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INVESTIGATION OF SULFUR-TOLERANT CATALYSTS FOR SELECTIVE SYNTHESIS OF HYDROCARBON LIQUIDS FROM COAL-DERIVED GASES. ANNUAL TECHNICAL PROGRESS REPORT, SEPTEMBER 19, 1979-SEPTEMBER 18, 1980

BRIGHAM YOUNG UNIV.
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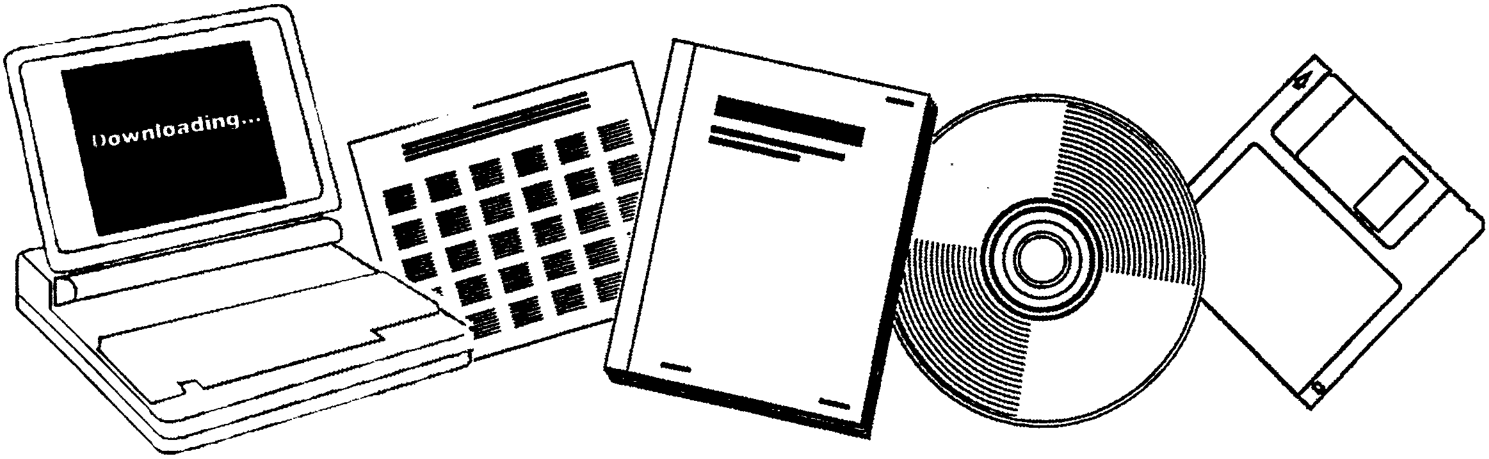

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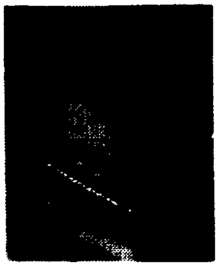

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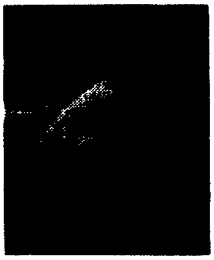

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INVESTIGATION OF SULFUR-TOLERANT CATALYSTS FOR SELECTIVE SYNTHESIS OF HYDROCARBON LIQUIDS FROM COAL-DERIVED GASES

Annual Technical Progress Report
For Period September 19, 1979 to September 18, 1980

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FOREWORD

This report summarizes technical progress during the first year (September 19, 1979 to September 18, 1980) of a three-year study conducted for the Department of Energy (DOE) under Contract No. DE-AC01-79ET14809. The principal investigator for this work was Dr. Calvin H. Bartholomew; Mr. Henry W. Pennline was the technical representative for DOE.

The following students contributed to the technical accomplishments and to this report: Glenn W. Davis, Jeffery L. Rankin, and Glen Witt. Mr. Rankin and Dr. Bartholomew were the principal authors. Lorelei Swingle provided typing services.

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ABSTRACT

During the first year, twelve supported iron and cobalt catalysts were prepared, including three boride promoted catalysts by a procedure developed previously in this laboratory. Each was characterized by H_2 and CO chemisorption measurements. Construction and testing of a high pressure laboratory microreactor system were completed. The system features a 0.65 cm tubular reactor, ice-temperature liquid traps, and a gas chromatographic system for complete product analysis. Eight catalysts were tested at 90 kPa, 450-500 K, $H_2/CO = 2$ to obtain product distribution, selectivity, and turnover number data. The results show that supports and promotors significantly affect specific activity and product selectivity of iron and cobalt in CO hydrogenation.

