

Report 5

INVESTIGATION OF SULFUR-TOLERANT CATALYSTS FOR  
SELECTIVE SYNTHESIS OF HYDROCARBON LIQUIDS FROM  
COAL-DERIVED GASES

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## Introduction

Although cobalt and iron-containing catalysts for the Fischer-Tropsch synthesis were developed several decades ago, their selectivity, activity, and stability properties leave much to be desired. Previous investigations were generally conducted on poorly characterized catalysts operating in heat/mass transfer-influenced regimes, and the effects of catalyst properties, promoters, supports, and additives were not well-defined.

Our work is a systematic investigation of catalyst metal-additive and metal-support interactions and their effects on activity, selectivity, and resistance to sulfur poisoning in Fischer-Tropsch synthesis. This investigation of catalysts for selective synthesis of hydrocarbon liquids began about 5 years ago. The major objectives of the project are three-fold:

First, to investigate the effects of supports and of sulfur, nitrogen, and boron additives on the activity and selectivity of cobalt and iron catalysts and their sulfur tolerance in  $\text{CO}/\text{H}_2$  synthesis.

Second, to correlate these activity/selectivity and sulfur tolerance properties with measurable properties of the active phases such as oxidation state, dispersion, and adsorption capacities.

Third, with this basic understanding, to seek more active, sulfur tolerant iron and cobalt catalysts for selective synthesis of premium hydrocarbon feedstocks.

The work is divided into three tasks. Task 1 is the preparation and characterization of promoted and unpromoted, supported and unsupported cobalt and iron synthesis catalysts. The second is the measurement of synthesis activity/selectivity properties of these catalysts under reaction conditions. The third is measurement of deactivation rates during synthesis in a reaction mixture containing dilute  $\text{H}_2\text{S}$ .

## Catalyst Preparation

Figure 1 shows the 28 catalysts to be prepared and characterized. This experimental grid was designed to systematically investigate effects

of alkali promoters and boron, nitrogen, and sulfur additives and the effects of five support materials, including the novel zeolites ZSM-5 and Silicalite.

The preparation of boride promoted catalysts has been refined in our laboratory, and utilizes the reactions shown in Figure 2. Since much of the borohydride is lost to hydrolysis (top reaction), a fourfold excess of sodium borohydride is used to reduce the metal salts to the dimetal boride (bottom reaction). A subsequent washing of the catalyst to free it of sodium impurities follows.

#### Catalyst Characterization

Catalyst characterization plans involve a comprehensive, multitool approach to the measurement of basic physical, chemical, and surface properties, and include adsorption measurements, temperature programmed desorption, and analysis by Moessbauer spectroscopy.

As outlined in Figure 3,  $H_2$  and  $CO$  chemisorption will be performed on all catalysts to determine active metal surface areas.  $CO_2$  adsorption is used to measure the concentration of alkali promoters on the catalyst surface.  $O_2$  titration gives oxidation states of the metals, and Moessbauer spectroscopy aids in identification of the phases present in the catalyst. Temperature programmed desorption of adsorbed reactants yields valuable information on the effects of promoters, additives, and supports on catalyst adsorption properties.

Our chemisorption experiments are carried out in a standard volumetric apparatus. The system is capable of  $10^{-6}$  torr and is equipped with a mercury driven gas buret and manometer. Adsorption isotherms are measured using 1 g samples of catalyst powders.

The samples are loaded into a pyrex reactor cell shown in Figure 4. Once loaded, the catalyst may be reduced in  $H_2$ , undergo chemisorption measurements, and be tested for activity without being reexposed to air.

The results of chemisorption measurements on several iron catalysts are shown in Figure 5. As expected, the 3% catalyst is less reducible and more dispersed than the higher loading 15% catalyst. By dispersion is meant the percent of metal atoms exposed to the catalyst surface. Dispersions are very small, in the range of 1 to 4%. The effect of

potassium promotion may be seen by comparing the 15% Fe/SiO<sub>2</sub> catalyst to the 15% FeK/SiO<sub>2</sub> catalyst results. As can be seen in the table, CO<sub>2</sub> adsorption increased substantially, at the expense of CO and H<sub>2</sub> adsorption. From this data, an apparent surface enrichment of K<sub>2</sub>O is nearly 25 times its bulk concentration of 3%. CO/H adsorption ratios of Fe/SiO<sub>2</sub> are near 0.4, while potassium promotion lowers this ratio to 0.3. Fe/ZSM-5 and Fe/Silicalite evidence particularly low CO/H ratios. Borided iron, while less disperse than the unborided catalysts, are sufficiently disperse to evidence similar activity, as will be seen later.

Studies of silica-supported cobalt catalysts have also been conducted. Figure 6 shows that cobalt catalysts are generally more disperse than the corresponding iron catalysts. CO/H ratios are very nearly 1 in the unpromoted catalysts. The percent reduction to metal ranges from 30 to 50% for the cobalt catalysts studied. CO/H ratios for borided catalysts are much lower than the pure cobalt catalysts.

Mossbauer spectroscopy shows additional evidence for metal-support interaction. Figure 7 indicates the presence of Fe<sup>2+</sup> in the 3% Fe/SiO<sub>2</sub> catalyst, with metal-support interaction indicated by the low recoil-free fraction. In contrast, as shown in Figure 8, the 15% Fe/SiO<sub>2</sub> catalyst spectrum shows the presence of Fe<sub>2</sub>O<sub>3</sub>, mainly in small particles. As expected, unsupported Fe consists of large particles of Fe<sub>2</sub>O<sub>3</sub>, as shown in Figure 9.

H<sub>2</sub> reduction for 36 hours at 723 K reduces the 3% Fe/SiO<sub>2</sub> catalyst only about 30%, in excellent agreement with O<sub>2</sub> titration data (Figure 10). The 15% Fe/SiO<sub>2</sub> catalyst is reduced nearly 100%, with the disappearance of the oxide peaks in the center of the spectrum. (Figure 11). The testing of the catalysts in a mixture of H<sub>2</sub> and CO in the reactor yields the commonly observed hexagonal carbide spectrum of Figure 12.

#### Activity/Selectivity Measurements

Once the catalysts have been characterized, they are tested in a laboratory reactor to determine activity/selectivity properties. The experiments outlined in Figure 13 have been designed to isolate, as much as possible, the effects on selectivity and activity of metal, metal loading, metal-support interactions, promoters and additives, including

sulfur, and the effects of increasing pressure from 1 atmosphere to near industrial conditions at 25 atmospheres.

A laboratory microreactor system has been made fully operational. The schematic in Figure 14 outlines its major features, which include gas purification by molecular sieve and deoxo units, a tubular furnace, a pair of liquid and wax traps, and a gas chromatographic analysis. The system is capable of 30 atmospheres, and is equipped with automatic flow controllers. Analysis is performed by a Hewlett-Packard 5834A gas chromatograph which is fully time-programmable. In addition, cryogenic operation to  $-50$  C is available by utilizing a liquid nitrogen feed to the oven space. This greatly enhances analysis of low-boiling hydrocarbon species.

The analysis of Fischer-Tropsch hydrocarbon products is a difficult problem, but simplified by our use of online gas sampling combined with capillary column operation. Hydrocarbons are eluted in nearly boiling point order, as typified by the chromatogram of Figure 15, providing an excellent "fingerprint" of the reaction products. Fixed gases, including  $H_2$ ,  $N_2$ ,  $CO$ ,  $CO_2$ ,  $CH_4$ ,  $C_2H_6$ ,  $C_2H_4$ ,  $E_2O$ , and others, are analyzed on a 6-foot Carbosieve B packed column. The total analysis requires about 1 hour.

Before analyzing activity/selectivity data, the catalysts are pretreated in the reactant mixture at reaction temperature for 12 to 20 hours until steady state is reached. Changes in selectivity are due to carbiding of surfaces and the filling of catalyst pores with an inventory of liquids. When steady state is reached, rates and product distributions are considered reliable for comparisons. Conversions are limited to less than 10% and finely crushed powders are used to avoid mass and heat transfer limiting reaction regimes.

Turnover numbers for several iron and cobalt catalysts are shown in Figure 16. As can be seen, the turnover numbers for 5 and 15%  $Fe/SiO_2$  are the same within a factor of 2, while the CO turnover number for 15%  $Co/SiO_2$  is a factor of 20 times larger than that of 5%  $Co/SiO_2$ , suggesting the effects of metal-support interaction. The borided catalysts are also generally less active than their unborided counterparts. Potassium addition had little effect on activity, while the zeolite catalysts were

a factor of 10 less active than silica-supported iron. In all cases, cobalt catalysts are an order of magnitude more active than their iron catalyst counterparts.

