

Report 14

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 activity, selectivity, and stability properties leave much to be desired. Previous investigations were generally made on poorly characterized catalysts operating in heat/mass-transport-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. Our investigation of catalysts for selective synthesis of hydrocarbon liquids began about 1 1/2 years ago and is scheduled to continue another 1 1/2 years. 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 CO/H₂ 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 uptakes.

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 iron and cobalt 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 H₂S. This paper will focus on recent progress in connection with Tasks 1 and 2, i.e. the preparation and characterization of iron and cobalt catalysts.

Figure 1 shows the 28 catalysts we plan to prepare and characterize in total. This experimental grid was designed to systematically investigate effects of potassium promotion and boron, nitrogen, and sulfur additives and the effects of the four support materials, including the novel zeolite supports, ZSM-5 and Silicalite. Approximately half of these catalysts have been prepared to date.

Catalyst Characterization

Catalyst characterization plans involve a comprehensive multi-tool approach to the measurement of basic physical, chemical and surface properties and include H₂ and CO chemisorption measurements, thermal gravimetric analysis, temperature programmed reduction, and analysis by Moessbauer spectroscopy.

As outlined in Figure 2, H₂ and CO chemisorption will be performed on all catalysts to determine metal surface areas. We have used CO₂ chemisorption to measure the concentration of alkali promoters on the catalyst surface. Both thermal gravimetric analysis and Moessbauer spectroscopy will aid in determining boride, nitride, and carbide formation during preparation and reaction, and reveal oxidation states of reduced metals. Temperature programmed desorption of adsorbed reactants will yield valuable information on the effects of promoters, additives, and supports on catalyst adsorption properties.

Our chemisorption experiments are carried out on 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

potassium. The potassium-promoted catalyst was also more difficult to reduce - the percent reduction dropped from 80 to 42%.

An estimate of the surface enrichment of potassium may be made as shown by the graph in Figure 5 from Jacobs of Princeton. He noted that CO_2 adsorption was a linear function of K/Fe atomic ratio. If one subtracts the quantity of adsorbed CO_2 on the unpromoted catalyst from the CO_2 uptake of the promoted catalyst, one obtains an estimate of the CO_2 adsorption of the K_2O . By this method, we calculate a surface enrichment of K_2O nearly 25 times its bulk concentration.

Studies of silica-supported cobalt catalysts have also been conducted. The data in Figure 6 suggest that once again a 36-hour reduction in H_2 is adequate, since the O_2 titration indicated 71% reduction of the 3% cobalt catalyst to the metal state, and a dispersion of 8%. A CO/H ratio of nearly 1 was observed for the 3% catalyst, while the 15% catalyst had a CO/H ratio of only 0.5. This suggests that due to its lower dispersion, bridged CO species were present on the surface of the higher loading catalyst. A similar behavior was also observed for unsupported cobalt boride catalysts. Currently, H_2 , CO, and CO_2 adsorption on potassium promoted cobalt are underway to compare the effects of potassium on cobalt to those on iron.

Figure 7 lists some data on cobalt boride catalysts. Once again, CO/H ratios varied from 0.5 to 0.6 a behavior typical of moderately or poorly dispersed cobalt catalysts. Nevertheless, in all cases, the cobalt catalysts are better dispersed than the iron, although dispersions are only 2 to 10%.

Activity/Selectivity Measurements

Once the catalysts have been characterized, they are tested in a laboratory reactor to determine activity/selectivity properties (Task 2). The experiments outlined in Figure 8, have been designed to isolate, as much as

possible, the effects on selectivity and activity of metal, metal loading, metal-support interactions, promoter and additives, including sulfur, and the effects of increasing pressure from 1 atmosphere to near industrial conditions at 25 atmospheres.

A laboratory microreactor system for testing Fischer-Tropsch catalysts has been made operational and is currently in use. The schematic in Figure 9 outlines its major features which include gas purification by molecular sieve and cesox units, a tubular furnace, a pair of liquid and wax traps, and a gas chromatographic analysis. The system is capable of pressures to 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 while allowing fast analysis of high molecular weight species.

The analysis of Fischer-Tropsch hydrocarbon products is a difficult problem. Our analytical scheme is diagrammed in Figure 10. Two columns are used in parallel to obtain a complete analysis of hydrocarbon and fixed gas components. Hydrocarbon analysis is performed on a 30 foot SP 2100 column, temperature programmed from 20 C to 200 C. When large amounts of oxygenates are produced, as when testing iron catalysts, an additional section of SP 2100 with 0.1% Carbowax additive improves the separation of the more difficult polar alcohols. The fixed gas analysis, including H₂, N₂, CO, CO₂, H₂O, and CH₄, is performed on a single column of Carbosieve B, programmed from 50 C to 200 C. Separation of these gases on one column is somewhat unique. The total analysis requires approximately two hours.

A typical hydrocarbon analysis for a low molecular weight product is

pictured in Figure 11. As can be seen, identification of all peaks would be a formidable task, but the boiling point order of elution of the normal alkanes makes a good "fingerprint" of the product. An order has been placed for a capillary column system which will greatly improve the peak analysis, especially for higher hydrocarbons, by removing the low upper temperature limit present for packed column baseline noise interference.

Before analyzing activity/selectivity data the catalysts are pretreated in the reactant mixture at or above reaction temperature for 12 to 20 hours, until steady state is reached. As shown by Figure 12 for 15% cobalt on silica, activity initially increases with time, then decreases to a nearly steady value. Simultaneously, selectivity to the various hydrocarbons is changing. This is due to the carbiding of surfaces, the filling of catalyst pores with liquid, and establishing steady state. The products are analyzed every 2 hours. When steady state is reached, rates and product distributions are measured and considered reliable for comparisons. Conversions are limited to 10% or less and finely crushed powders are used to avoid mass and heat transport limiting reaction regimes.