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I. OBJECTIVES AND SCOPE

A. Background

Cobalt and iron catalysts find wide application in the oil, gas and chemical industries, particularly in ammonia synthesis, hydrotreating and hydrocarbon synthesis reactions. They are expected to find even broader application in future energy technologies, especially in production of synthetic fuels from coal.

Although cobalt and iron containing catalysts for synthesis of aliphatic and aromatic hydrocarbons from coal-derived gases (Fischer-Tropsch Synthesis) were developed 2-3 decades ago and are even used on a very limited basis commercially to produce gasoline, their activity, selectivity and stability properties leave much to be desired. Most Fischer-Tropsch (FT) catalysts, for example evidence poor selectivity for highly desirable products such as gasoline (C_6-C_{12}) or chemical (C_2-C_5) feedstocks; that is, the hydrocarbon products range from gases to heavy waxes. Thus, there is clearly a need to find more selective catalysts. Since much of the recent work has been directed at synthesis of gaseous hydrocarbons for chemical feedstocks, there is clearly a need to focus on catalysts selective for the production of liquid aliphatics and aromatics, particularly in the C_6-C_{12} gasoline feedstock range.

With the exception of a few recent studies, previous investigations have emphasized a trial and error (screening) approach to finding the best FT catalysts. Much of the previous work was carried out using large catalyst beds under conditions such that the kinetics were influenced by diffusional resistance, temperature gradients and heat/mass transport effects. Generally, there was relatively little characterization of the physical and chemical properties of the catalysts. Yet recent evidence indicates that FT catalysts are complex, multiphase solids and that structural and chemical promoters and surface additives (including sulfur) can profoundly influence the activity, selectivity and stability of these catalysts (1-3). Moreover, poisoning by sulfur compounds at levels as low as 1 ppm can result in rapid significant losses of activity and dramatic changes in selectivity; yet there has been very little definitive work to characterize the effects of sulfur poisoning. Therefore, the need is evident for a comprehensive, systematic scientific investigation of these phenomena which includes careful characterization of bulk and surface catalytic properties and activity studies under chemical-reaction-controlled conditions.

B. Objectives

This report describes recent progress in a comprehensive, quantitative investigation of catalyst metal-additive interactions and their effects upon activity, selectivity and resistance to sulfur poisoning in Fischer-Tropsch Synthesis, the objectives of which are to:

1. Determine and explain the effects of the interaction of sulfur, nitrogen and boron additives with unsupported and supported cobalt and iron catalysts (promoted and unpromoted) on activity, selectivity and sulfur tolerance in Fischer-Tropsch synthesis.

2. Correlate the activity/selectivity and sulfur tolerance properties for hydrocarbon synthesis with the oxidation state, dispersion and adsorption properties of the catalytically active phases in iron and cobalt catalysts.

3. Seek more active, sulfur tolerant Fe and Co metal/metal oxide catalysts for selective production of premium feedstocks such as C_2-C_5 hydrocarbons or C_6-C_{12} hydrocarbons, with emphasis on gasoline liquids.

C. Technical Approach

In order to accomplish the above listed objectives, the proposed work has been divided into three areas of study (three tasks) to be completed over a period of three years:

Task 1. Preparation and characterization of promoted and unpromoted, supported and unsupported cobalt and iron synthesis catalysts.

Task 2. Measurement of hydrocarbon synthesis activity/selectivity properties of cobalt and iron catalysts under typical reaction conditions.

Task 3. Measurement of the deactivation rates of cobalt and iron catalysts during synthesis in a reaction mixture containing dilute H_2S.

The experimental approach for each of these tasks is described below.

