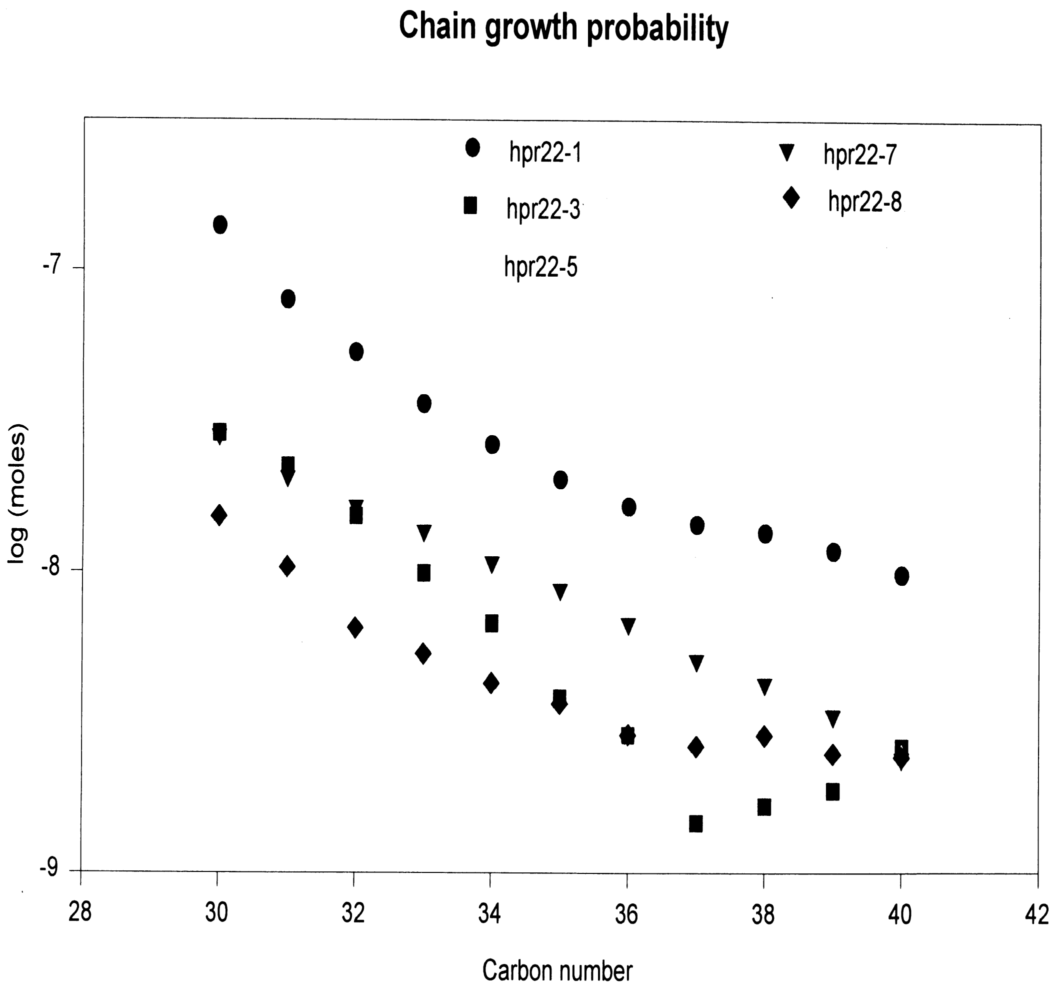


Figure 3. Carbon number product distribution for HPR-22

