carbides (carbides with carbon atoms in trigonal prismatic interstices, χ -$Fe_{2.5}C$ and Fe_3C). The formation and distribution of these phases depend on the reaction conditions, reaction times, and state of the catalyst (reduced/unreduced, supported/unsupported , etc.). However, the role of each of these phases during the reaction has not been resolved. As has been discussed earlier, the various phase changes which occur for Fe during pretreatment and reaction may play a significant role in the catalyst attrition.

1.6 Project Objectives

The objectives of the project were to (1) develop a better understanding of the parameters affecting attrition resistance of Fe F-T catalysts suitable for use in SBCRs and (2) incorporate this understanding into the design of Fe catalysts having superior attrition resistance. The goal was to develop an Fe catalyst, without sacrificing FTS activity and selectivity, which can be used in a SBCR having only an internal filter for separation of the catalyst

2.0 DESCRIPTION OF PROJECT TASKS

TASK 1: Catalyst Preparation

The objectives of this task were to prepare precipitated iron catalyst with various levels of binder and precipitated silica. Several parameters were varied in the catalyst preparation to study their effect on the catalyst attrition, activity and selectivity. Section 3.1 describes the detailed catalyst preparation procedure employed in this study.

TASK 2: Catalyst Performance Evaluation

The objectives of this task were to evaluate the performance of various catalyst compositions under similar conditions in a fixed-bed microreactor. Section 3.3 describe the experimental apparatus and procedures employed throughout the project. Catalyst comparisons were carried out at the following operating conditions:

Pretreatment:	CO, 280°C, 16h
Temperature:	250°C
Pressure:	1.48 MPa
SV:	2 nL/(g of cat/h)
H_2/CO:	0.67

The catalyst was tested over a period of 100 to 125 h.

TASK 3: Catalyst Characterization

The objectives of this task were to characterize the fresh, reduced and used catalysts. Section 3.2 describes the various analytical techniques employed for catalyst characterization throughout the project. A detailed attrition study of the catalysts is reported in Appendix A.

TASK 4: Slurry Reactor Testing

The objectives of this task were to determine the catalyst performance (activity, selectivity, longevity and attrition) in a slurry reactor.

3.0 EXPERIMENTAL APPROACH

3.1 Catalyst Preparation

A standard Ruhrchemie precipitated Fe catalyst (Identified as Batch 52119) was obtained from the U.S. Department of Energy (DOE) as a benchmark catalyst. The composition of this catalyst was 100 Fe/5 Cu/4.2 K/25 SiO_2. It contained 25 parts by weight (pbw) precipitated silica. It was obtained as a 1/8 in. extrudate and was crushed to 50 to 100 μm particles prior to use.

In this study, all catalysts were prepared with the same ratio of iron, copper, and potassium (100 Fe/ 5 Cu/4.2 K) as the benchmark catalyst, but with differing levels of binder and precipitated silica. Three types of catalysts were prepared as shown in

Table 1.

Table 1. Catalyst Designation and Binder Content

Catalyst Series	Binder Silica (wt %)	Precipitated Silica (pbw)
Fe-bSi(x)	x	0
Fe-pSi(y)	12	y
Ruhrchemie	0	25
HPR	Proprietary Composition	

Catalyst preparation involved four steps: preparation of the iron, copper, and silica (when added) precursor; incorporation of potassium; addition of binder silica; and finally spray drying. Two types of silica-containing iron catalysts were prepared and the procedure is shown in Figure 1. The first series of catalyst contained binder silica but no precipitated silica and had a composition of 100Fe/5Cu/4.2 (plus binder silica). The binder silica preparation and addition method is proprietary. These catalysts were prepared by coprecipitation using an aqueous solution containing $Fe(NO_3)_3.9H_2O$ and $Cu(NO_3)_3.2.5H_2O$ in the desired Fe/Cu atomic ratio, which was precipitated by adding 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 the undried, reslurried Fe/Cu coprecipitate. To this catalyst, five different levels of binder silica were added: 4,8,12,16 and 20 %. These catalysts were then spray dried at 250°C using a large bench-scale Niro spray dryer, 3 ft diameter x 6 ft high. Finally, the spray dried catalyst was calcined at 300°C for 5 h in a muffle furnace. These catalysts are designated Fe-bSi(x), denoting that they contain x % binder silica.