Turnover numbers for supported iron and cobalt catalysts tested to date are shown in Figure 13. As can be seen, turnover numbers for catalyst Fe-S-102 with 15% metal loading, and catalyst Fe-S-103 with 3% metal loading are close, i.e. within a factor of 2, but activation energies differ substantially. It is possible that the low activation energies for the low loading catalyst may be due to metal-support interactions. The addition of potassium to the iron had little effect on turnover number, while the boride catalysts showed relatively low activity. Since this figure was prepared an iron boride catalyst of higher activity has been prepared and tested with greater success. Our work establishes that cobalt/silica catalysts have

greater activity than iron/silica catalysts in the Fischer-Tropsch synthesis. For example, CO turnover number for Co-S-101 of 5.9×10^{-3} at 463 K may be compared to the turnover number of 0.64×10^{-3} at 460 K for the iron catalyst Fe-S-102 under the same conditions. This is nearly an order of magnitude difference in activity.

Figure 14 contains product selectivity data for samples of the same catalysts tested under two different H_2/CO ratios. It is evident that decreasing H_2/CO ratio from 2 to 1 increased the average molecular weight of the product in the case of both iron/silica catalysts. This was accomplished by reducing methane yield. Also, CO_2 selectivity increased significantly. The 3% iron/silica catalyst Fe-S-103 produced more methane and a significantly lower molecular weight product than the 15% iron/silica catalyst. Its selectivity to CO_2 was much lower also. This illustrates how metal-support interactions and differences in the state of reduction of the catalyst can significantly influence selectivity for Fischer-Tropsch synthesis on iron. The addition of potassium to the 15% iron/silica shifted carbon numbers of the product from methane and ethane to the C_5+ range. CO_2 production also increased. This promoter effect will be shown more graphically later. The iron boride catalyst was relatively inactive and produced large amounts of methane and ethane. No products beyond C_4 were detected. Cobalt/silica produced higher molecular weight products than any of the iron catalysts at 1 atmosphere pressure. The selectivity of 34% to C_5+ is especially interesting considering no other promoters besides silica were present; the low selectivity to CO_2 is typical of cobalt in the Fischer-Tropsch synthesis. Recently we have completed testing a cobalt boride catalyst which had unusually good selectivity (non Schuit-Flory) to the C_4 to C_{10} range. This interesting behavior is undoubtedly due to the boride additive.

Preliminary tests have been performed also with iron supported on the zeolites ZSM-5 and Silicalite. The results are summarized in Figure 15. The performance of these catalysts is very different from the silica-supported metal. At 1 atmosphere, iron on ZSM-5 produces predominantly methane, and very little C_{2+} . However, the silicalite catalyst produced more C_2-C_4 than the silica catalyst of similar metal loading. A more thorough investigation of these catalysts is planned for the near future, but it is clear that in these catalysts a combination of metal-support interactions and shape selectivity affect activity and selectivity in Fischer-Tropsch synthesis.

The hydrocarbon distribution for 3% cobalt on silica shown in Fig. 16 appears to follow the Schultz-Flory distribution, albeit with some data scatter at C_4 . The very low C_2 yield typical of cobalt catalysts is quite evident from these data. The cobalt boride catalyst, however, evidenced non-Schultz-Flory behavior, yielding nearly equal amounts of C_5 to C_{10} products.

Olefin/paraffin separation is achieved with some difficulty on packed columns, but the data in Figure 17 demonstrate the results that have been obtained so far. The cobalt catalysts appear to produce predominantly saturated hydrocarbons, while each of the iron catalysts show olefin production. The high yield of olefins from the iron/silicalite catalysts, especially in the low carbon number ranges, is significant.

Summary

Some major observations and conclusions based on the 15 catalysts prepared to date are summarized here. From adsorption studies, it is evident that iron and cobalt on silica have relatively poor dispersions in the range of 2 to 10%, though cobalt catalysts are generally more highly dispersed. A 36-hour reduction in H_2 of these catalysts was found to be adequate to achieve near maximum reduction to the metallic state. We have observed that CO/H

adsorption ratios on iron/silica are near 1, ranging from 0.7 to 1. This is a completely new observation, we believe. Potassium promotion of the iron lowers this ratio to 0.2. On the other hand, CO/H ratios for cobalt are near 0.5. Experiments with CO₂ chemisorption have shown that K₂O is concentrated on the catalyst surface to as much as 25 to 30 times its bulk concentration.

From atmospheric reactor tests of eight supported catalysts in our microreactor system, the following conclusions may be drawn:

-at atmospheric pressure, cobalt produces a higher molecular weight product than iron.

-decreasing H₂/CO ratio causes the average molecular weight of the hydrocarbons to increase by reducing the methane yield.

-iron catalysts produce alcohols, olefins, and large amounts of ethane relative to cobalt catalysts.

-potassium promotion of iron/silica shifts carbon numbers to higher molecular weights at the expense of C₁-C₂ production.

-and significant differences in selectivity are observed in iron-silica catalysts due to differences in state of reduction, and are evidence of metal-support interactions affecting selectivity.

References

1. Bartholomew, C.H., "Investigation of Sulfur-Tolerant Catalysts for Selective Synthesis of Hydrocarbon Liquids from Coal-Derived Gases," Annual Technical Progress Report, FE-14809-4, October 10, 1980.
2. Bartholomew, C.H., "Investigation of Sulfur-Tolerant Catalysts for Selective Synthesis of Hydrocarbon Liquids from Coal-Derived Gases," Quarterly Technical Progress Report, DOE-ET-14809-5, January 10, 1981.
3. Bartholomew, C.H., "Investigation of Sulfur-Tolerant Catalysts for Selective Synthesis of Hydrocarbon Liquids from Coal-Derived Gases," Quarterly Technical Progress Report, DOE-ET-14809-6, April 20, 1981.