Product selectivities for iron catalysts are summarized in Figure 17. It is evident that decreasing  $H_2/CO$  ratio from 2 to 1 increased the average molecular weight of the product by decreasing methane production. Also,  $CO_2$  selectivity increased significantly. The 3% Fe/SiO<sub>2</sub> catalyst produced more methane and a lower molecular weight product than the 15% Fe/SiO<sub>2</sub> catalyst. The addition of potassium to the 15% iron catalyst shifted carbon numbers of the product from methane and ethane to the C<sub>5+</sub> range.  $CO_2$  production also increased. Iron boride catalysts produced hydrocarbon distributions similar to unborided catalysts, with a tendency toward high C<sub>5+</sub> yields and low  $CO_2$  make. Fe/Silicalite produced high olefin yields, especially in the low carbon numbers.

Similar data for three cobalt catalysts are shown in Figure 18. Cobalt/silica catalysts produce higher molecular weight products than iron catalysts at 1 atm pressure. The high yield of alcohols from several unsupported cobalt boride catalysts is especially interesting, along with the unusual high selectivity to  $CO_2$  over the same catalysts.

Figure 19 shows a product selectivity plot for cobalt/silica. The very low C<sub>2</sub> yield is typical of cobalt catalysts. Figure 20 shows the same data for iron/silica. Higher C<sub>2</sub> yields are evident over iron, and the effects of the addition of potassium are shown graphically by the decrease of C<sub>1</sub> and C<sub>2</sub> fractions and increased C<sub>3+</sub> fractions.

### Sulfur Poisoning Tests

Task 3 is the measurement of the effects of dilute H<sub>2</sub>S on catalyst activity and selectivity during synthesis. During the tests, 4-6 ppm of H<sub>2</sub>S was added to the feed stream after an initial period of 24 hours in sulfur-free reactants.

The effect of sulfur on selectivity over Co/SiO<sub>2</sub> is illustrated in Figure 21. The product distribution of the partially poisoned catalyst shows a marked shift towards higher molecular weight products. This effect is maximized at about 50% activity and 50% sulfur coverage,

but then appears to diminish as sulfur coverage approaches saturation.  $\text{CO}_2$  selectivity decreases continuously with CO conversion activity. In the case of  $\text{Fe/SiO}_2$  these effects are not observed.

Figure 22 shows the normalized activity of the catalysts tested to date with increasing sulfur exposure. In the case of  $\text{Co/SiO}_2$ ,  $\text{Fe/SiO}_2$ , and  $\text{FeK/SiO}_2$ , deactivation is rapid and extensive. Apparently,  $\text{Fe/SiO}_2$  is more sulfur tolerant than  $\text{Co/SiO}_2$ , and the addition of  $\text{K}_2\text{O}$  does lengthen the lifetime of  $\text{Fe/SiO}_2$  catalysts. Particularly important is the extended stability of borided iron in sulfur-containing reactants. Little deactivation was observed, even after 5 days exposure to 6 ppm  $\text{H}_2\text{S}$ .

### Summary and Conclusions

#### Task 1

1. Using techniques developed in our laboratory, it is possible to prepare adequately dispersed iron and cobalt boride catalysts.
2. Silica supported iron and cobalt catalysts evidence relatively poor metal dispersions in the range of 1 to 10%. Cobalt/silica is more dispersed than iron/silica.
3.  $\text{O}_2$  titration shows 36-hour reduction of  $\text{Fe/SiO}_2$  and  $\text{Co/SiO}_2$  catalysts in flowing  $\text{H}_2$  is adequate.
4. Because of metal-support interaction, lower loading catalysts are less reducible than higher loading catalysts.
5.  $\text{CO/H}$  adsorption ratios observed for  $\text{Fe/SiO}_2$  are near 0.4. Potassium promotion lowers this ratio to 0.5.  $\text{CO/H}$  adsorption ratios for cobalt are near 1.
6.  $\text{CO}_2$  chemisorption has shown that  $\text{K}_2\text{O}$  is concentrated on the surface of promoted iron catalysts to as much as 30 times its bulk concentration.
7. Moessbauer spectroscopy of iron catalysts gives evidence for metal-support interactions.

#### Task 2

1. A microreactor system and analysis scheme for  $\text{C}_1$  to  $\text{C}_{30}$  hydrocarbons and fixed gases has been made fully operational.

2. Cobalt catalysts produce a higher molecular weight product and are more active than corresponding iron catalysts at 1 atm.
3. Decreasing  $H_2/CO$  ratio from 2 to 1 causes the average molecular weight of the hydrocarbon product to increase by reducing methane yield.
4. Potassium promotion of  $Fe/SiO_2$  shifted carbon numbers to higher molecular weights at the expense of  $C_1-C_2$  production.
5. Iron catalysts produce larger amounts of  $C_2$ , alcohols, and olefins relative to cobalt catalysts.
6. Borided catalysts produce product distributions similar to unpromoted catalysts, though  $CoB$  shows promise as an alcohol producer.

#### Task 3

1.  $H_2S$  poisoning of  $Co/SiO_2$  causes a shift to higher molecular weights in the product. This does not occur with  $Fe/SiO_2$ .
2. Potassium extends the life of  $Fe/SiO_2$  in the presence of  $H_2S$ .
3.  $FeB$  is extremely resistant to poisoning by  $H_2S$ .
4.  $Fe/SiO_2$  is more  $H_2S$  poison resistant than  $Co/SiO_2$ .



CATALYST PREPARATION PLANS

<u>Metal-Support Combination</u>	<u>Unpromoted</u>	<u>Promoted</u>		<u>Additive Pretreatments</u>			<u>No. Catalysts</u>
		<u>K<sub>2</sub>O</u>	<u>ZnO</u>	<u>B</u>	<u>N</u>	<u>S</u>	
Fe (Unsupported)	X	X		X	X	X(2) <sup>c</sup>	6
Co (Unsupported)	X			X		X	3
Fe/SiO <sub>2</sub>	X(2) <sup>a</sup>	X <sup>b</sup>	X <sup>b</sup>	X	X <sup>b</sup>	X(3) <sup>b,c</sup>	9
Co/SiO <sub>2</sub>	X(2) <sup>a</sup>	X <sup>b</sup>		X			4
Fe/Al <sub>2</sub> O <sub>3</sub>	X						1
Fe/ZSM-5	X						1
Fe/Silicalite	X	X				X <sup>d</sup>	3
Fe/C	X						1
						Total	28

<sup>a</sup> 3 and 15 wt. % Loadings

<sup>b</sup> 15 wt. % Loading Only

<sup>c</sup> Unpromoted and Promoted

<sup>d</sup> Promoted Only

FIGURE 1

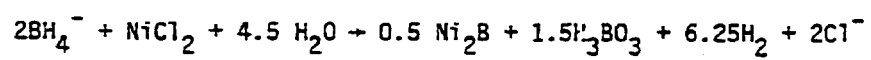
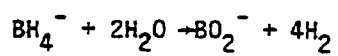


FIGURE 2

TASK 1 EXPERIMENTAL PLAN

DESCRIPTION	PURPOSE OF STUDY	CATALYSTS
A. H <sub>2</sub> and CO Chemisorption Measurements	Determine Active Metal Surface Areas	All Catalysts
B. CO <sub>2</sub> Chemisorption Measurements	Determine Alkali Promoter Surface Concentrations	Fe, FeK, Fe/SiO <sub>2</sub> , FeK/SiO <sub>2</sub> , Fe/Silicalite FeK/Silicalite, FeZ/SiO <sub>2</sub> , Co/SiO <sub>2</sub> , CoK/SiO <sub>2</sub>
C. O <sub>2</sub> Titration Measurements	Determine Degree of Metal Reduction	All Catalysts
D. Moessbauer Spectroscopy	Determine Oxide, Carbide, Nitride Phase Formation Under Preparation and Reaction Conditions	Fe Catalysts
E. Temperature Programmed Desorption	Determine Effects of Promoters and Supports on Reactant Adsorption	Fe/SiO <sub>2</sub> , Fe/Al <sub>2</sub> O <sub>3</sub> , Fe/Silicalite, Fe/ZSM-5, Fe/C, FeK/SiO <sub>2</sub> , FeZ/SiO <sub>2</sub> , FeN/SiO <sub>2</sub> , FeS/SiO <sub>2</sub> , Co/SiO <sub>2</sub>

