Title: Modified Ferrisilicates for Synthesis Gas Conversion

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Objective: Preparation and characterization of a family of modified iron silicate compositions with the zeolite ZSM-5 structure and subsequent determination of their effectiveness as synthesis gas conversion catalysts.

Abstract: Great strides have been made in the synthesis of silicate-based molecular sieves with the ZSM-5 structure containing catalytically-important elements, such as Fe, Co and Ga. The framework stability of these metal-containing molecular sieves has been found to be limited. However, such instability has been advantageously used in the selective generation of high dispersions of catalytic metal deep within the pores of the constrained-pore zeolite. The catalytic application of the iron-containing materials for synthesis gas conversion has been examined in this phase of the project. Mild hydrothermal treatment (one hour at 550°C in 100% steam) results in very high, nearly monatomic dispersion of iron within the pores of the zeolite (active iron: 1.01% by weight) which has been characterized by Mossbauer spectroscopy, magnetic susceptibility measurements, high resolution electron microscopy, as well as tested as a catalyst using the shape-selective probe reaction: the conversion of ethyltoluene to methylstryrene. With longer steam treatment (four hours at 550°C in 100% steam) more of the iron is removed from the framework and small clusters of iron particles begin to form (active iron: 1.2% by weight). Testing of both the one-hour and four-hour steam-treated materials in the syn-gas unit revealed distinctly different activities as well as selectivities. The catalyst prepared from one-hour steam treatment showed 20% conversion to hydrocarbon products with little variation over the 80 hour run time. Only the

C5 yield varied from the standard Anderson-Shulz-Flory distribution and selectivity was limited to C5 and lower hydrocarbons. The four-hour treated catalyst exhibited twice the activity with little change after 18 days on-stream with a product distribution which deviated substantially from Anderson-Shulz-Flory distribution with strong selectivity for the production of C8 and C9 hydrocarbons. Regeneration of this catalyst showed no major loss in activity and selectivity.

Experimental Conditions A schematic diagram of the experimental set-up used in this study is shown in Figure 1. The catalysts were packed in a high pressure reactor which was placed in an oven designed to keep the catalyst bed at a constant temperature. The reactor was made of 316 stainless pipe (0.75 inc ID). Gases, including He, H_2, and CO, were fed into the reactor; the outlet stream passed through a series of condensers and was analyzed by a gas chromatograph (GC).

Following a series of preliminary tests to determine the effects of reaction temperature and catalyst treatment on product gas composition, the experimental set-up was modified to improve product collection and analysis. The changes, which were made downstream of the reactor, included the installation of two product sampling lines leading to the GC, and the addition of a gas flowmeter before the inlet to the GC. As shown in Figure 2, one sampling line was heat-traced to prevent wax and heavy hydrocarbon condensation in the line, and was used to determine the distribution of products between the various hydrocarbon compounds (C1-C5 versus C5+; and olefins or aromatics versus paraffins). In the other sampling line, the effluent gas passed through a water-cooled condenser, a dririte adsorber bed, an ice-cooled condenser, and an ascarite adsorber bed, before entering the GC.

Typical reaction conditions are shown in Table 1. As shown in Figure 3, about ten grams of pelletized catalysts were usually packed in the middle of the reactor. Glass wool and a fine mesh stainless steel screen were used to support the catalyst bed and ceramic balls were used to fill the empty space. The catalysts tested include:

1. silicalite: used to establish a baseline catalytic activity for comparison with the ferrisilicate catalysts.

2. [Fe(90)H+]: the calcined, hydrogen form of the iron silicate with the ZSM-5 structure. The SiO_2/Fe_2O_3 mole ratio for this ferrisilicate was 90.

3. [Fe(90)H+; 1hr]: the ferrisilicate catalyst after one hour of hydrothermal treatment at 550°C.

4. [Fe(90)H+; 4hr]: the ferrisilicate catalyst after four hours of hydrothermal treatment at 550°C.

Before each test, the catalysts were activated with He for one hour at 500°C, at 1 atm pressure; then with H_2 for one hour at 500°C, at 1 atm. After catalyst activation, the reaction gas mixture was introduced to the reactor. Inlet gas flow rates were maintained at 200cc/min H_2 and 200 cc/min CO for an hourly space velocity of around 800 hr^{-1} and at 100 cc/min H_2 and 100 cc/min Co for a space velocity of 400 hr^{-1}. The molar ratio of CO to H_2 was equal to 1 (CO:H2=1:1).