Catalyst Preparation Plans

<u>Metal-Support Combination</u>	<u>Unpromoted</u>	<u>Promoted</u>		<u>Additive Pretreatments</u>			<u>No. Catalysts</u>
		<u>K₂O</u>	<u>ZnO</u>	<u>S</u>	<u>N</u>	<u>B</u>	
Fe (unsupported)	x	x		x(2) ^b	x	x	6
Co (unsupported)	x			x		x	3
Co/SiO ₂	x(2) ^c	x				x	4
Fe/SiO ₂	x(2) ^c	x	x	x(3) ^b	x	x	9
Fe/Al ₂ O ₃	x						1
Fe/ZSM-5	x	x		x ^d			3
Fe/Silicalite	x	x					<u>2</u>
						Total	28

Figure 1

TASK 1 EXPERIMENTAL PLAN

DESCRIPTION	PURPOSE OF STUDY	CATALYSTS
A. H ₂ and CO Chemisorption Measurements	Determine Active Metal Surface Areas	All Catalysts
B. CO ₂ Chemisorption Measurements	Determine Alkali Promoter Surface Concentrations	Fe, FeK, Fe/SiO ₂ , FeK/SiO ₂ , Co/SiO ₂ , CoK/SiO ₂ , Fe/ZSM-5, FeK/ZSM-5, Fe/Silicalite, FeK/Silicalite
C. Thermal Gravimetric Analysis and Monsebauor Spectroscopy	Determine effects of support on state of metal reduction and investigate carbide, nitride formation under reaction conditions	Co/SiO ₂ , Fe, Fe/SiO ₂ , Fe/Al ₂ O ₃ , Fe/ZSM-5, Fe/Silicalite
D. Temperature Programmed Desorption	Determine effects of promoters and supports on reactant adsorption properties	Fe/SiO ₂ , FeK/SiO ₂ , FeS/SiO ₂ , FeN/SiO ₂ , Fe/Silicalite, Fe/Al ₂ O ₃ , Fe, Co/SiO ₂ , Co, CoK/SiO ₂

Figure 2

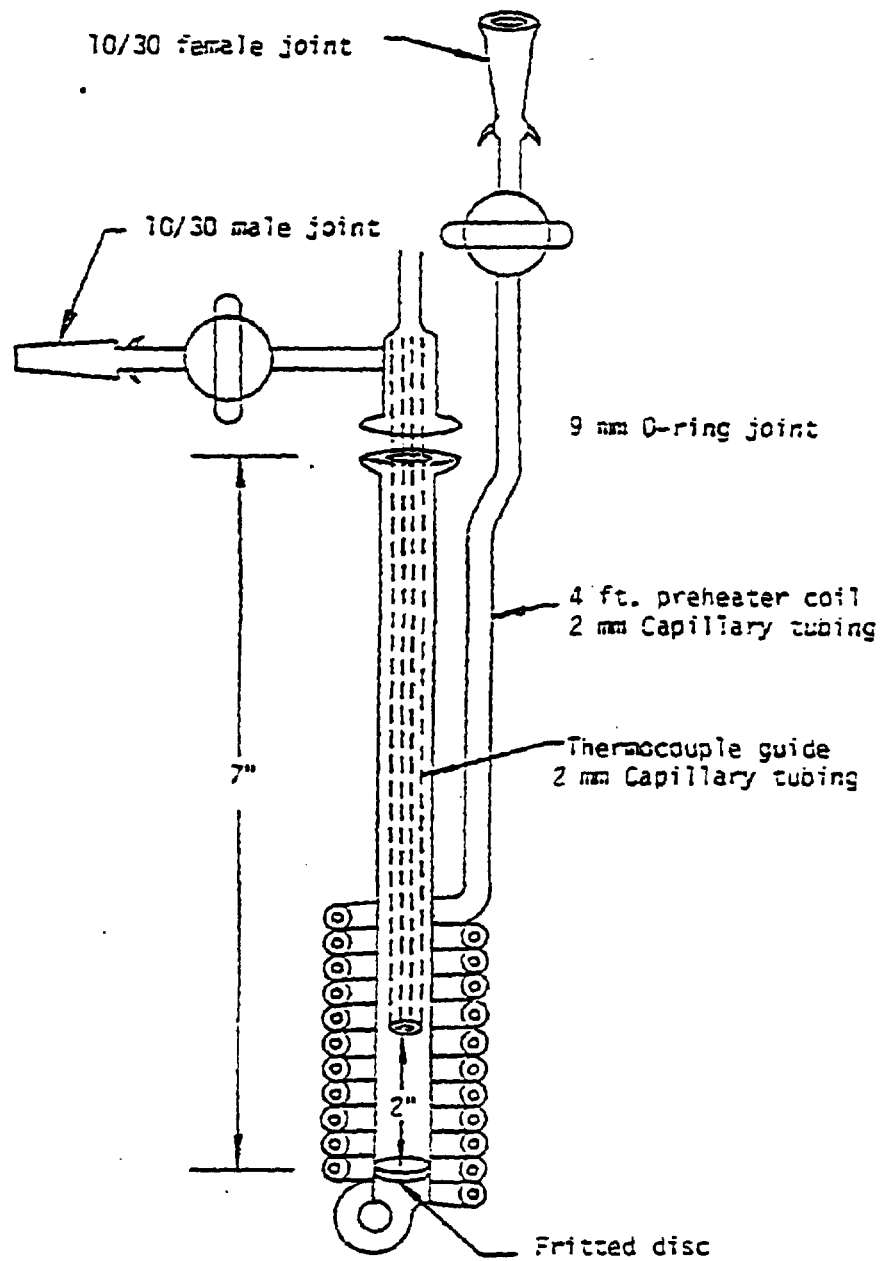


Figure 3. Laboratory Pyrex Reactor.