FIGURE 3

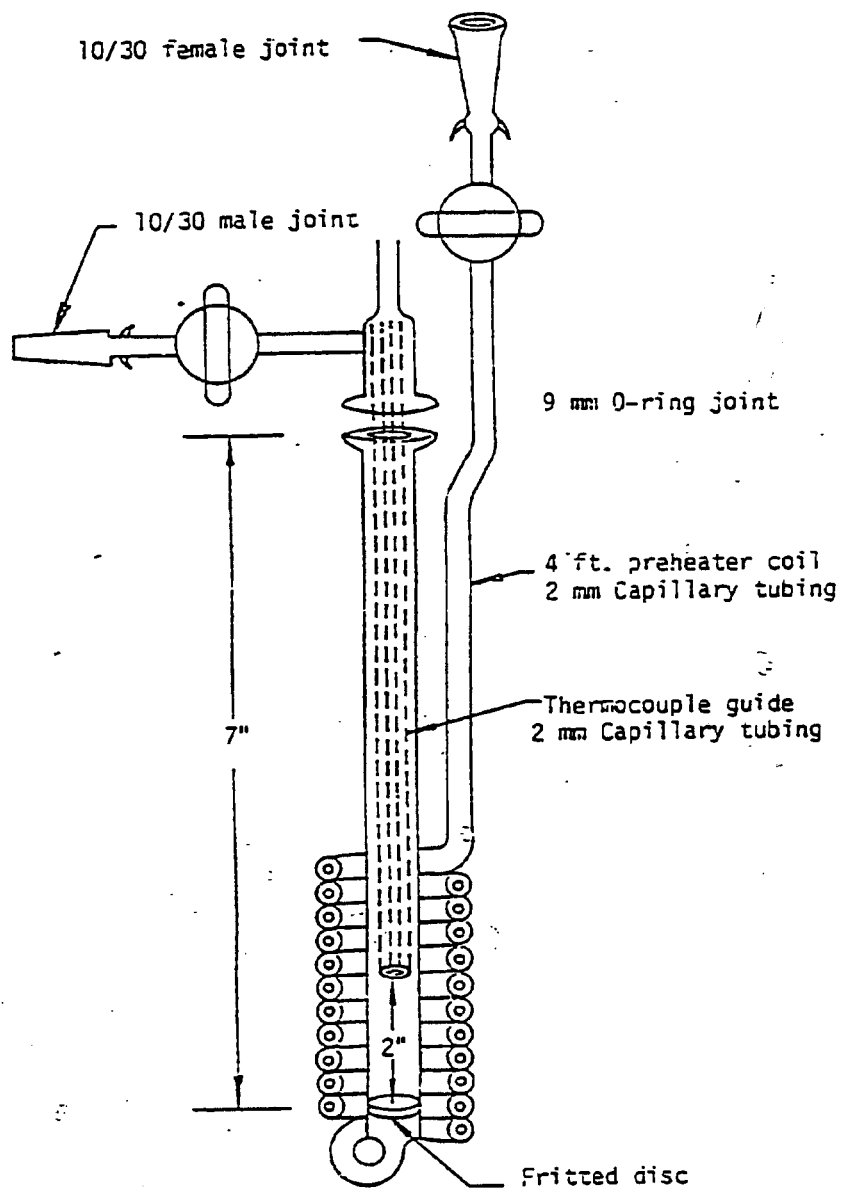


Figure 4. Laboratory Pyrex Reactor.

FIGURE 5  
 $H_2$ ,  $CO$ ,  $CO_2$ , and  $O_2$  Uptakes on Iron Catalysts

Catalyst	$H_2$ Uptake <sup>a</sup> ( $\mu\text{moles/g}$ )	$CO$ Uptake, <sup>b</sup> ( $\mu\text{moles/g}$ )	$CO_2$ Uptake <sup>c</sup> ( $\mu\text{moles/g}$ )	$O_2$ Uptake <sup>d</sup> ( $\mu\text{moles/g}$ )	% Reduction <sup>e</sup>	% Dispersion <sup>f</sup>	DET Area <sup>g</sup> ( $m^2/g$ )
3% Fe/SiO <sub>2</sub>	2.36	1.21	-----	91.6	23	3.86	-----
15% Fe/SiO <sub>2</sub>	23.3	17.5	28.2	-----	--	-----	-----
15% Fe/SiO <sub>2</sub>	16.0	12.2	1.09	1590	79	1.51	-----
15% Fe-K/SiO <sub>2</sub>	9.11	4.94	6.56	856	43	-----	-----
14.7% Fe/ZSM-5	22.8	7.68	-----	-----	--	-----	-----
8.3% Fe/Silicelite	20.4	4.55	-----	-----	--	-----	-----
Fe-B/SiO <sub>2</sub>	10.7	3.58	-----	-----	--	-----	-----
Fe-B	4.13	1.85	-----	-----	--	-----	61.7

<sup>a</sup> At 298 K

<sup>b</sup> At 298 K

<sup>c</sup> At 373 K

<sup>d</sup> At 673 K

<sup>e</sup> Based on  $Fe_2O_3$  stoichiometry

<sup>f</sup> Percent Metal Atoms Exposed

<sup>g</sup> By  $N_2$  Adsorption

FIGURE 6 H<sub>2</sub>, CO, CO<sub>2</sub>, and O<sub>2</sub> Uptakes on Cobalt Catalysts

Catalyst	H <sub>2</sub> Uptake <sup>a</sup> ( $\mu\text{moles/g}$ )	CO Uptake <sup>b</sup> ( $\mu\text{moles/g}$ )	CO <sub>2</sub> Uptake <sup>c</sup> ( $\mu\text{moles/g}$ )	O <sub>2</sub> Uptake <sup>d</sup> ( $\mu\text{moles/g}$ )	% Reduction <sup>e</sup>	% Dispersion <sup>f</sup>	BET Area <sup>g</sup> ( $\text{m}^2/\text{g}$ )
3% Co/SiO <sub>2</sub>	18.8	55.5	-----	-----	-----	-----	-----
15% Co/SiO <sub>2</sub>	52.4	89.9	17.9	641	38	10.9	-----
Co-B/SiO <sub>2</sub>	21.2	24.4	-----	-----	-----	-----	-----
Co-B	47.5	32.6	-----	-----	-----	-----	90.9