<u>Effects of Reaction Temperature and Catalyst Treatment on Product Gas Composition</u>: Results from the preliminary test runs in the high-pressure catalytic reactor are shown in Figures 4-7. In Figure 4, the product gas composition, as analyzed by the GC, is plotted versus reaction temperature for silicalite. Silicalite was used in the reactor to establish a baseline catalytic activity for comparison with the ferrisilicate catalysts. Silicalite was also used as a filler to dilute the ferrisilicates. As shown in Figure 4, with silicalite, ethane and ethylene, which are not observed until 350°C, were produced in small quantities at 400°C. Minute amounts of propylene and propane were recorded at 350°C and 400°C. Figure 5 shows the gas composition versus temperature for the calcined ferrisilicate. Of interest here is the appearance of a noticeable amount of ethane at 350°C. Small quantities of propane,

isobutane, and butane were observed at 350°C and 400°C. There was no alkene detected with this catalyst. Figure 6 shows the gas composition versus temperature for the catalyst which had been hydrothermally-treated for one hour. With this catalyst, ethane and propane appeared at a low temperature (250°C). Ethylene, which was not detected with the calcined catalyst was recorded at 300°C. Butane and isobutane appeared at 350°C.

Figure 7 shows the effects of catalyst and catalyst treatment on the carbon number of the product hydrocarbons. At 400°C, the production of all hydrocarbons from C1 to C4 appeared higher for the hydrothermally-treated iron silicate than for the calcined iron silicate. Based on previous catalyst characterization with Mossbauer Spectroscopy, magnetic moment measurements, and compositional analysis, the hydrothermally-treated material had greater than 50% of the iron in the catalyst present as active iron, compared to about 12% active sites for the calcined ironsilicate. From these preliminary studies it appears that control over product specificity in the reaction between CO and H_2 could be achieved through modification of the iron silicates and that hydrothermal treatment induces as more active form of the iron in the material for the production of hydrocarbons.

Catalytic activity: [Fe(90)H+,1hr] has an iron concentration in the catalyst of 1.8 weight percent of which 0.77% is tied up in the framework, leaving 1.01% as catalytically-active iron located inside the pores. As shown in Table 2, where K+/Fe mole ratio indicates the fraction of iron in the iron silicate framework, the calcined catalyst has 88% of the total iron present as part of the framework and 12% as active iron located inside of the pores. The catalyst, hydrothermally treated for one hour, has 57% of the iron as active species while four hours treatment in the presence of steam shows only a slight increase in the number of active iron species from 57% to 67%.

11.5 grams of [Fe(90)H+; 1hr] were charged into the high-pressure catalytic reactor and the conversion of CO and H_2 (CO:H_2 =1:1) was studied at 1.5 MPa (230 psig), two different temperatures

(350°C and 280°C), and two different hourly space velocities (413 hr^{-1} and 825 hr^{-1}). The system was in operation for 141 hours and the following results were obtained.

The CO conversion after 84 hours of operation at the higher temperature 350°C, 1.5 MP and 413 hr^{-1}, was 21% as shown in Figure 8 and Table 3. The fraction Co conversion was calculated according to the following equation:

$$\text{Conversion} = \frac{(\text{moles of CO in} - \text{moles CO out})}{(\text{moles of CO in})}$$

Product distribution based on the n-paraffins from methane to pentane followed the Anderson-Shulz-Flory (AFS) statistics, with a progression coefficient of 0.16 as shown in Figure 9. However, a significant amount of pentene was also produced (Table 5) which added to pentane, made the total amount of C5 hydrocarbons deviate from ASF distribution and points to high alkene selectivity for C5. The Fischer-Tropsch synthesis has been characterized as a reductive oligomerization of Carbon monoxide. Thus the product distribution laws developed for cligomerization or polymerization can be applied, in which the weight fraction Wn decreases according to a geometric progression:

$$Wn = na(N-1)(1-a)2$$

where a, the progression coefficient. According to ASF statistics, a semi-logarithmic plot of Wn/n against the carbon number n is a straight line, whose slope is equal to log a. Deviations from the ASF distribution are possible if secondary reactions such as cracking on acidic supports or insertion of product olefins into the growing chain occur. More alkenes were recorded with the catalyst [Fe(90)H+,1hr] at the higher space velocity and lower temperatures as shown in Table 4.