**H₂, CO, CO₂ and O₂ Uptakes on Iron Catalysts After
36-hour Reductions in Hydrogen**

<u>Catalyst Code</u>	<u>% Metal Loading</u>	<u>H₂ Uptake^a (μmoles/g)</u>	<u>CO Uptake^b (μmoles/g)</u>	<u>CO₂ Uptake^c (μmoles/g)</u>	<u>O₂ Uptake^d (μmoles/g)</u>	<u>% Reduction</u>
Fe-S-102 ^f	16	20.19	3.52	--	--	--
Fe-S-102	15	17.10	24.80	1.16	1622	80.5
Fe-S-103	3	3.10	4.82	--	50.16	12.5
FeK-S-100 ^g	15	9.11	4.94	6.56	856	42.5
Fe8-S-101 ^h	10	6.37	--	--	--	--

^a Al 298 K

^b Al 298 K

^c Al 373 K

^d Al 673 K

^e Based on Fe₂O₃ stoichiometry

^f After 20 hour reduction in H₂

^g Containing 3% K₂O promoter

^h Containing Boride promoter

Figure 4

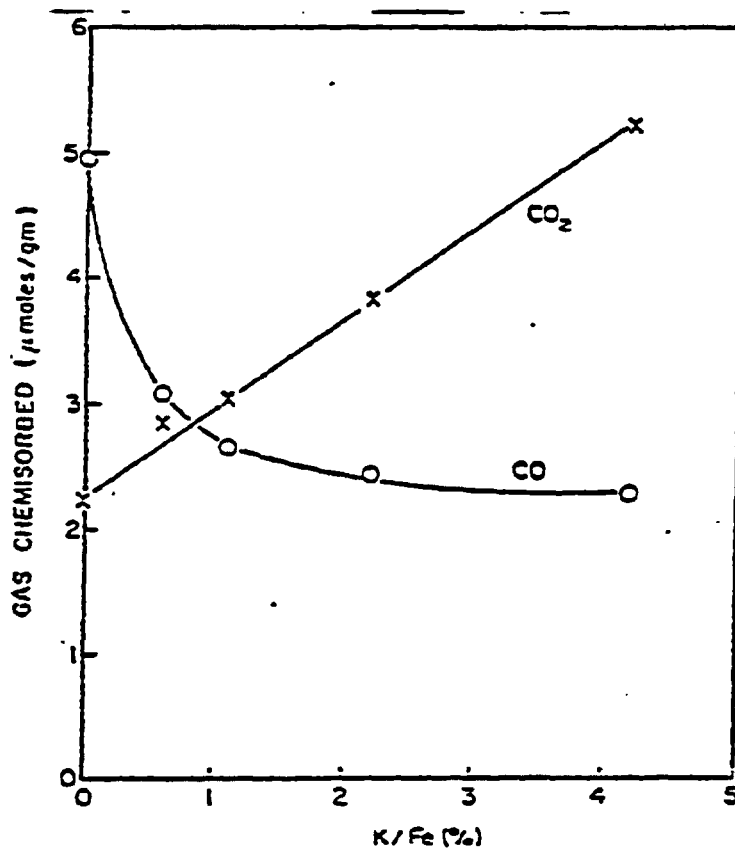


Figure 5

**H₂, CO, and O₂ Uptakes on Cobalt Catalysts After
36-hour Reductions in Hydrogen**

<u>Catalyst Code</u>	<u>%Metal Loading</u>	<u>H₂ Uptake^a (mmoles/g)</u>	<u>CO Uptake^b (mmoles/g)</u>	<u>O₂ Uptake^c (mmoles/g)</u>	<u>% Reduction^d</u>
Co-S-101	3	13.24	24.00	241	71.2
Co-S-102	15	35.95	31.93	--	--
CoD-X-102 ^e	--	47.50	32.50	--	--

-
- ^a At 290 K
 - ^b At 298 K
 - ^c At 623 K
 - ^d Based on CO₂ stoichiometry
 - ^e Containing Borole promoter

Figure 6

CHEMISORPTION DATA
Cobalt Boride Catalysts

<u>Catalysts</u>	<u>H₂ Uptake</u>	<u>CO Uptake</u>	<u>CO/H</u>
Co-B/Al ₂ O ₃	59 67 ^a	74 66 ^a	0.63 0.49
Co-B/SiO ₂	56	60	0.54

^aAfter 24 hour reactor test. (μmoles/g)

TASK 2 EXPERIMENTAL PLAN

DESCRIPTION	PURPOSE OF STUDY	CATALYSTS
Activity/Selectivity Measurements	Effects of Metal	Co, Fe
	Effects of Support	Co/SiO ₂ , Co, Fe, Fe/SiO ₂ , Fe/Al ₂ O ₃ , Fe/ZSM-5, Fe/Silicalite
	Effects of Metal Loading	3 and 15% Fe/SiO ₂ , 3 and 15% Co/SiO ₂
	Effects of Promoter	K ₂ O Promoted Fe, Fe/SiO ₂ , Co/SiO ₂ , Fe/ZSM-5, Fe/Silicalite
	Effects of Nitriding, Boriding	Fe and Fe/SiO ₂ (nitrided and borided), Co and Co/SiO ₂ (borided)
	Effects of Sulfiding	Fe, Fe/SiO ₂ , Fe/SiO ₂ , Fe/ZSM-5, Fe/SiO ₂ (sulfided), and Co (sulfided)
Reactor Runs at 25 atm	Effects of Pressure	5 "best" catalysts based on runs at 1 atm