<sup>a</sup> At 298 K

<sup>b</sup> At 298 K

<sup>c</sup> At 373 K

<sup>d</sup> At 573 K

<sup>e</sup> Based on Co<sub>3</sub>O<sub>4</sub> Stoichiometry

<sup>f</sup> Percent Metal Atoms Exposed

<sup>g</sup> By N<sub>2</sub> Adsorption

FE-S-103 CALCINED 373K 11-9-81

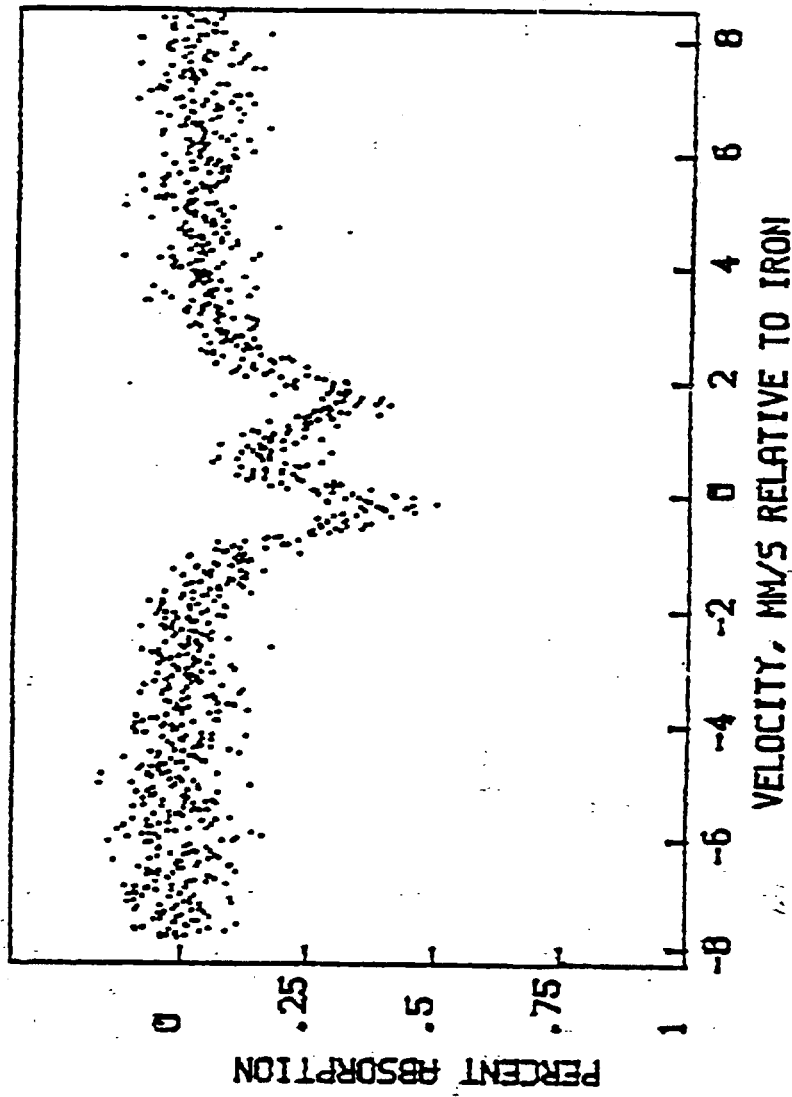


FIGURE 7

FE-S-102 CALCINED 373K 12-28-81

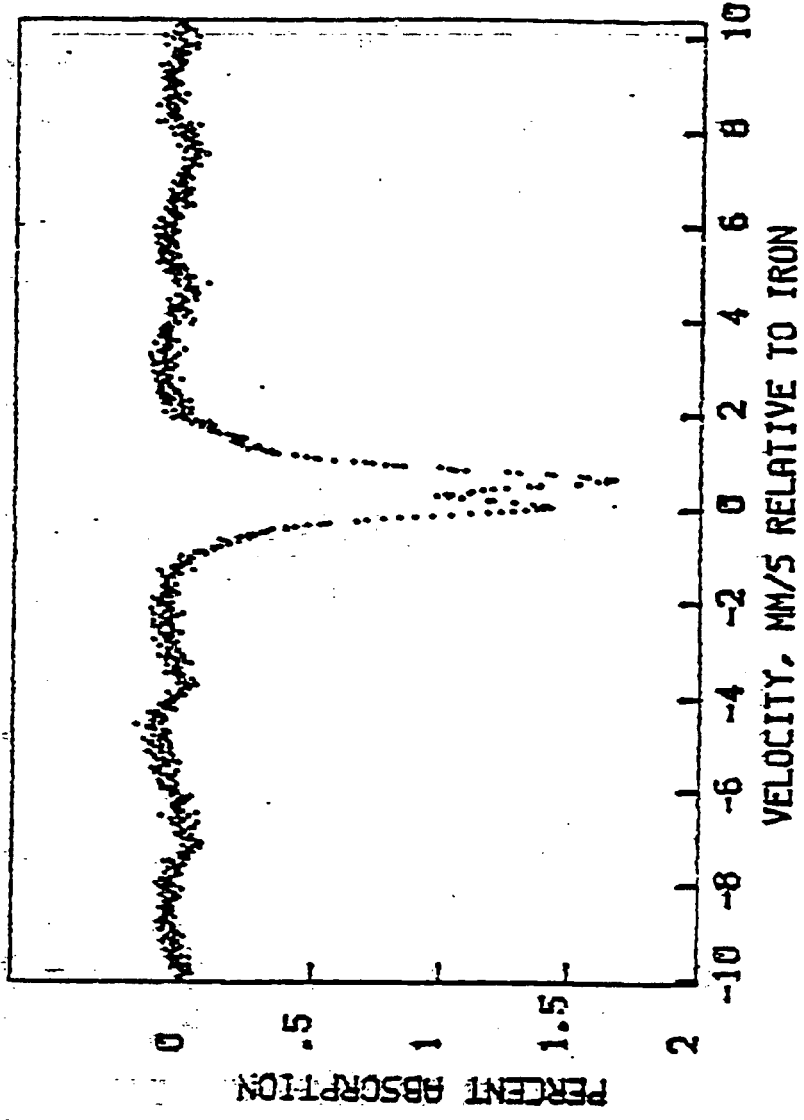


FIGURE 8



FE-X-100 CALCINED AT 473K 7-26-82

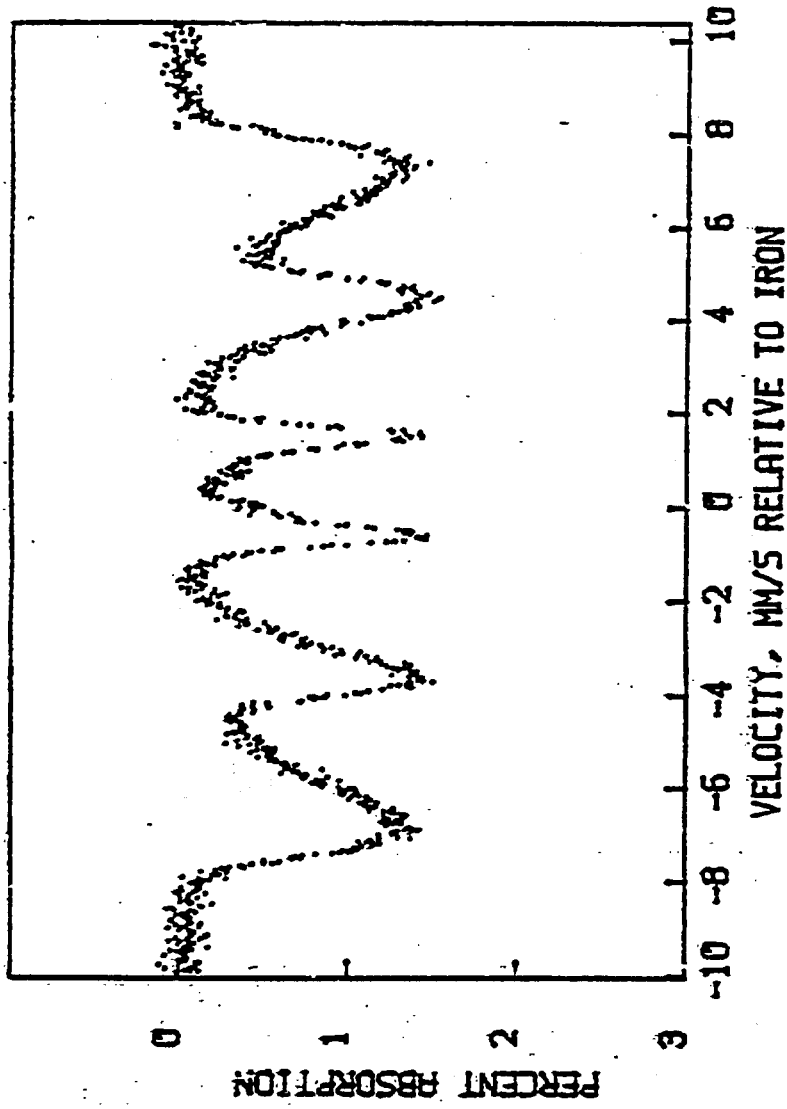


FIGURE 9

Fe-5-103 Reduced 723K 36 Hrs. 1-9-82

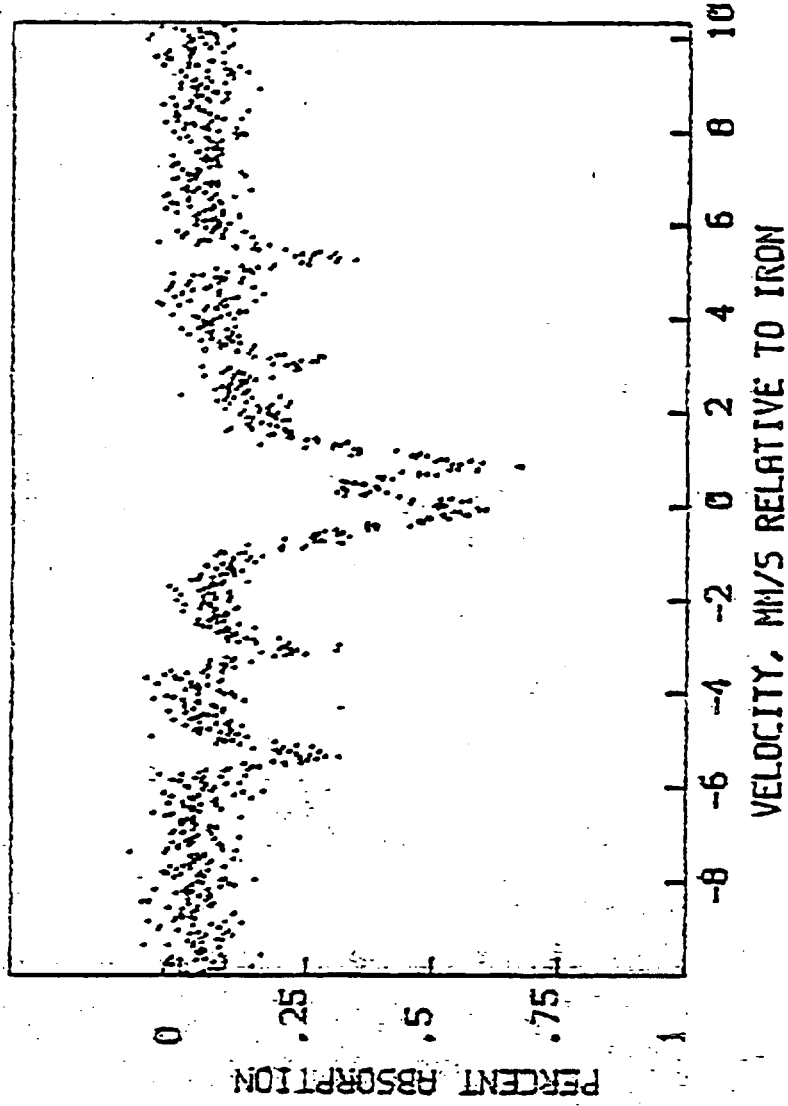


FIGURE 10

FE-S-102 REDUCED 729K 36 HRS. 1-6-82

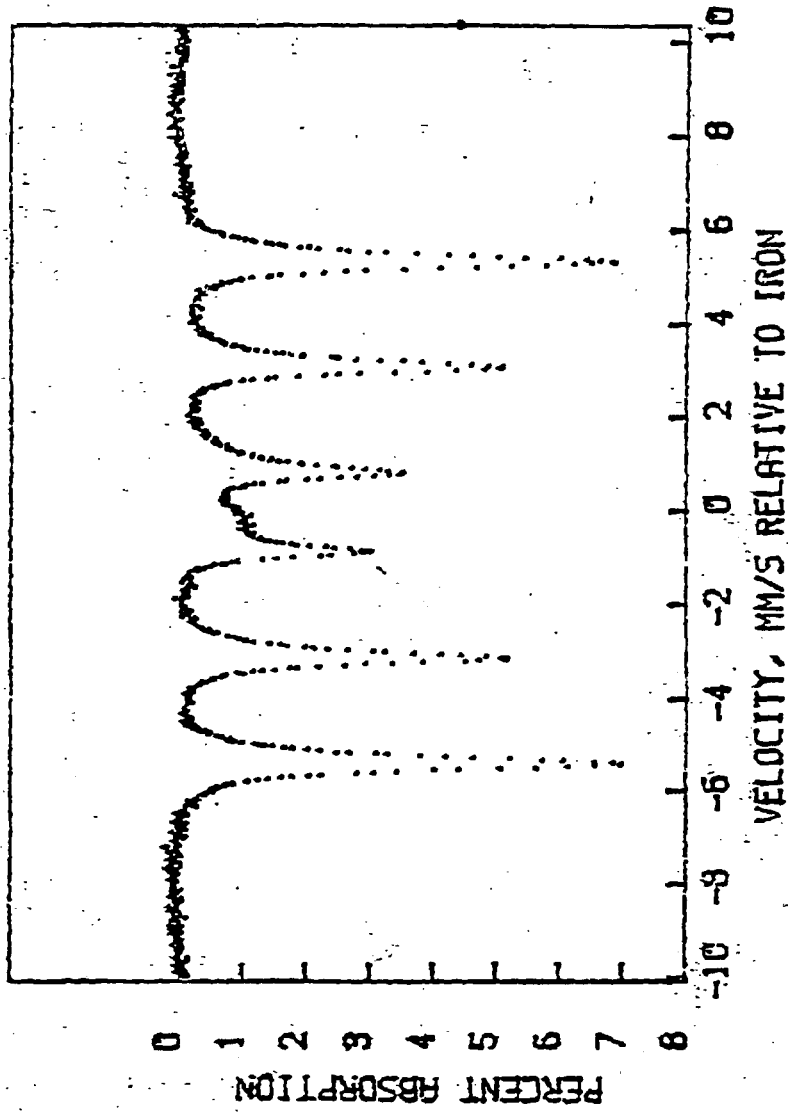


FIGURE 11

SAMPLE C6 REDUCED & REACTOR TESTED

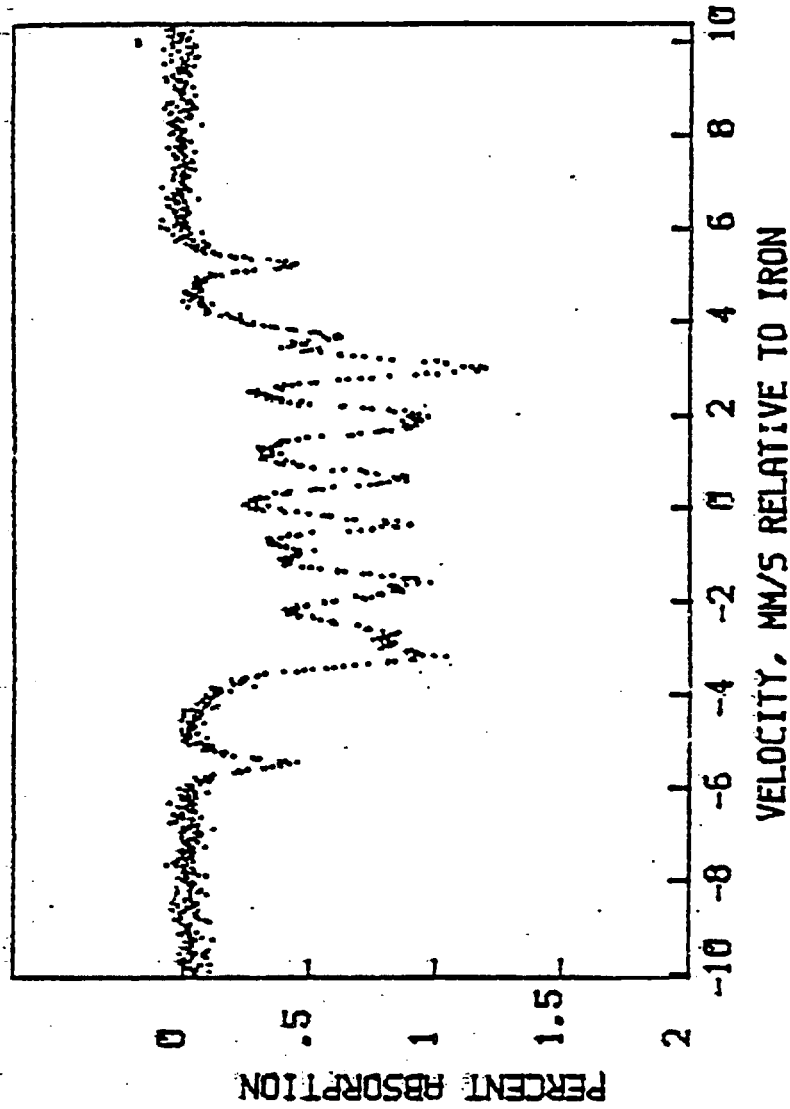


FIGURE 12

TASK 2 EXPERIMENTAL PLAN