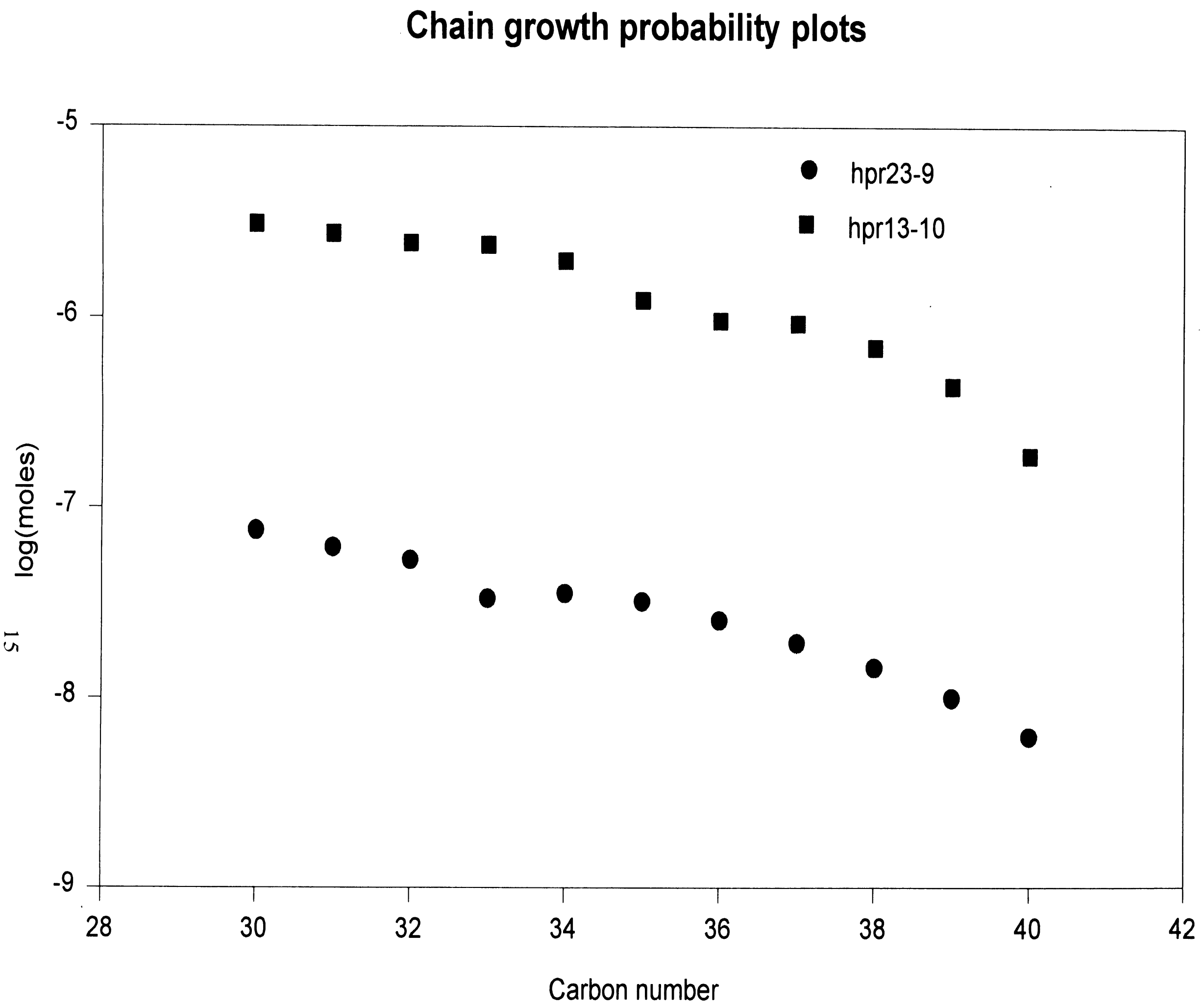
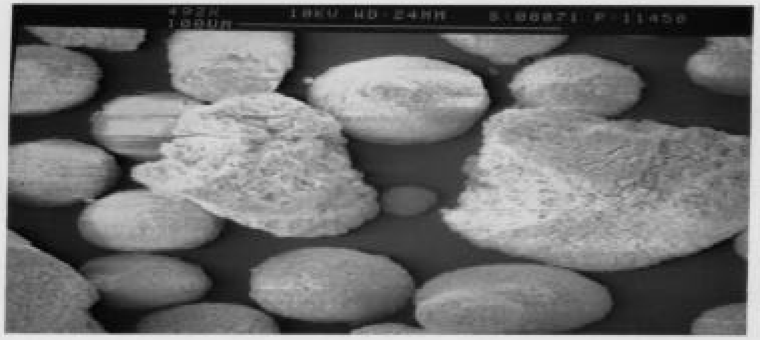
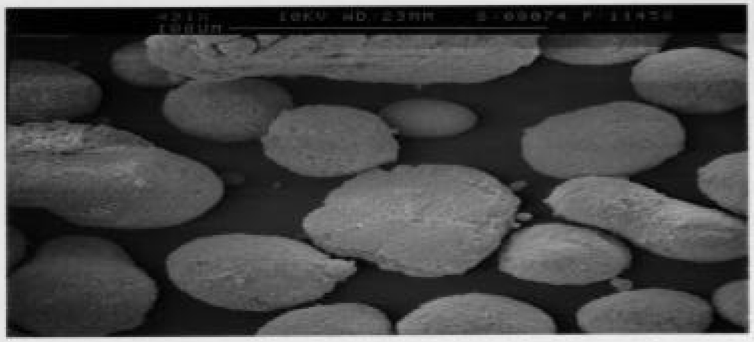