Task 1: Catalyst Preparation and Characterization

Catalysts to be prepared as part of this study are listed in Table 1. Except for a 3 wt.% Fe/Al_2O_3, all of the catalysts will have metal loadings of approximately 15 wt.%. The alumina-supported catalysts will be prepared mainly by impregnation of an alkali-free γ-Al_2O_3, (Conoco) with aqueous solutions of cobalt and iron nitrates. Co/SiO_2 and Fe/SiO_2 will be prepared by a modification of a new developed controlled-pH precipitation technique which results in very high nickel dispersions in Ni/SiO_2 catalysts. The Al_2O_3 and SiO_2 supported catalysts will be dried directly without precalcination and all catalysts will be reduced in flowing hydrogen 12-16 hours at 725 K. Promoted catalysts will be prepared by separating each of the dried catalysts into two batches and reimpregnating one batch of each kind with a solution of KNO_3 or $Zn(NO_3)_2$ in such proportions as to obtain 3.0% K_2O and 15% ZnO in the final product.

Table 1

Catalyst Preparation Plans[a] (Task 1)

Metal-Support Combination	Unpromoted	Promoted		Additive Pretreatments			No. Catalysts
		K_2O	ZnO	S	N	B	
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_2O_3	x						1
Fe/ZSM-5	x	x		x[d]			3
Fe/Silicalite	x	x					2
						Total	28

[a] 15 wt.% metal unless otherwise noted; 3 wt.% K_2O, 15% ZnO.

[b] Promoted and unpromoted catalysts will be sulfided.

[c] 3 and 15 wt.% metal loadings.

[d] Promoted catalyst will be sulfided.

Catalysts will be sulfided by passing a gaseous mixture of 3% H_2S/H_2 over reduced samples at 575 K for a period of 12-16 hours. They will be nitrided by exposing the reduced catalyst to ammonia at 625 K for 12-16 hours followed by treatment in H_2 at 575 K for 12-16 hours to remove all traces of ammonia; thus preventing formation of urea during synthesis. Silica supported iron boride will be prepared according to special techniques recently developed in this laboratory for preparation of supported cobalt and nickel borides (1,2). This approach involves a nonaqueous, low temperature reduction of the impregnated or deposited metal nitrate/ support with sodium borohydride followed by washing, drying and high temperature reduction in hydrogen.

The catalysts prepared in this study will be characterized by a number of different techniques including H_2 and CO chemisorption, chemical analysis, x-ray diffraction, thermal gravimetric analysis, Moessbauer Spectroscopy and ESCA. Metal dispersions will be measured using hydrogen adsorption at 298 K and will be checked in selected cases using CO chemisorption at 298 K and x-ray line broadening. X-ray diffraction scans will also be used to establish the various catalytic phases. The extent of reduction to the metallic state and bulk oxidation states will be determined by thermal gravimetric analysis and Moessbauer spectroscopy. Selected samples will be sent to Austin Science Associates, Austin, Texas for Moessbauer Analysis. ESCA and X-ray diffraction scans will also be performed at the University of Utah. Chemical analysis will be taken by Rocky Mt. Geochemical Corp.

Characterization experiments to be performed in the Principal Investigator's laboratory are summarized in Table 2. Experiments to determine the effects of promoters and sulfur poisoning on the adsorption of CO and H_2 have also been included. These experiments should also reveal how the chemical states of the metal are affected by surface additives. Gravimetric Analysis will also be used to determine the kinetics of carbiding under reaction conditions. A TGS-2 Thermogravimetric analyzer is already available in the Catalysis laboratory.

Task 2: Activity/Selectivity Measurements

The experimental plan in Table 2 summarizes the catalysts to be tested and the purpose of their study. The conditions proposed for the activity/selectivity measurements are 525 K (and 500 K in selected cases), 1 atm, (25 atm in the case of the 4-5 most promising catalysts), $H_2/CO = 2$ and space velocities in the range of 2,000 to 30,000 h^{-1}. The space velocity will be adjusted in each test so that the CO conversion at 525 K is in the range of 5-10% in order that intrinsic activities may be obtained in the absence of diffusional influences (4-22, Appendix A). Catalyst samples will be crushed to fine particles in order to otherwise minimize diffusional influences; small samples on the order of 0.5 to 2 g and the use of high space velocities will minimize thermal gradients in the catalyst bed. Samples will be reduced *in situ* for 2 hours and then conditioned under the reaction conditions for a period of 6-18 hours during which time chromatograph samples will be carried out intermittently. From previous