The second series of catalysts contained both precipitated and binder silica. Four such catalyst were prepared containing 5,10,15 and 20 pbw precipitated silica (yielding catalysts of the composition 100Fe/5Cu/4.2K/ySiO_2, where y is 5,10,15 or 20). The precipitated silica was added as a dilute solution of $Si(OC_2H_5)_5$ to the nitrate solution described above. To each of these catalysts, 12 % binder silica was added. These catalysts are designated Fe-pSi(y). These catalysts were then spray dried and calcined in the same way as those above. Finally, HPR series of iron precipitated catalyst was prepared. The preparation of HPR series of catalyst were proprietary.

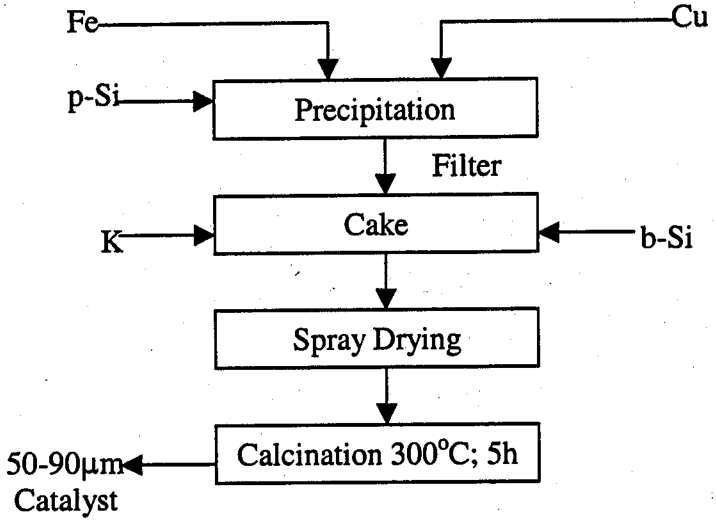

Fig: 1 Catalyst Preparation Procedure

3.2 Catalyst Characterization

Detailed physical and chemical characterization of the fresh, reduced and used catalysts were carried out using the following analytical techniques.

The BET surface area of the catalysts was 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 SEM micrograph was taken using a Cambridge Stereoscan 100. 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.

For determination of the reduction behavior and the reducibility of the catalysts, TPR experiments were carried out using a Micromeritics 2705 TPR/TPD system. A sample close to 0.2 g 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 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.

The attrition of the catalysts was measured using a three-hole air-jet attrition tester per ASTM-D-5757-95. This test method is applicable to spherically or irregularly shaped particles that range in size between 10 and 180 micrometers, have skeletal densities between 2.4 and 3.0 g/cm^3, and are insoluble in water. Particles less than 20 microns are considered fines. The heart of the system is the vertical attriting tube, a stainless steel tube 710 mm long with an inside diameter of 35 mm. There is an orifice plate attached to the bottom of this tube with three 2-mm long drilled sapphire square-edged nozzles. The nozzles are precision drilled 0.381+/- 0.005 mm in diameter. Above the attriting tube is the settling chamber, a 300-mm long cylinder with a 110-mm inside diameter. Finally, there is a fines collection assembly made up of a 250-mL filtering flask and an extraction thimble. There is additional peripheral equipment required to provide the source of humidified air (30-40% relative humidity) that the test method requires. To conduct a test, a sample of dried powder is humidified and attrited by means of three high velocity jets of humidified air. The fines are continuously removed from the attrition zone by elutriation into a fines collection assembly. The attrition index (AI) is calculated from the elutriated fines to give a relative estimate of the attrition resistance of the powdered catalyst as may be observed in commercial use.

The full test protocol calls for 45 g of a screened and dried representative sample to be humidified with 5 g of demineralized water to produce 50 g of water equilibrated sample. This sample is run in the apparatus for 5 hours, with an intermediate change of the fines filter at one hour elapsed time. The AI is based on the fines loss after 1 hour and 5 hours.

3.3 Apparatus and Procedures

The catalysts prepared were tested in a laboratory scale high-pressure and high temperature fixed bed reactor which is shown in Figure 2. Briefly, the fixed-bed reactor was constructed of 1-c.m-i.d. stainless steel tube. The iron F-T catalysts were pretreated under flowing CO at 280°C for 16 h before reaction. Following catalyst pretreatment, the reactor temperature was decreased to 50°C. CO flow was stopped, and synthesis gas was introduced at a gas space velocity of 2.0 NL/g-cat/h. The synthesis gas was a premixed gas of CO and H_2 (H_2/CO=0.67) containing 5 % Ar as an internal standard for product analysis. The reactor system was then pressurized to 1.48 MPa. The reactor temperature was then increased gradually to 250°C. This is referred to as the conditioning period. After achieving, the desired process condition 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 100 to 125 h.