Figure 8

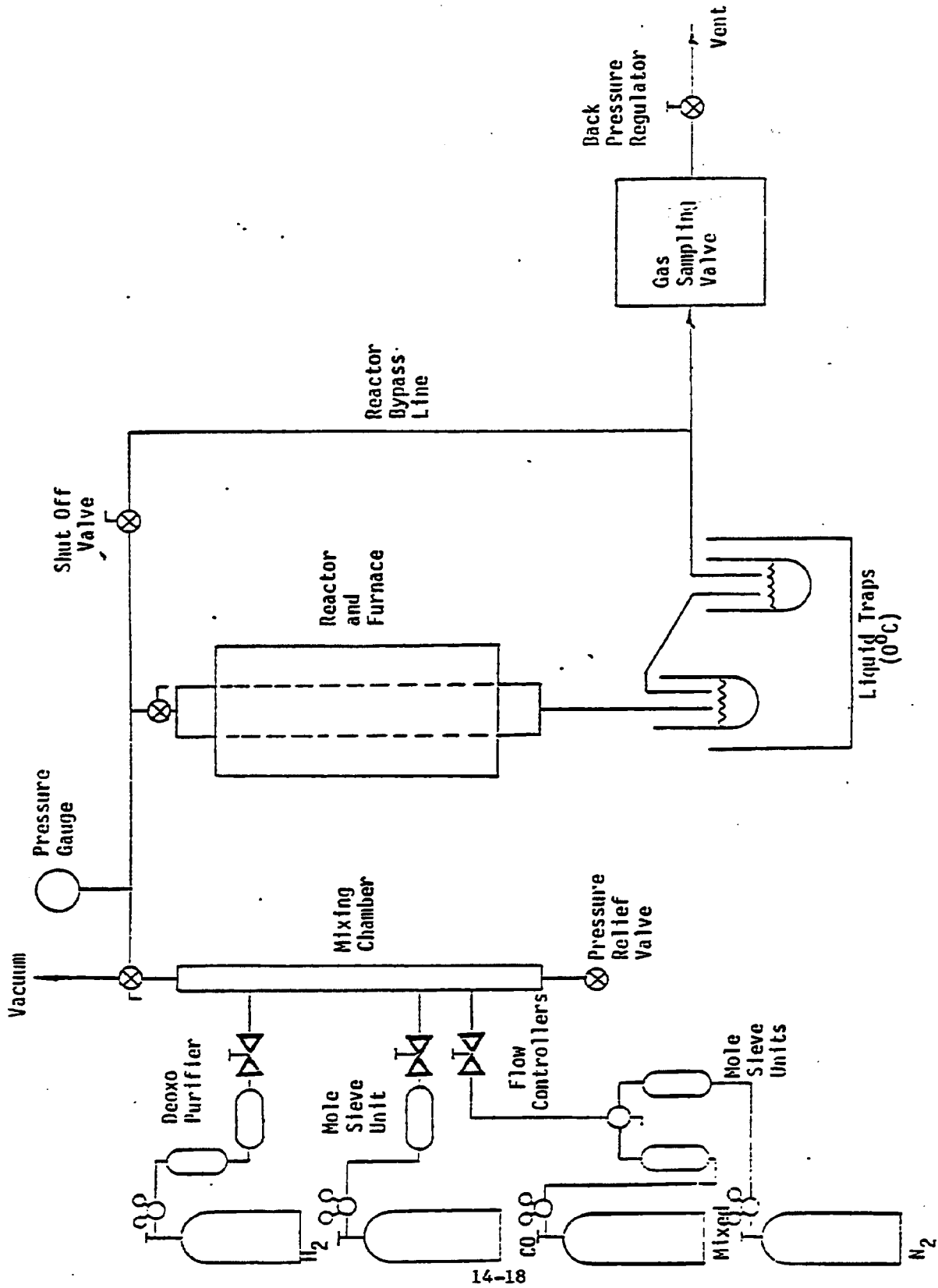


Figure 9. Fischer-Tropsch Reactor-System.