Catalytic Activity of [Fe(90)H+,4hr]: 11.05 grams of [Fe(90)H+,4hr] were charged into the high pressure catalytic reactor and the reaction temperature was set at 35 °C. The reactant gas space velocity was 413 hr^{-1}. The system was operated for 424 hours (17.7 days) when an electrical failure forced a shutdown. The catalyst was subsequently regenerated at 500°C and 100 cc/min, first in a flow of He for one hour, than in a flow of air for four hours, a flow of He for another hour and finally a flow of H_2 for one hour. After regeneration, the reactant gas mixture (H_2:CO=1:1) was introduced into the reactor, at an hourly space velocity of 413 hr^{-1} and the reaction proceeded at a temperature of 350°C for 408 hours (17 days).

The CO conversion of [Fe(90)H+,4hr] before regeneration was 53% after 17.7 days, as shown in Table 5 and Figure 10. The conversion decreased from 49% to 30% after 12 days, but picked up again and the conversion at the end of 17.7 days of operation was 53%. The dip in conversion could be due to temperature or flow rate fluctuations within the system. After regeneration, the catalyst activity started high at around 48% and slowly decreased to 37% after 17 days on-stream, as shown in Figure 11.

Product distribution of [Fe(90)H+.4hr], before regeneration, and after 17.7 days on-stream, deviated substantially from ASF distribution and indicated strong selectivity for the production of C8 (octane) and C9 (cumene) hydrocarbons, as shown in Figure 12. Similarly, product distribution after regeneration and after 17 days, showed marked deviation from ASF statistics and strong selectivity towards C8 and C9 as shown in Figure 13. The absence of C6 compounds from the product distribution was also noted. Figure 14 summarizes the improvement in conversion observed with progressive modification of the iron silicate catalyst with steam.

Table 1: Typical Reaction Conditions for Fischer-Tropsch Synthesis, with Ferrisilicates

- Catalyst weight = 10 g
- Catalyst pretreatment = 1 hr in He flow and 1 hr in H_2 flow at 500° C, 1 atm.
- Inlet gas flow rates = 200 cc/min H_2 and 200 cc/min CO (H_2:CO = 1:1 ; hourly space velocity = 800 hr^{-1})
  100 cc/min H_2 and 100 cc/min CO (H_2:CO =1:1; hourly space velocity = 400 hr^{-1})
- Reaction Temperature = 250,350,400° C
- Reaction Pressure = 15-20 atm

Table 2: Chemical Composition of Fe(90)

	Calcined	Steamed at			
		500° C			700°
		1 hr	2 hr	4 hr	4 hr
Wt % K	1.10	0.53	0.41	0.38	0.01
K^+/Fe mole ratio	0.88	0.43	0.33	0.31	0.01

Wt % Fe = 1.78; Wt % Si = 41.1

Table 3: CO Conversion with [Fe(90)H+,1hr]

Time on stream	CO in	CO out	Conversion
12	0.00286	0.00224	0.217
22	0.00286	0.00233	0.185
46	0.00286	0.00236	0.175
71	0.00286	0.00227	0.206
84	0.00286	0.00226	0.210

Table 4: Hydrocarbon Mole Fraction
in Product Gas of Fischer-Tropsch Synthesis
with [Fe(90)H+,1hr]