DESCRIPTION	PURPOSE OF STUDY	CATALYSTS
Activity/Selectivity Measurements	Effects of Metal	Fe/SiO <sub>2</sub> and Co/SiO <sub>2</sub>
	Effects of Metal Loading	3 and 15% Fe/SiO <sub>2</sub> , 3 and 15% Co/SiO <sub>2</sub>
	Effects of Support	Fe, Fe/SiO <sub>2</sub> , Fe/Al <sub>2</sub> O <sub>3</sub> , Fe/Silicalite, Fe/ZSM-5, Fe/C, Co, Co/SiO <sub>2</sub>
	Effects of Alkali	K <sub>2</sub> O Promoted Fe, Fe/SiO <sub>2</sub> , Fe/Silicalite, Co/SiO <sub>2</sub> ZnO Promoted Fe/SiO <sub>2</sub>
	Effects of Nitriding and Boriding	Fe, Fe/SiO <sub>2</sub> (nitrided and borided), Co, Co/SiO <sub>2</sub> (borided)
	Effects of Sulfiding	Fe, FeK, Fe/SiO <sub>2</sub> , FeK/SiO <sub>2</sub> , FeZ/SiO <sub>2</sub> , FeK/Silicalite, Co (sulfided)
Reactor Runs at 25 atm	Effects of Pressure	5 "best" catalysts based on atmospheric tests