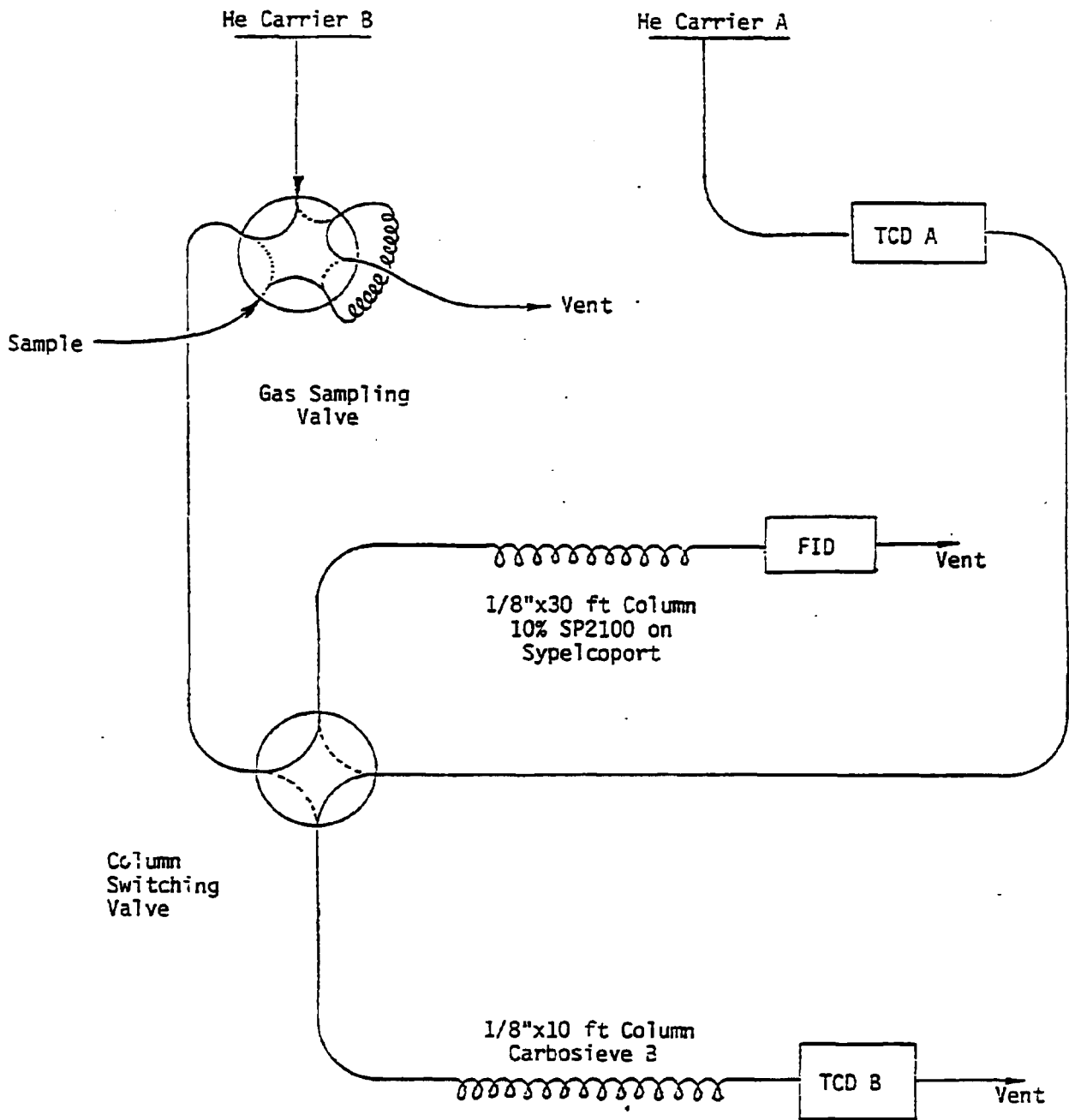


Figure 10

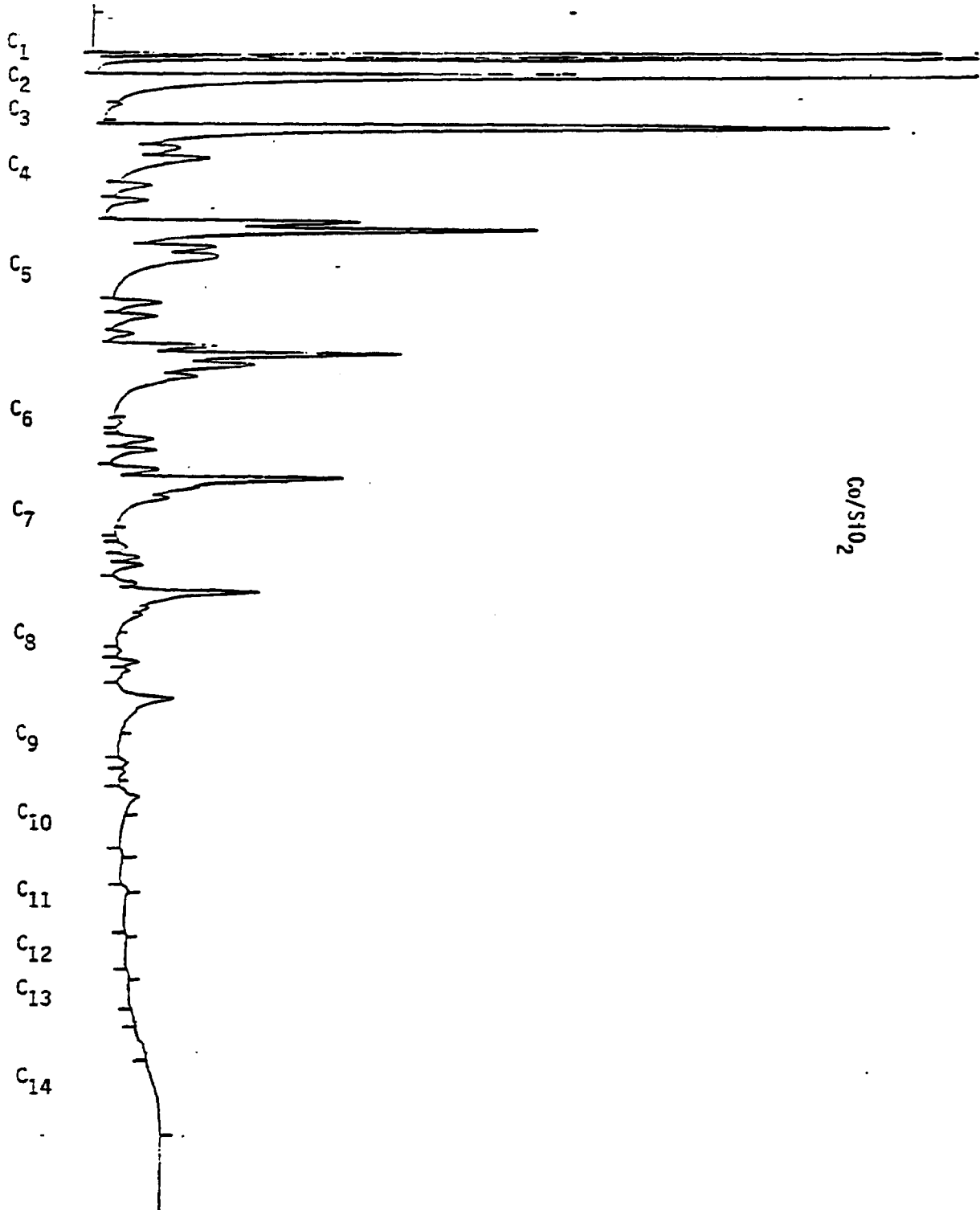


Figure 11
14-20