Time From Start hr	Temp C°	Space Velocity hr^{-1}	Mole Fractions								
			Methane	Ethylene	Ethane	Propylene	Propane	Butene	Butane	Pentene	Pentane
12	350	413	0.916	--	0.0619	--	0.0162	--	0.0020	0.0012	0.0004
22	--	--	0.912	--	0.0665	--	0.0192	--	0.0024	--	--
46	--	--	0.901	--	0.0735	--	0.0268	--	0.0028	0.0016	0.0006
71	--	--	0.905	--	0.0719	--	0.0204	--	0.0025	--	--
84	--	--	0.908	--	0.0677	--	0.0192	--	0.0024	0.0019	0.0005
93	350	825	0.874	0.0417	0.0598	0.0046	0.0154	--	0.0025	0.0016	0.0004
99	--	--	0.875	0.0414	0.0605	0.0037	0.0150	--	0.0020	0.0015	0.0004
105	--	--	0.874	0.0417	0.0612	0.0035	0.0151	--	0.0020	0.0014	0.0004
110	--	--	0.874	0.0423	0.0613	0.0034	0.0150	--	0.0018	0.0016	0.0004
117	280	825	0.984	--	0.0120	0.0012	0.0023	--	0.0003	--	--
140	--	--	0.938	0.0376	0.0163	0.0033	0.0037	0.0008	0.0006	--	--

Table 5: Co Conversion with [Fe(90)H^+,4hr]

Time From Start (day)	(Co)in mol/min	(Co)out mol/min	Conversion
(Before Regeneration)			
1	0.002679	0.001489	0.44
4		0.001572	0.41
5		0.001772	0.34
6.2		0.001763	0.34
11		0.001878	0.30
12		0.00190	0.29
15		0.00144	0.46
16		0.001306	0.51
17		0.001228	0.54
17.7		0.001269	0.53
(After Regeneration)			
4	0.002679	0.001383	0.48
9		0.001522	0.43
10		0.001526	0.43
11		0.001650	0.38
12		0.001693	0.37
13		0.001583	0.41
14		0.001915	0.28
15		0.001753	0.34
16		0.001866	0.30