FIGURE 15

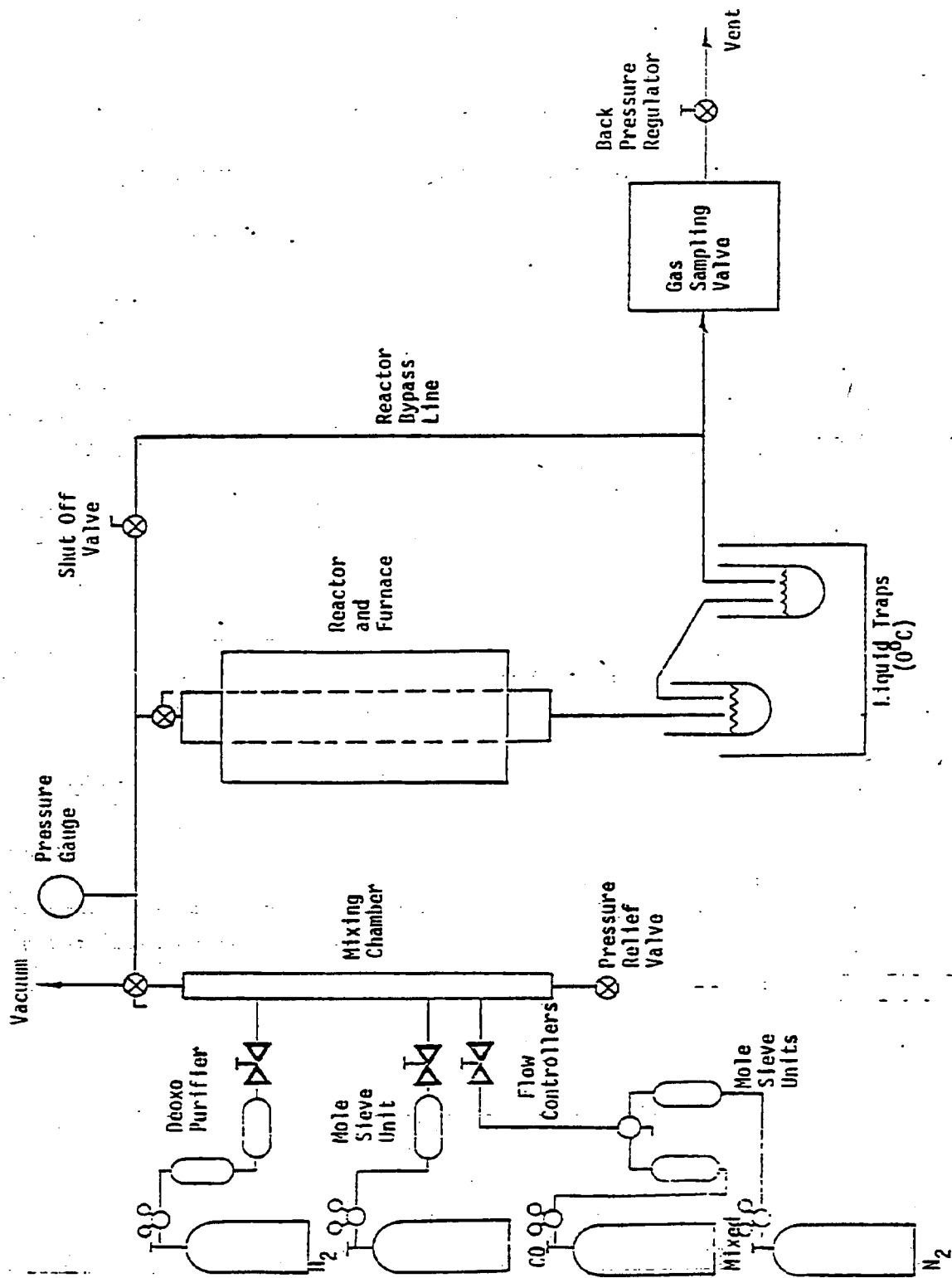


Figure 14. Fischer-Tropsch Reactor System.

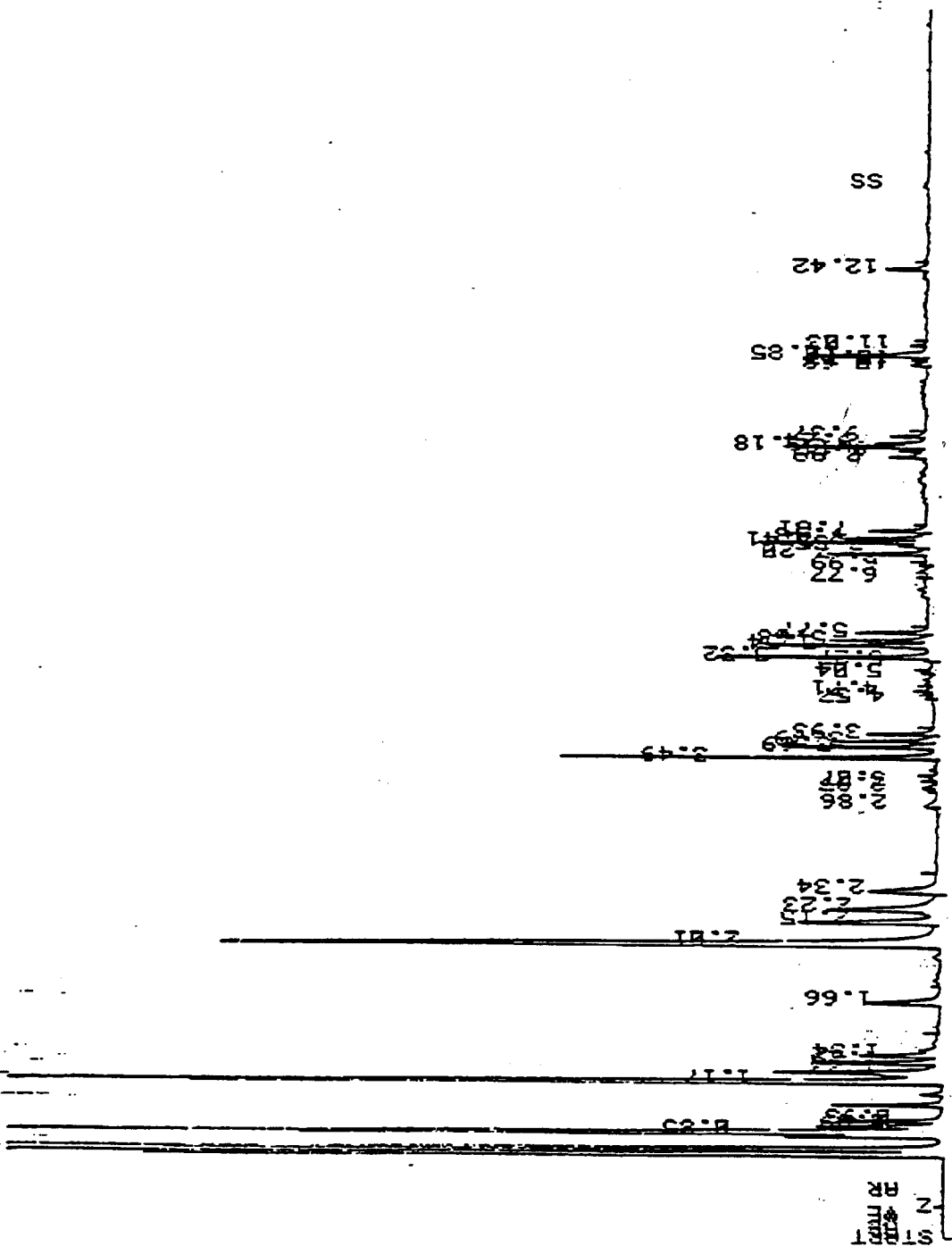


FIGURE 15

## CO TURNOVER NUMBERS

<u>Catalyst</u>	<u>H<sub>2</sub>/CO</u>	<u>Temperature (K)</u>	<u>Turnover Number (N<sub>CO</sub> x 10<sup>3</sup>)</u>	<u>Activation Energy (kJ/gmole)</u>
3% Fe/SiO <sub>2</sub>	2	498	7.0	82.8
	1	498	7.0	80.8
15% Fe/SiO <sub>2</sub>	2	498	3.9	92.5
	1	498	2.5	99.3
15% FeK/SiO <sub>2</sub>	2	498	6.6	---
14.7% Fe/ZSM-5	2	500	0.45	---
8.3% Fe/Silicalite	2	500	0.24	---
FeB	2	483	8.1	81.4
FeB/SiO <sub>2</sub>	2	498	0.33	---
3% Co/SiO <sub>2</sub>	2	450	3.0	---
15% Co/SiO <sub>2</sub>	2	450	64	---
CoB	2	485	1.55	140
CoB/SiO <sub>2</sub>	2	504	17	154

FIGURE 16



PRODUCT SELECTIVITY DATA FOR IRON  
(1 ATM, 498 K)