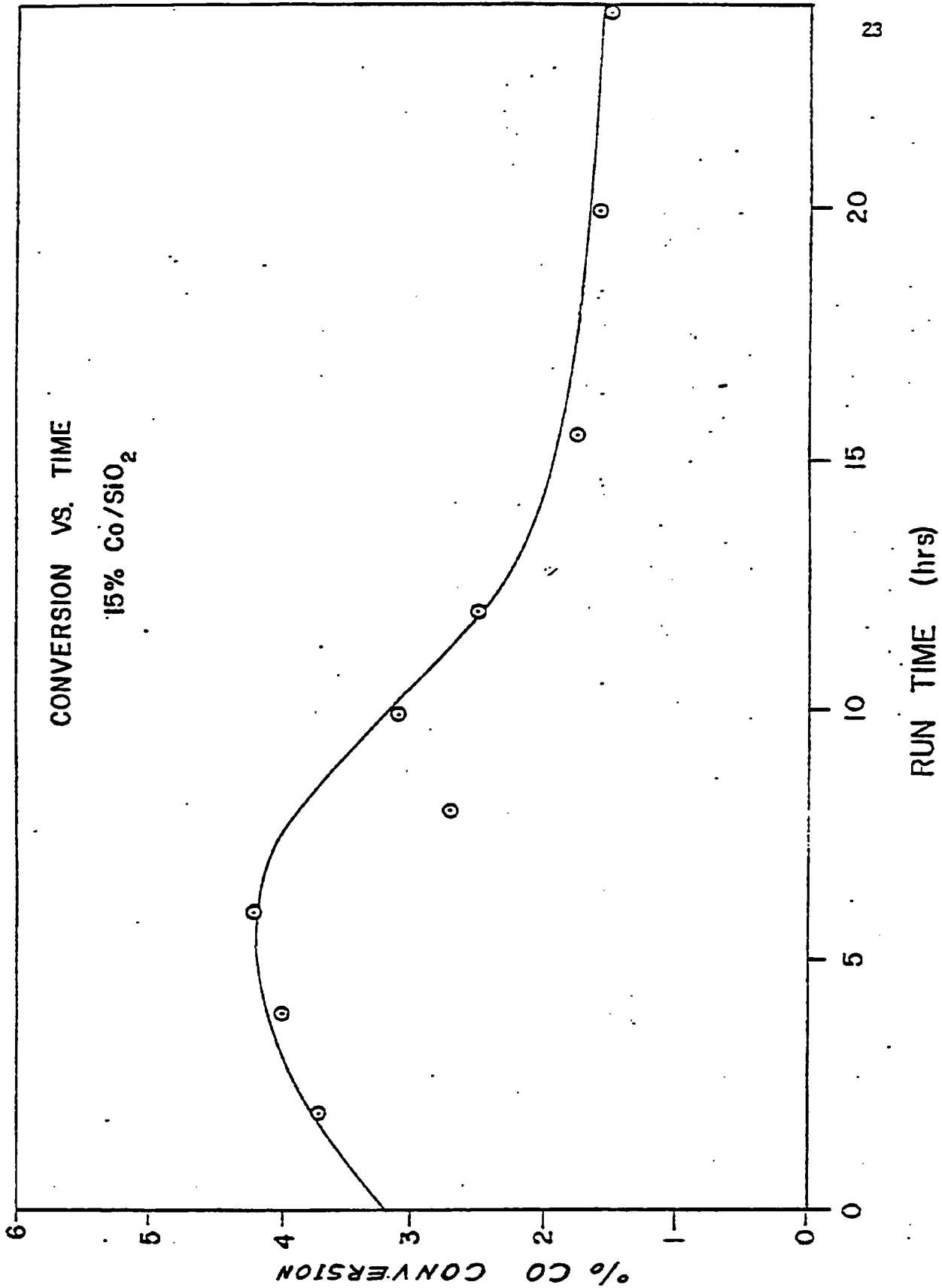


Figure 12. Percent CO Conversion vs. Reaction Time for Co-S-102.