Table 2

Experimental Plan

Task	Purpose of Study	Catalysts
1-Characterization:		
a. H_2 and CO Chemisorption Measurements	Determine Active Metal Surface Areas	H_2 Adsorption on All Catalysts; CO adsorption on Fe, Fe/SiO_2; Fe/Al_2O_3, Fe/MgO, Co and Co/SiO_2
b. H_2 and CO Adsorption Measurements on K_2O Promoted and Presulfided Catalysts	Determine effects of promoters and sulfur poisoning on reactant adsorption	Fe, Fe/SiO_2, Co, Co/SiO_2
c. Thermal Gravimetric Analysis and Moessbauer Spectroscopy	Determine effects of support on state of metal reduction; investigate carbide, nitride formation under reaction conditions.	Co/SiO_2, Fe, Fe/SiO_2, Fe/Al_2O_3 (2 loadings) Fe/ZSM-5[a] and Fe/Silicalite[a]
2-Activity/Selectivity Measurements	Effects of support	Fe, Fe/SiO_2, Fe/MgO Fe/Al_2O_3, Fe/ZSM-5, Fe/Silicalite, Co, Co/SiO_2
	Effects of metal	Co, Fe
	Effects of metal loading	3 and 15% Fe/Al_2O_3
	Effects of Promoter	K_2O promoted Fe, Fe/SiO_2, Co/SiO_2; ZnO promoted Fe/SiO_2
	Effects of Sulfiding	Fe, Fe/SiO_2 9unpromoted and K_2O promoted); Fe/SiO_2 ZnO promoted) and Co
	Effects of Nitriding, Boriding	Fe and Fe/SiO_2 (nitrided and borided), Co and Co/SiO_2 (borided)
	Effects of Pressure (Runs at 25 atm)	5 "best" catalysts based on runs at 1 atm

3-In situ H_2S Deactivation	Effects of support	Fe/SiO_2, Fe/MgO, Fe/Al_2O_3
	Effects of metal	Co, Fe, Co/SiO_2 and Fe/SiO_2
	Effects of metal loading	3 and 15% Fe/Al_2O_3
	Effects of Promoter	K_2O promoted Fe and Fe/SiO_2;ZnO promoted Fe/SiO_2 (sulfided and unsulfided)
	Effects of Sulfiding	Fe, Fe/SiO_2 (unpromoted and K_2O promoted)
	Effects of Nitriding, Boriding	Nitrided and Borided Fe, Fe/SiO_2; Borided Co and Co/SiO_2
	Effects of Pressure (Runs at 25 atm)	5 "best" catalysts based on runs at 1 atm
	Kinetics of Deactivation	Fe/SiO_2 and Co/SiO_2

---

[a] Fe/ZSM-5 and Fe/Silicalite samples have been obtained from the Pittsburgh Energy Technology Center.

investigations it is clear that in the case of small samples 6-18 hours reaction in the synthesis gas mixture is adequate to reach a steady state catalyst condition, although we will be able to check this experimentally.

Since much of the recent scientific work has been carried out at 1 atm but the FT process in normally run at 20-30 atm in industry, the proposed testing of the most important catalysts at both 1 and 25 atm will combine the advantages of both worlds. That is, specific activity/selectivity properties of iron and cobalt catalysts can be compared with those from other scientific laboratories and the performance of these same catalysts can be compared with commercial catalysts tested under industrial relevant conditions. At least one representative catalyst will be tested over a range of pressure from 1-25 atm so that effects of pressure can be determined and the results at 1 atm can be extrapolated to higher pressure. It is also possible that some of the catalyst will have more desirable selectivity properties at lower pressures and this approach will reveal such a phenomenon.

Most of the activity/selectivity tests will be carried out in a tubular, differential reactor system capable of 300-1300 K, 1-30 atm operation and equipped with mass flow meters, a CO NDIR analyzer and an HP-5834 chromatograph with TCD and FID detection. Glass reactors suitable for pretreating and activity testing samples at 1 atm are already available. A tubular reactor suitable for testing of powdered samples at 25 atm will be fabricated. The reactor system will be modified by adding a trap for hydrocarbon liquids in addition to the presently available water trap. Gaseous, liquid and aqueous phase hydrocarbons will be collected and analyzed using 10 foot Porapak Q, 5% Carbowax/ Chromosorb W and Chromosorb 102 columns. Selected runs will be carried out over the temperature range 500-575 K in a Berty Autoclave mixed flow reactor in order to determine conversion-temperature selectivity-temperature behavior and the effects of pressure.