Figure 4. Carbon number product distribution for HPR-23

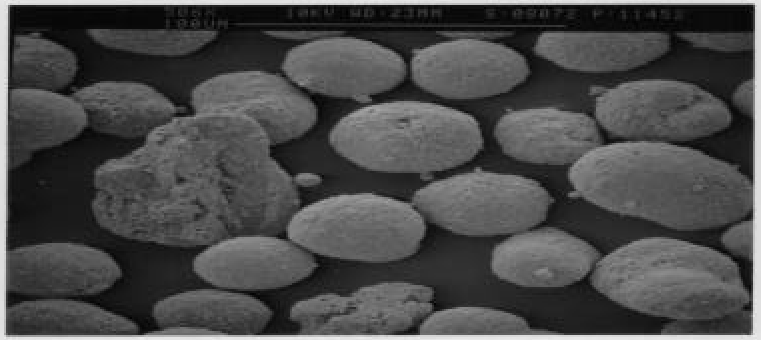


HPR-22

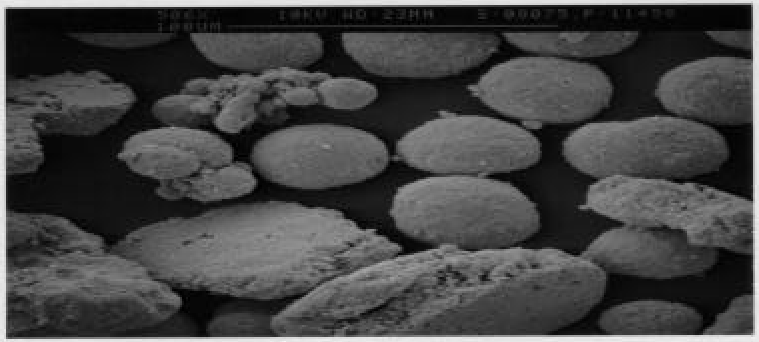


HPR-23

Figure 5. SEM micrographs of the fresh iron catalysts (a) HPR-22 (b) HPR-23



HPR-22



HPR-23

Figure 6. SEM micrographs of the reduced iron catalysts (a) HPR-22 (b) HPR-23

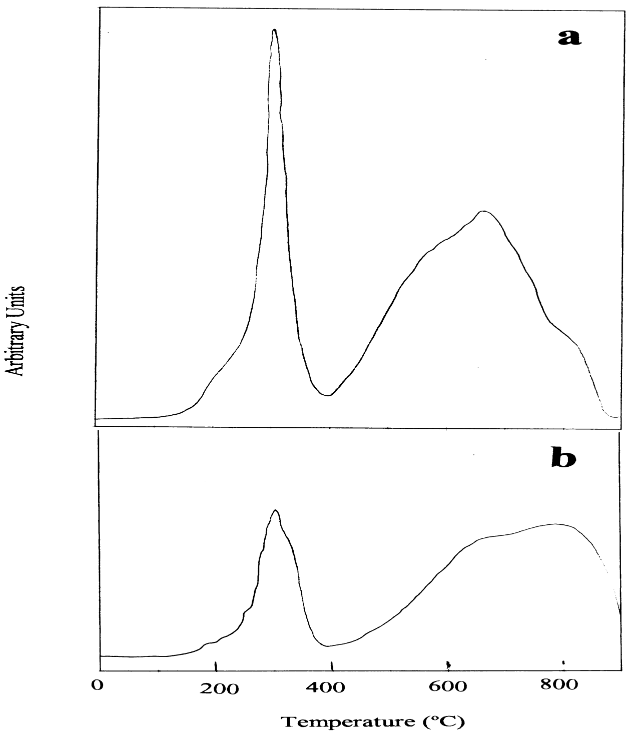


Figure 7. Hydrogen consumption during temperature-programmed reduction (a) HPR-22 (b) HPR-23.