Catalyst	H <sub>2</sub> /CO	CH <sub>4</sub>	C <sub>2</sub> -0 <sub>4</sub>	C <sub>5</sub> ±	CO <sub>2</sub>	Alcohols	Olefin/Paraffin
3% Fe/SiO <sub>2</sub>	2	0.25	0.33	0.04	0.30	0.08	0.31
	1	0.20	0.31	0.03	0.36	0.10	-----
15% Fe/SiO <sub>2</sub>	2	0.16	0.27	0.03	0.47	0.07	0.33
	1	0.12	0.23	0.02	0.56	0.07	-----
15% FeK/SiO <sub>2</sub>	2	0.08	0.19	0.03	0.65	0.05	-----
14.7% Fe/ZSM-5	2	0.94	0.03	0.03	0	0	0.02
8.3% Fe/Silicalite	2	0.27	0.51	0.04	0.09	0.09	0.66
FeB	2	0.17	0.44	0.23	0.10	0.06	-----
FeB/SiO <sub>2</sub>	2	0.26	0.19	0	0.55	0	-----

FIGURE 17

PRODUCT SELECTIVITY FOR COBALT  
(1 ATM, 473 K)

<u>Catalyst</u>	$\frac{H_2}{CO}$	$\frac{CH_4}{C_2H_4}$	$\frac{C_2H_6}{C_2H_4}$	$\frac{C_3H_8}{C_2H_4}$	$\frac{CO_2}{CO}$	<u>Alcohols</u>	<u>Olefin/Paraffin</u>
3% Co/SiO <sub>2</sub>	2	0.27	0.24	0.34	0.04	0.11	0
CoB	2	0.18	0.11	0.17	0.40	0.15	-----
0.01/SiO <sub>2</sub>	2	0.31	0.26	0.31	0.06	0.06	-----

FIGURE 18

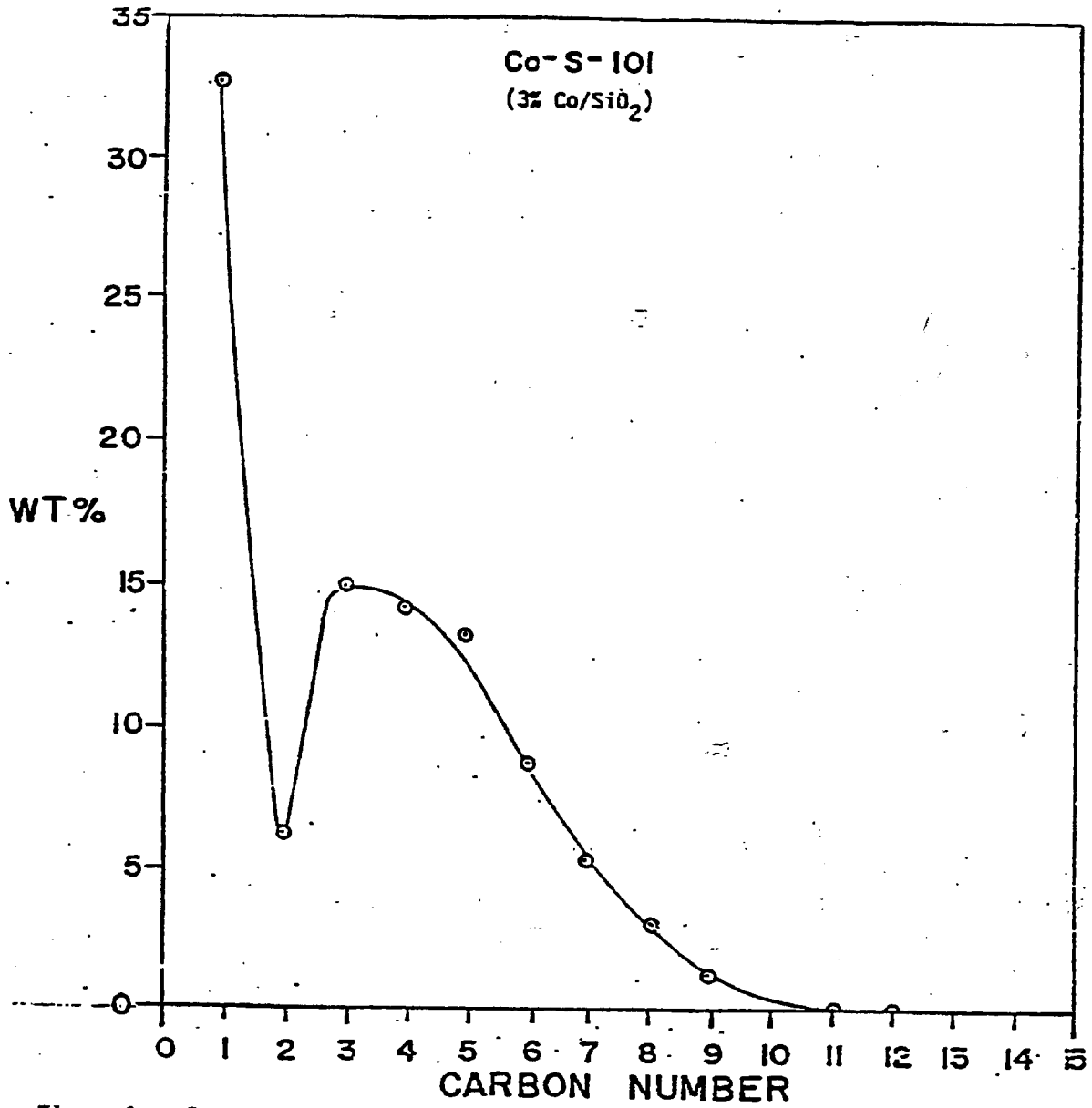
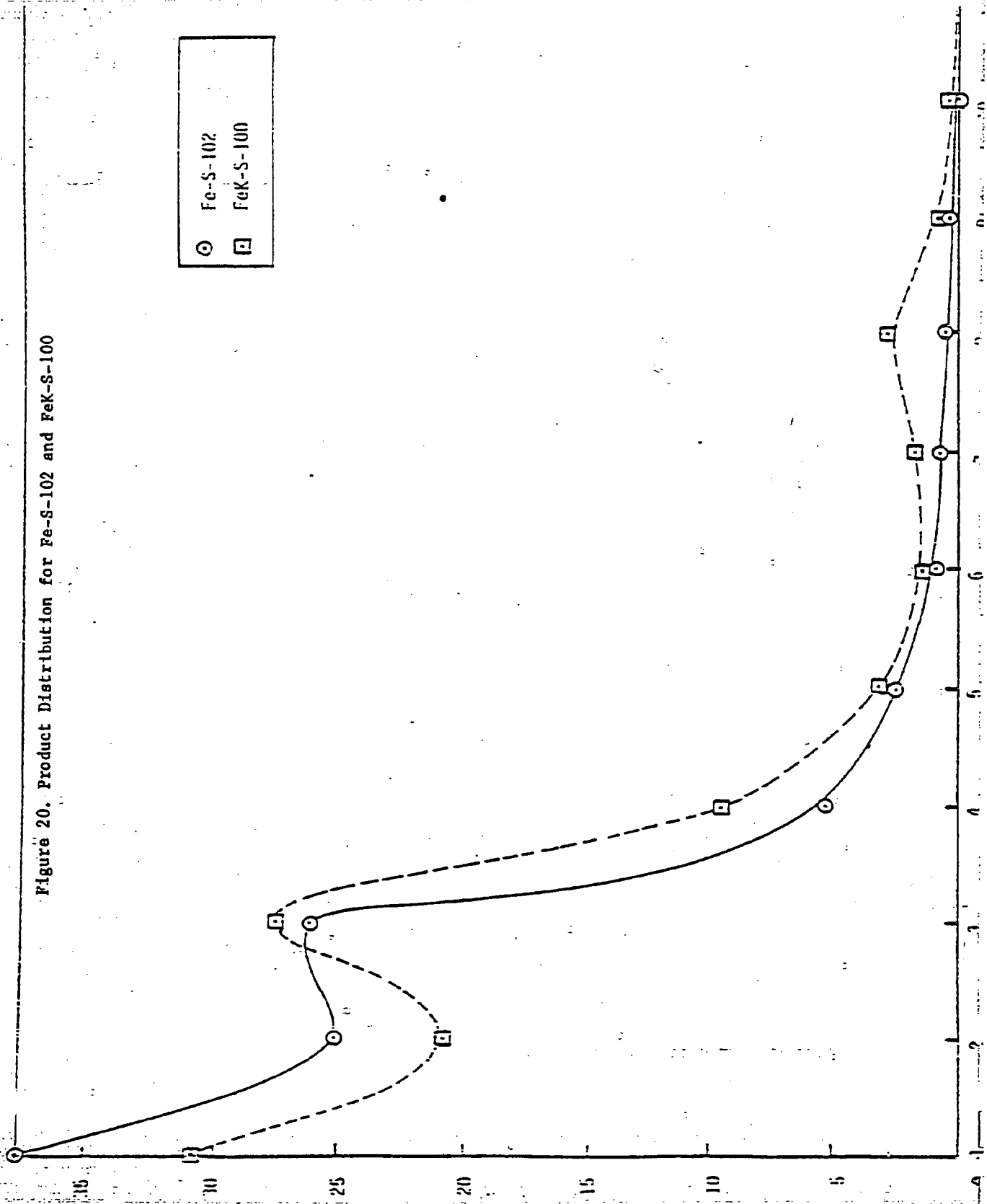


Figure 19. Product distribution for Co-S-101.