Task 3: In situ H_2S Poisoning Measurements

The catalysts to be studied for sulfur tolerance are listed in Table 2 along with the purpose for investigation. Activity measurements will be made as a function of time during reaction at 525 K, 1 atm (again the 4-5 most promising catalysts also at 25 atm), $H_2/CO = 2$ and space velocities of 5,000 to 30,000 hr^{-1} with 10 ppm H_2S in the reactant mixture. The analysis of gaseous hydrocarbons will be made intermittantly using chromatography over a period of 24 hours. Liquid hydrocarbons will be analyzed at the beginning (following 6-8 hours of conditioning) and the end of the 24 hour deactivation runs. During the majority of tests, each catalyst will be housed in a Pyrex differential tubular reactor cell. Selected runs with Fe/SiO_2 and Co/SiO_2 will be made using (i) a quartz mixed flow reactor at 1 atm and 525-575 K to determine the kinetics of deactivation and (ii) an aluminized stainless steel tubular reactor at 25 atm, 525 K to determine effects of pressure.

To ensure reproducibility in both activity and poisoning experiments, chromatographic samples will be analyzed repeatedly until consistent results are obtained. Duplicate samples of the same catalyst will be tested in selected instances.

II. SUMMARY OF PROGRESS

A project progress summary is presentd in Figure 1 and accomplishments during the past year are summarized below. Figure 1 shows that progress is on schedule at the end of the first year.

Accomplishments and results from the past year are best summarized according to task:

Task 1. Twelve supported iron and cobalt catalysts were prepared, including three boride promoted catalysts. Each was characterized by H_2 and CO chemisorption measurements.

Task 2. Construction and testing of a high pressure laboratory microreactor system were completed. The system features a 0.65 cm diameter tubular reactor with wax and liquid traps. A gas chromatographic system for complete product analysis was designed and made operational. Eight catalyst were tested at 90 kPa, 450-500 K, and $H_2/CO = 2$. Product distributions, selectivity, and CO turnover numbers were obtained. The results show that promoters and supports can significantly affect the specific activity and selectivity of cobalt and iron in CO hydrogenation.

Task 3. Sulfur poisoning studies are scheduled to begin in March 1981.

Misc. Technical communications were established and maintained with other laboratories doing similar work. The PI visited - laboratories and companies while receiving 6 visitors. The PI and students also attended and presented papers at 6 technical meetings. Three students (1 Ph.D., 1 M.S. and 1 B.S. Candidate) were supported, trained and educated as part of this contract.