CO TURNOVER NUMBERS FOR SUPPORTED CATALYSTS

Catalyst Code	H ₂ /CO Ratio	Temperature (K)	Turnover Number (N _{CO} × 10 ³)	Activation Energy (kJ/o mole)
Fe-S-102	2	460	0.64	97.1
	2	483	2.5	
	2	498	3.9	
	1	449	0.19	50.9
	1	483	1.4	
	1	498	2.5	
Fe-S-103	2	448	0.72	49.4
	2	483	3.2	
	2	498	7.0	
	1	442	0.79	54.0
	1	473	2.3	
	1	498	7.0	
FeK-S-100	2	498	6.6	—
FeS-S-101	2	498	0.33	—
CoE-A-101	2	500	1.4	—
Co-S-101	2	463	5.9	—

Figure 13

PRODUCT SELECTIVITIES FOR SUPPORTED CATALYSTS

Catalyst Code	Selectivity			Ave. Molecular Weight Hydrocarbon Product
	$\frac{C_{11}A}{C_{2-6}A}$	$\frac{C_5}{C_{2-6}A}$	$\frac{CO_2}{Alcohols}$	
Fe-S-102 ^a	0.16	0.27	0.47	27.77
Fe-S-102 ^b	0.12	0.23	0.56	20.60
Fe-S-103 ^a	0.25	0.33	0.30	26.27
Fe-S-103 ^b	0.20	0.31	0.36	27.54
FeK-S-100 ^a	0.08	0.19	0.65	30.26
FeS-S-100 ^a	0.26	0.19	0.55	20.25
Co-S-101 ^a	0.27	0.24	0.04	31.21

^a $H_2/CO = 2$

^b $H_2/CO = 1$

Figure 14 .

PRODUCT DISTRIBUTIONS
Fe Catalysts

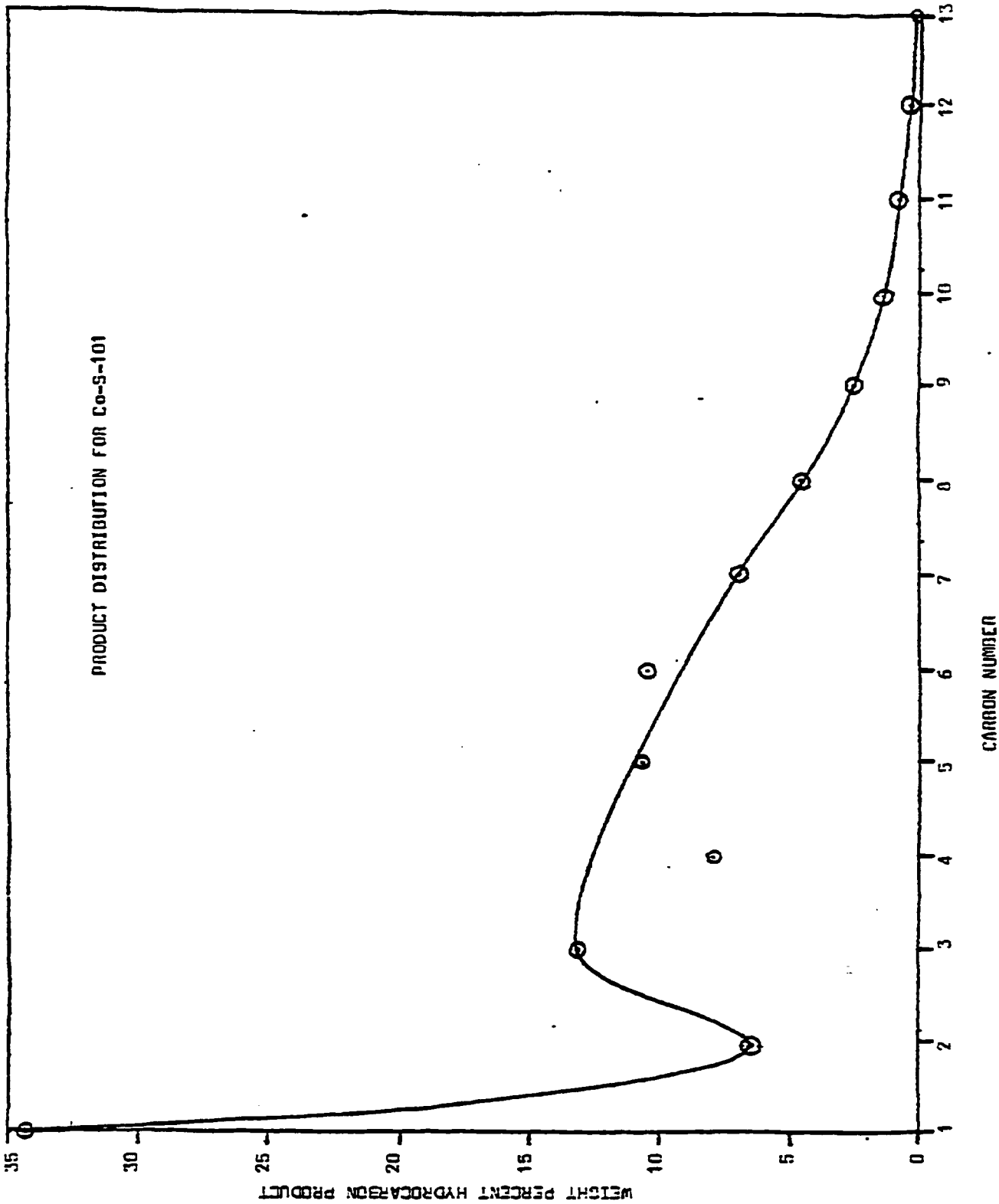
% Yield^a

<u>Catalyst</u>	<u>CH₄</u>	<u>C₂-C₄</u>	<u>C₅+</u>	<u>Alcohols</u>	<u>CO₂</u>
15% Fe/SiO ₂	55	38	4	3	4
14.7% Fe/ZSM-5	94	3	3	0	0
8.3% Fe/Silicalite	27	51	4	9	9

^a225°C, 90 kPa, H₂/CO = 2

Figure 15

PRODUCT DISTRIBUTION FOR Co-S-101



Olefin/Paraffin Ratios

<u>Catalyst</u>	<u>O/P</u>
15% Co/SiO ₂	0
15% Fe/SiO ₂	0.34
14.7% Fe/ZSM-5	0.013
8.3% Fe/Silicalite	0.66

Figure 17