Figure 20. Product Distribution for Fe-S-102 and FeK-S-100



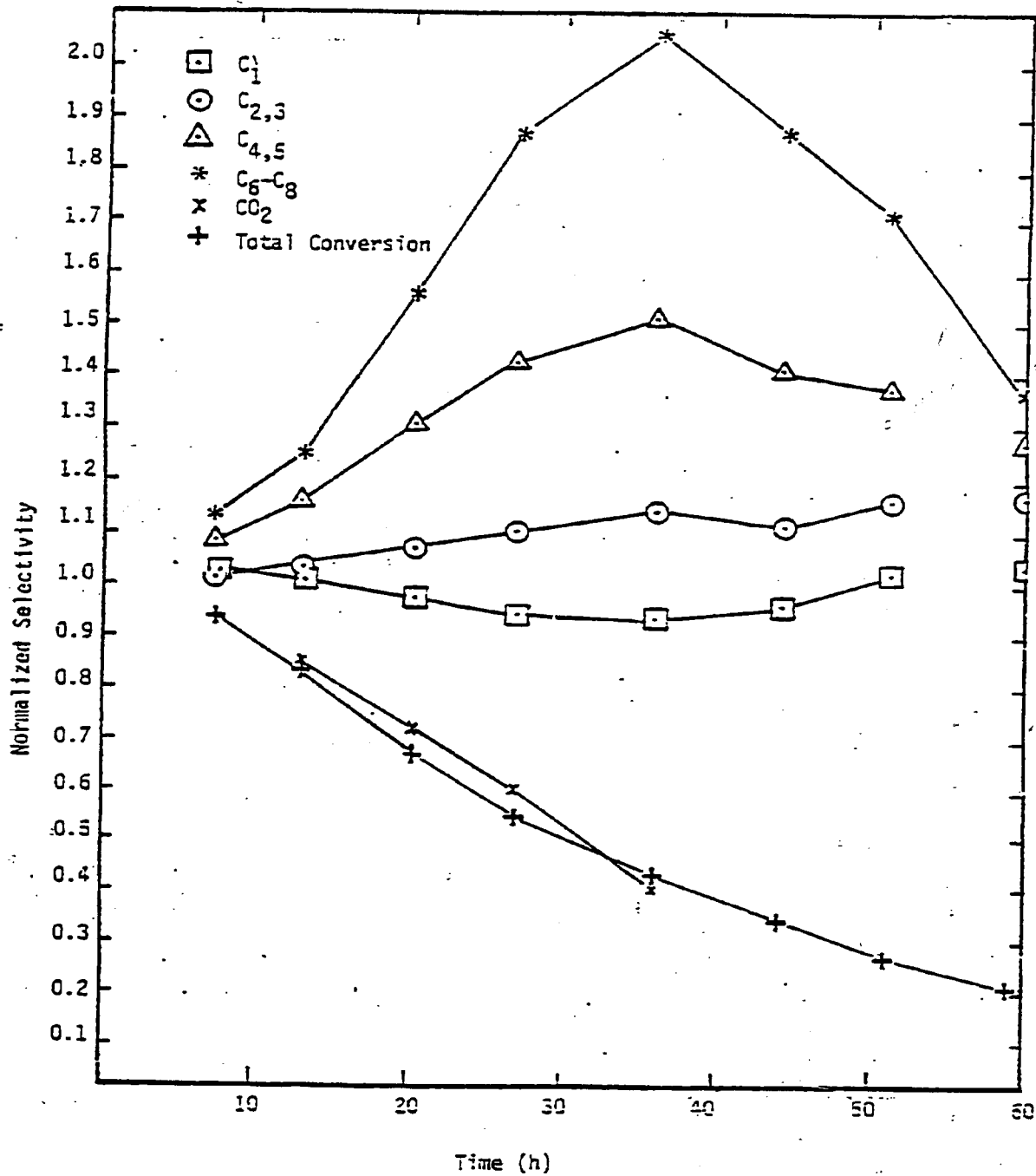


FIGURE 21

Product Selectivity as a Function of Time of Exposure to H<sub>2</sub>S.

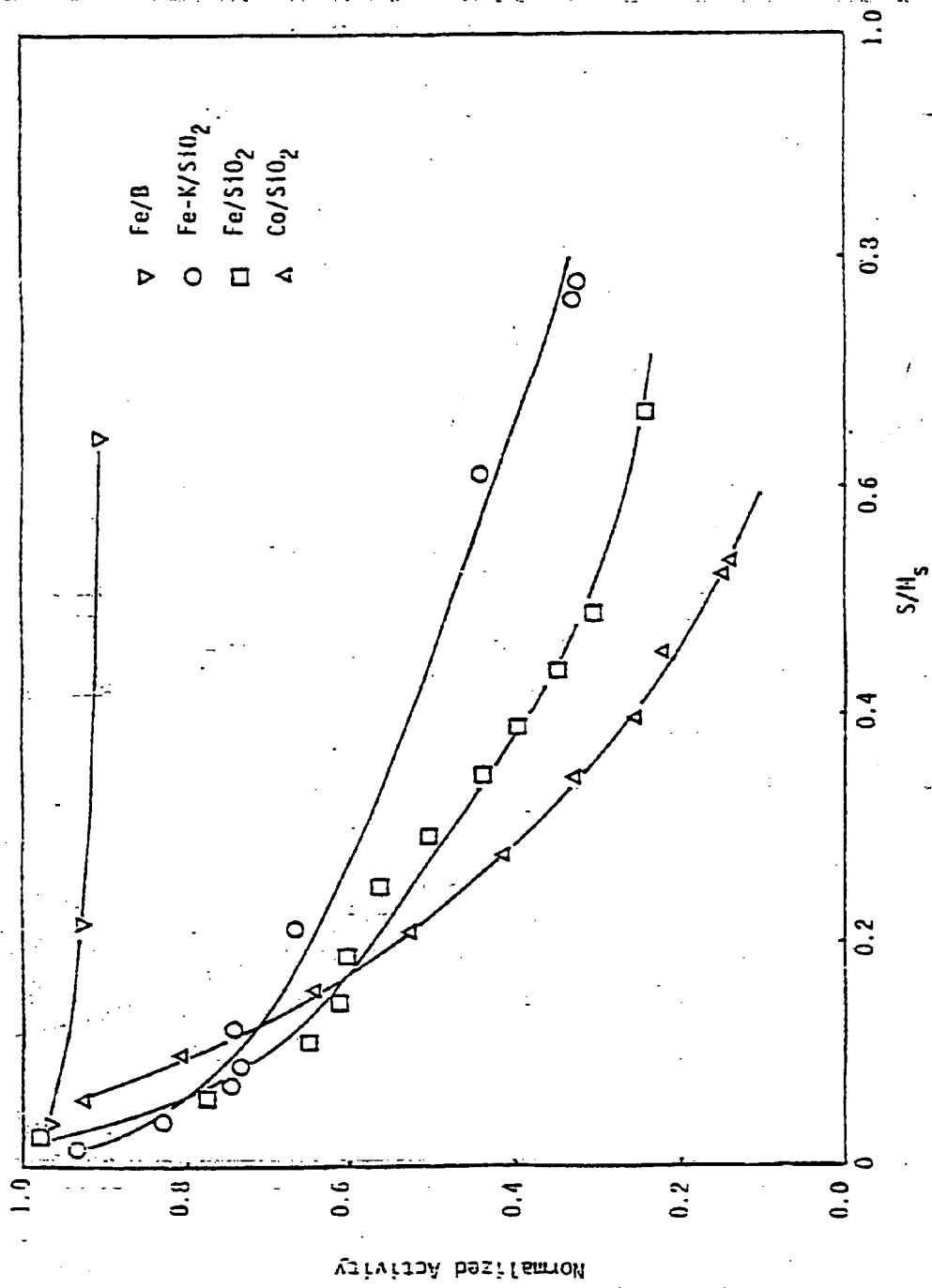


FIGURE 22 Normalized Activity Versus Sulfur Coverage (atoms of S adsorbed/metal surface atom) during in situ poisoning by 4-6 ppm H<sub>2</sub>S (500 K, 1 atm, H<sub>2</sub>/CO = 2).