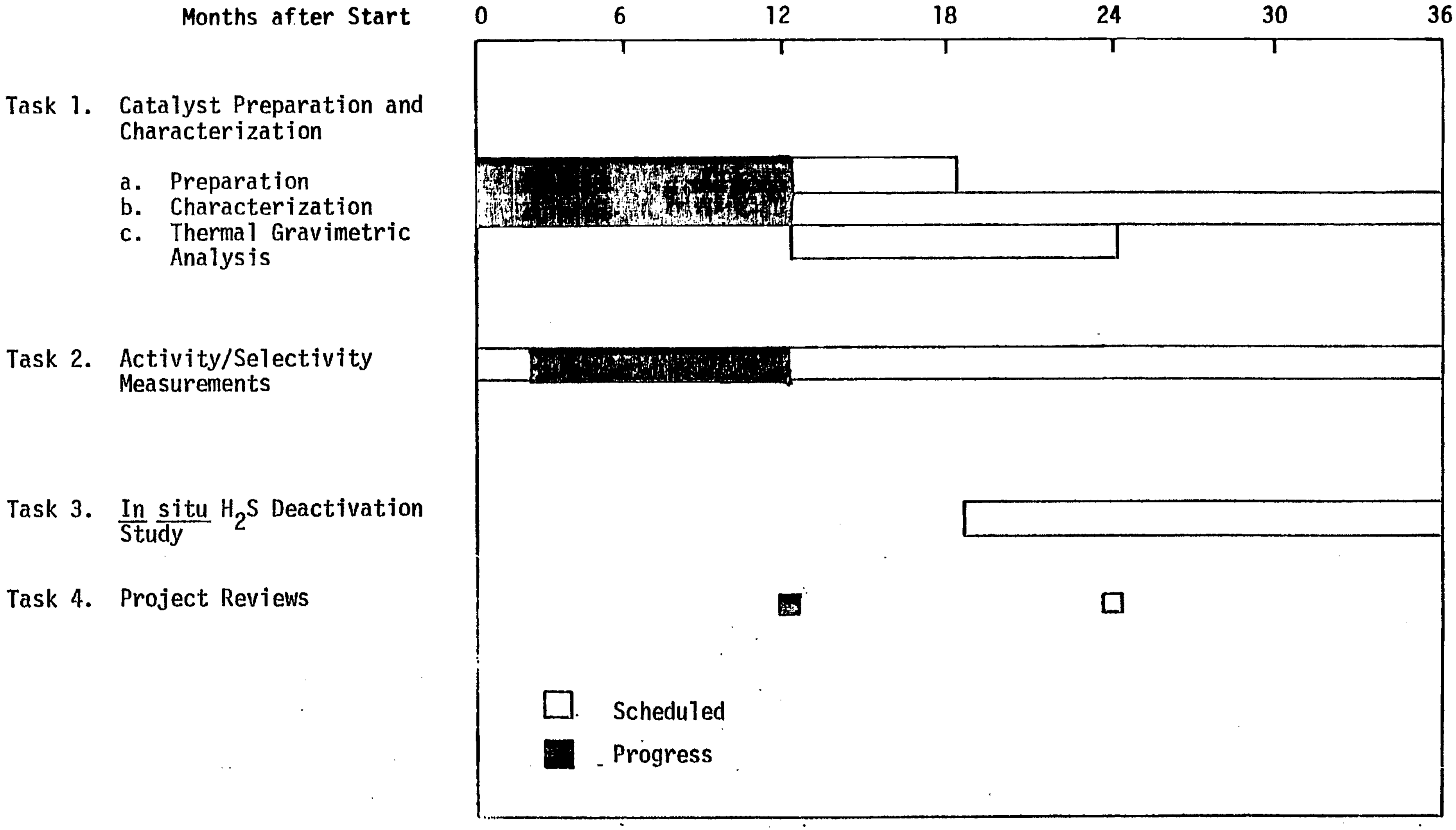

Figure 1. Schedule of Proposed Research Activities and Progress.

III. Detailed Description of Technical Progress

A. Task 1: Catalyst Preparation and Characterization

1. Catalyst Preparation

Table 3 lists the catalysts prepared during the first year of this study with their designated codes and compositions. A brief description of their preparation follows (23, 24, 25):

The boride-promoted catalysts were prepared under a N_2 atmosphere in a sealed reaction vessel to avoid the formation of boron oxide, which cannot be reduced in flowing H_2 even at 675 K(1) . Enough support was used so that, if all the metal adhered to the support, 18% metal loading would result. From previous experience we estimate a loading of about 10 wt.%; this is currently being checked by chemical analysis.

After drying the alumina or commerical Cab-O-Sil silica support material at 873 K and cobalt or iron nitrate in vacuo at about 340 K to remove most of the water of hydration, the metal salt was added to a slurry of support and dried acetone. The solution was then completely dried and added to a reaction vessel with dried isopropanol as the reaction medium. $NaBH_4$ was added in a ratio of 4 moles $NaBH_4$ to 1 mole of metal nitrate and the mixture was allowed to react at 298 K for 4 days. The resulting fine particles were washed several times with methanol over a period of 20 days. The catalysts were then stored in deaerated isopropanol.

To avoid exposing the catalyst to air during transfer to the reduction cell, a system was devised for loading the cobalt and iron boride catalysts into the Pyrex reactor in an inert atmosphere. Approximately 0.5 g of the catalyst was dried to paste in a glove box that was thoroughly purged with N_2 and then loaded into the reactor in the glove box after which the reactor was sealed until the H_2 reduction.

Because some isopropanol was still present in the catalyst, it had to be dried prior to reduction. This was accomplished by evacuating the sample at 475 K for 2 days. The catalyst was then reduced in flowing H_2 for 16 hours at 725 K and a space velocity of 2000 h^{-1}.

Preparation of the metal and potassium oxide promoted catalysts was by simple impregnation of support to incipient wetness with aqueous metal salt solutions. Several impregnations were necessary to ensure a uniform deposition of the metal salt, each followed by intermediate drying. After the final impregnation, the catalysts were dried in an oven at 355-375 K for 24 hours. These samples were reduced in flowing H_2 at 725 K and 2000 h^{-1} space velocity to prepare them for chemisorption trials.

The K atom to metal atom ratio of 0.2 was used as a guideline for potassium promoted catalyst composition. This is based on findings of Bell et al. (26) indicating that a 20 K/100 Fe atomic ratio maximizes the effects of the K_2O promoter.