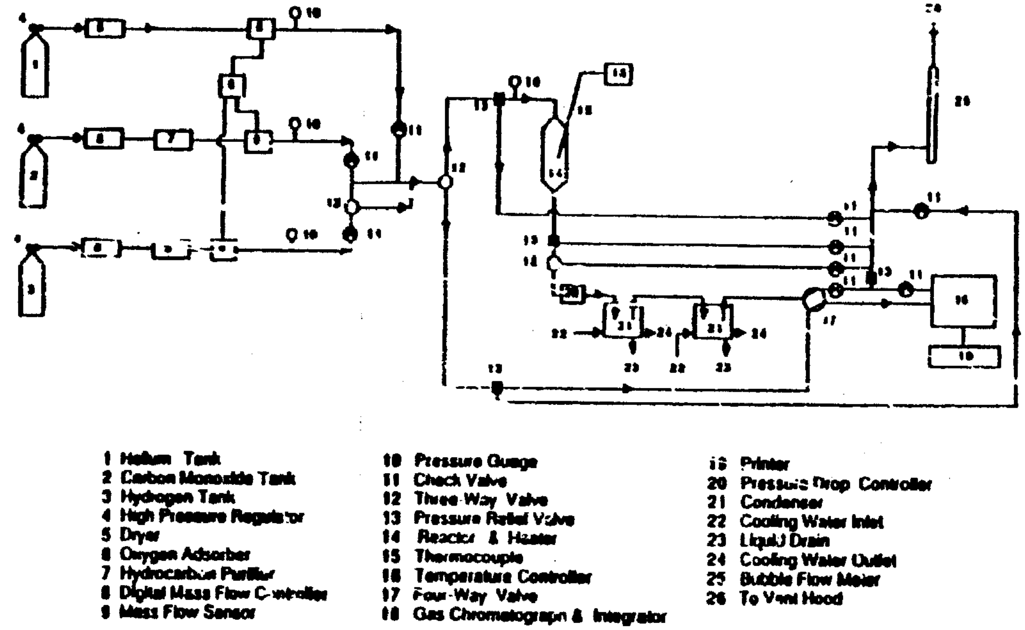

Figure 1: Flow Diagram of Reactor System for Syn-Gas Conversion

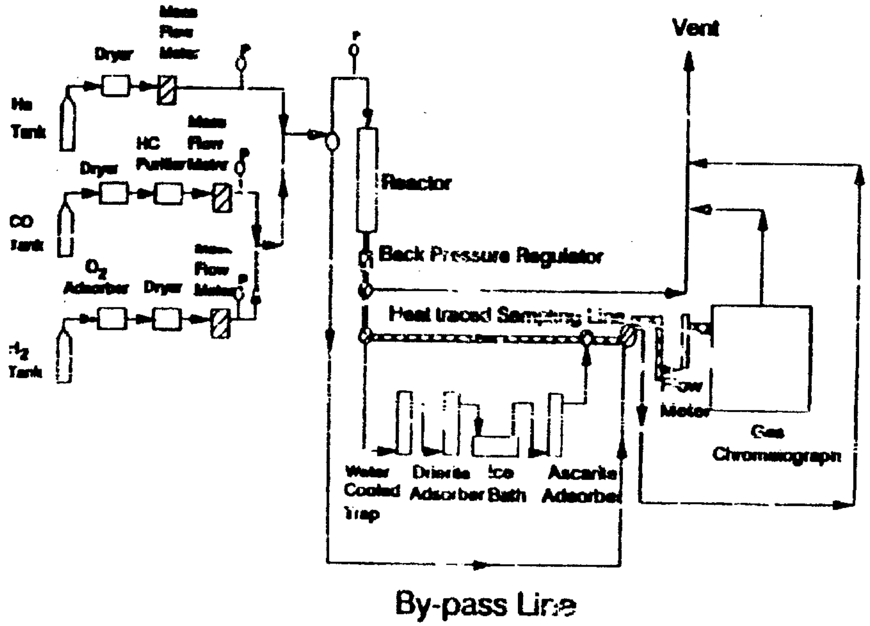

Figure 2: Schematic Flow Diagram of High Pressure

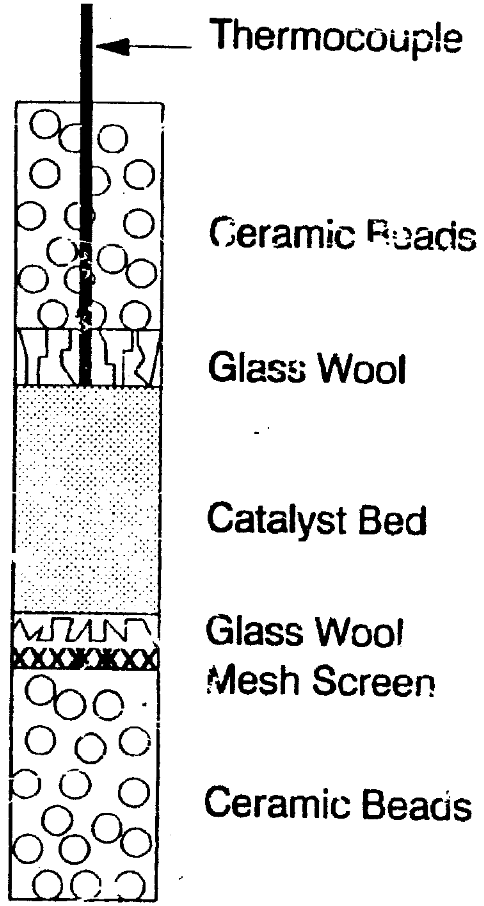

Figure 3: Schematic Diagram of the Packed-bed Reactor

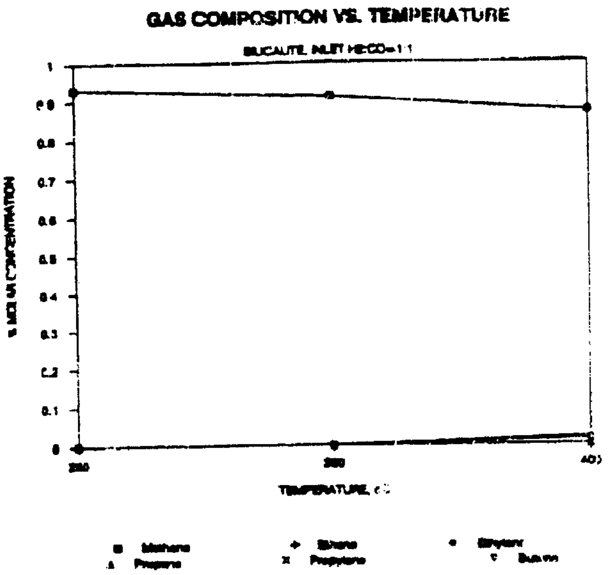