The product gas was analyzed by an online Hewlett-Packard (HP) 5890 Series II plus gas chromatograph (GC), with advanced Chemstation control and capabilities. The hydrocarbons C_1-C_{15} and the oxygenates were analyzed using an HP-1 100 m x 0.25 mm x 0.5 μm capillary column and detected by a flame ionization detector (FID). The CO, CO_2, and Ar were separated by a 2.6 ft x 1/8 in. Haysep Q column detected by TCD.

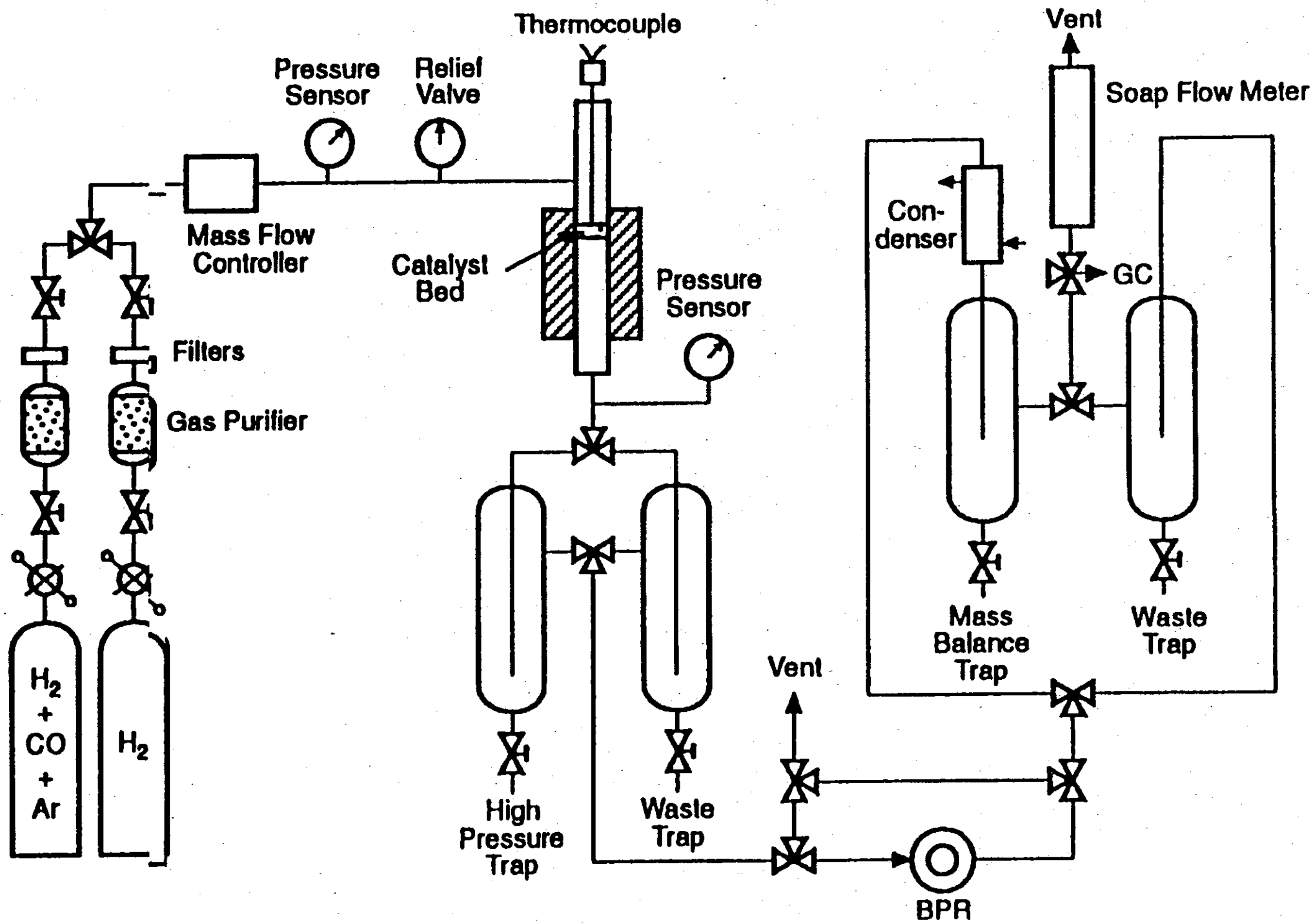

Figure 2. Schematic Diagram of the Laboratory-Scale Fixed-Bed Reactor