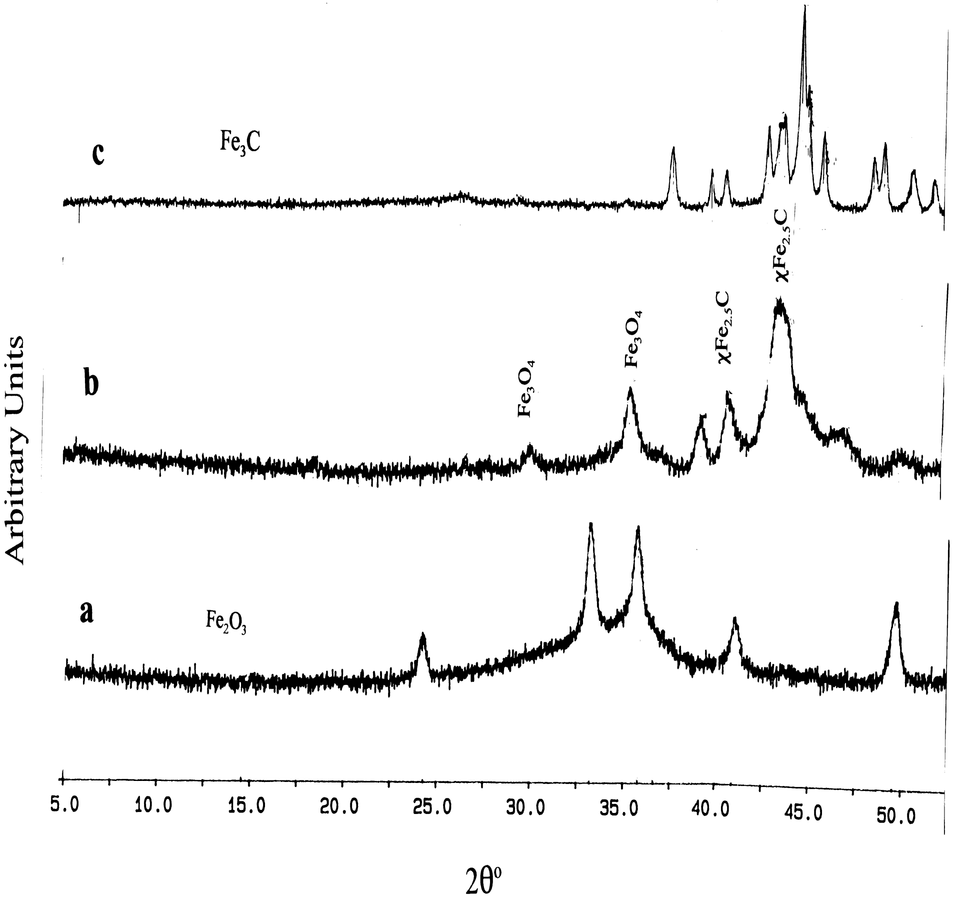
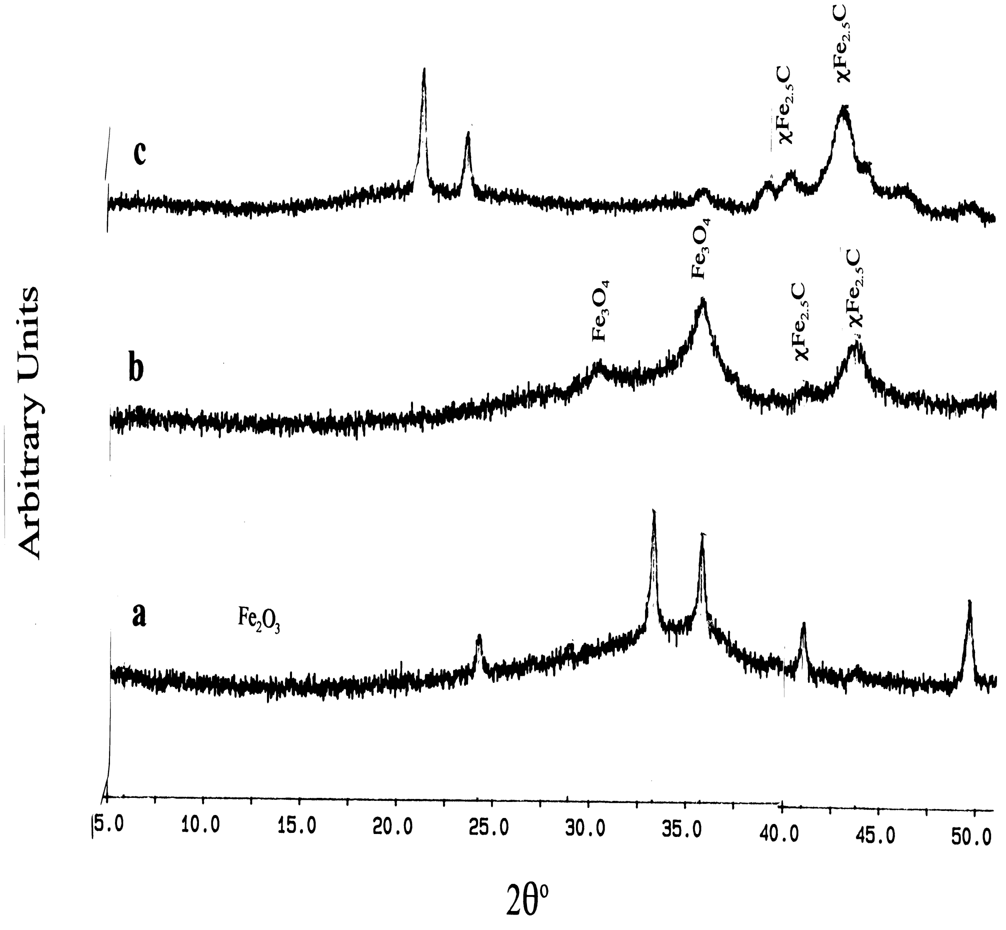


Figure 9. XRD spectra of the HPR-23 catalysts (a) fresh (b) reduced (activation in CO for 16 h at 280°C (c) used (activation in CO followed by FT synthesis for 100 h at 250°C.



Arbitrary Units
c
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χFe$_{2.5}$C
b
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Fe$_3$O$_4$
χFe$_{2.5}$C
χFe$_{2.5}$C
a
Fe$_2$O$_3$
5.0
10.0
15.0
20.0
25.0
30.0
35.0
40.0
45.0
50.0
2θ°