FIGURE 4 - Product gas composition versus temperature for silicalite

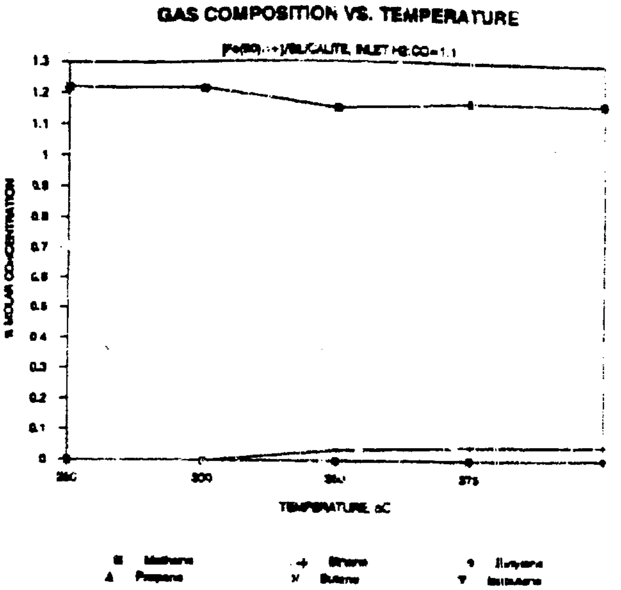

FIGURE 5 - Product gas composition versus temperatur . for [Fe(90)H+]

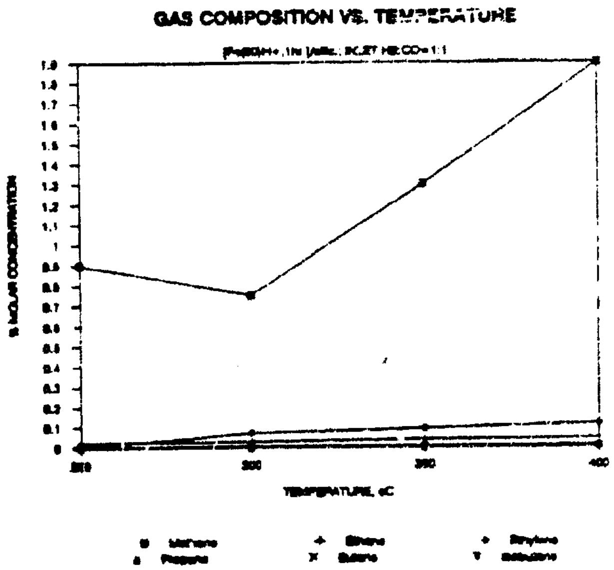

FIGURE 6 - Product gas composition versus temperature for [Fe(90)H+, 1 hr.]

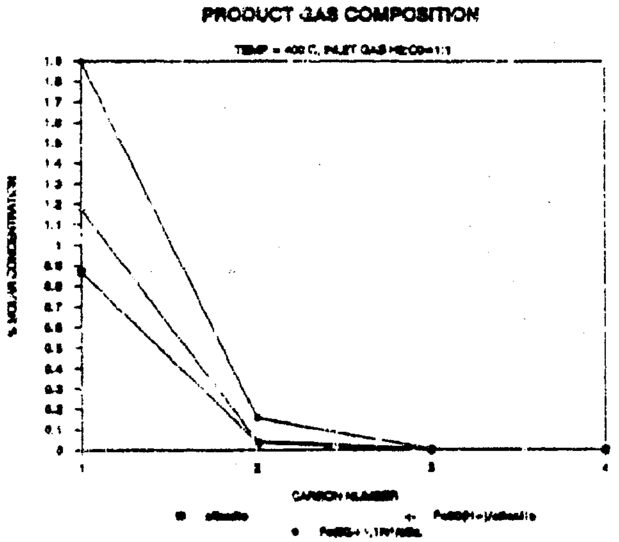

FIGURE 7 - Effects of catalyst and catalyst treatment on product gas composition

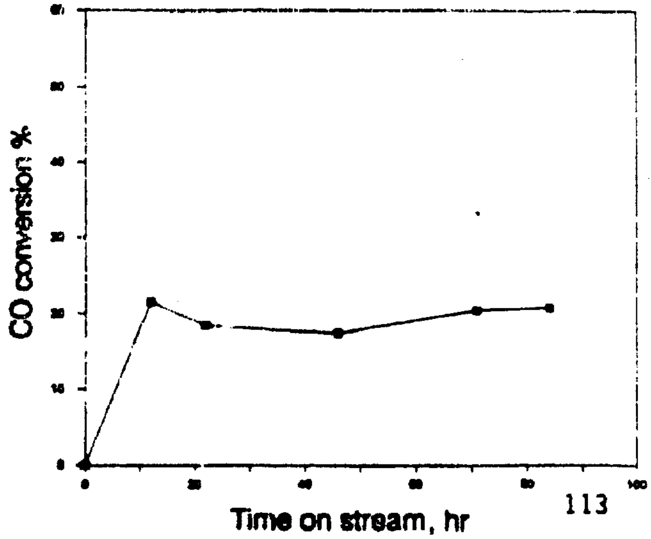

Figure 8 : CO conversion with [Fe(90)H+,1hr]

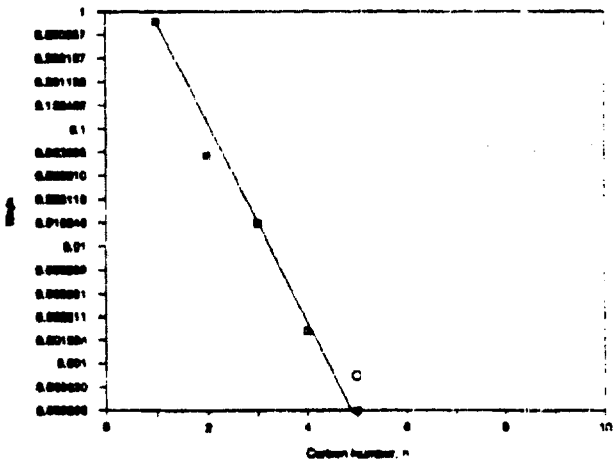

Figure 9 : ASF Product Distribution, with [Fe(90)H+,1hr]

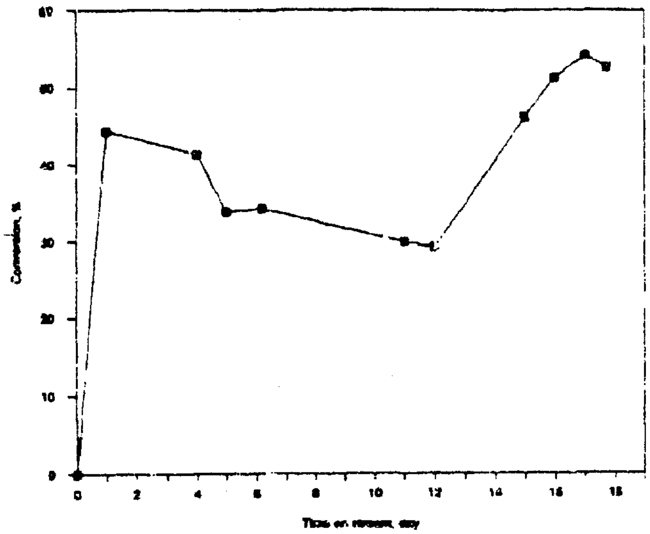

Figure 10 : CO conversion, with [Fe(90)H+,4hr] before regeneration

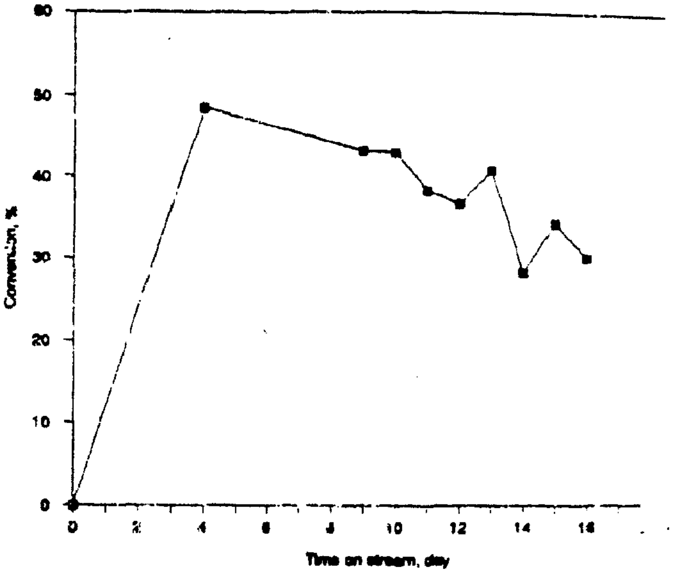

Figure 11 : CO Conversion, with [Fe(90)H+,4hr] after regeneratic

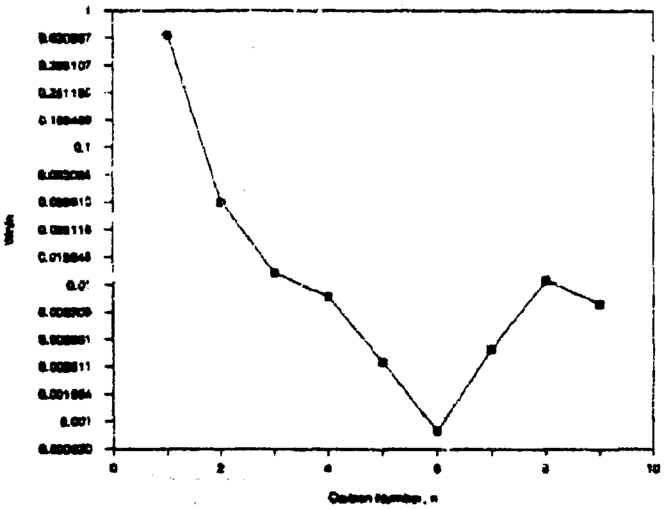

Figure 12 : ASF Product Distribution, with [Fe(90)H+,4hr]

Before Regeneration

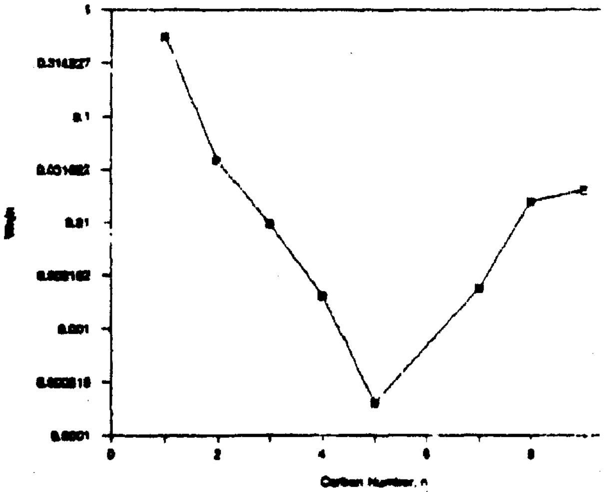

Figure 13 : ASF Product Distribution with [Fe(90)H+,4hr]

After Regeneration

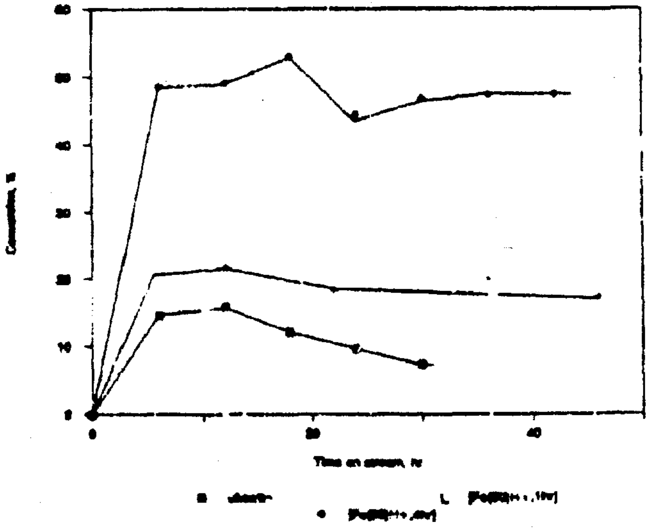

Figure 14 : Effect of Active Iron Concentration on CO conversion of Ferrisilicates