TABLE 3

Catalyst Compositions and Codes

Code[a]	Metal Loading(%)	Promoter Loading(%)
Co-S-101	3	-
Co-S-102	15	-
Co-K-S-100	15	3
Fe-S-100	3	-
Fe-S-101	15	-
Fe-S-102	15	-
Fe-K-S-100	15	3
Fe-ZSM-5	14.7	-
Fe-Silicalite	8.3	-
Co-B-A-101	∿10	-
Co-B-S-101	∿10	-
Fe-B-101	∿10	-

---

[a] A and S refer to alumina (Conoco dispal) and silica (Cab-O-Sil) supports respectively.

The two novel zeolite catalysts Fe-ZSM-5 and Fe-Silicalite, were obtained by Dr. Bartholomew from the Pittsburgh Energy Technology Center (23).

2. Catalyst Characterization

Metal surface areas were measured for all freshly reduced catalyst by hydrogen chemisorption at 298 K using a conventional volumetric apparatus. Following reduction, catalysts were evacuated to 10^{-6} Torr for two hours at 675 K. Hydrogen uptakes were measured as a function of pressure and the isotherm was extrapolated to obtain the adsorption at zero pressure.

CO chemisorption measurements were performed in a similar manner. A second titration of the gas followed to make correction for physisorption of CO on the catalyst. The difference between the two extrapolated uptakes was taken as the chemisorption uptake. Similar experiments on samples of pure silica support showed that both chemisorption and physisorption on the support are negligible.

Results of the chemisorption measurements are listed in Table 4. From the uptake data for the iron catalysts it is apparent that long reduction times (> 24 hours) are necessary to obtain adequate metal surface area. Calcination in air, followed by reduction also improved surface area slightly (25). CO/H ratios are unexpectedly low for the Co/SiO_2, K-promoted Fe/ SiO_2, Fe/ZSM-5, and Fe/Silicalite catalysts. The relatively large hydrogen uptakes for boron promoted cobalt indicate that boron may be a promoter for improving cobalt dispersion.

We have received samples of silicalite support from Union Carbide for further preparation of promoted iron silicalite catalysts. Samples of ZSM-5 support are presently being obtained for further catalyst preparation. The preparation of a 15% Fe on Al_2O_3, unsupported Fe, Co, Fe-boride, and Fe-potassium catalysts is also planned.

B. Task 2: Activity/Selectivity Measurements

1. Equipment Construction

During the past year, several reactor system designs were examined and considered. The system diagramed in Figure 2 resulted. Presently, the system is fully operational, though automatic flow controllers are still on order.

The design incorporates a 0.64 cm diameter stainless steel tubular reactor capable of withstanding pressures up to 25 atm. It includes a metal ring to facilitate heat transfer from the tube furnace used as a heater. A diagram of the reactor is shown in Figure 3. This reactor was constructed in the University's machine shop (24).

TABLE 4

H_2 and CO Chemisorption Uptakes at 298 K - Iron and Cobalt Catalysts

Catalyst Code	H_2 Uptake (µmoles/g)	CO Uptake (µmoles/g)	$\frac{CO}{H}$
Co-S-101	17.10^a	-	-
	61.44^b	6.46^b	0.053
Co-S-102	44.48^a	-	-
	57.61^b	10.34^b	0.090
Co-K-S-100	11.73	-	-
Fe-S-100	2.10^a	2.69^a	0.640
	23.17^b	0.35^b	0.008
Fe-S-101	3.50^a	4.66^a	0.666
	9.92^c	-	-
Fe-S-102	3.61^a	9.80^a	1.36
	59.22^b	-	-
	57.93^d	-	-
	20.19^e	3.52^e	0.087
Fe-K-S-100	11.23^c	7.23^c	0.322
Fe-ZSM-5	22.76^b	7.68^b	0.169
Fe-Silicalite	20.37^b	4.55^b	0.117
Co-B-A-101	59^a	74^a	0.63
	67^d	66^d	0.49
Co-B-S-101	56^a	60^a	0.54

---

[a] After 12 hr reduction in H_2

[b] After 24 hr reduction in H_2

[c] After 2 hr calcination in air, 20 hr reduction in H_2

[d] After 24 hr reactor run

[e] After 20 hr reduction in H_2

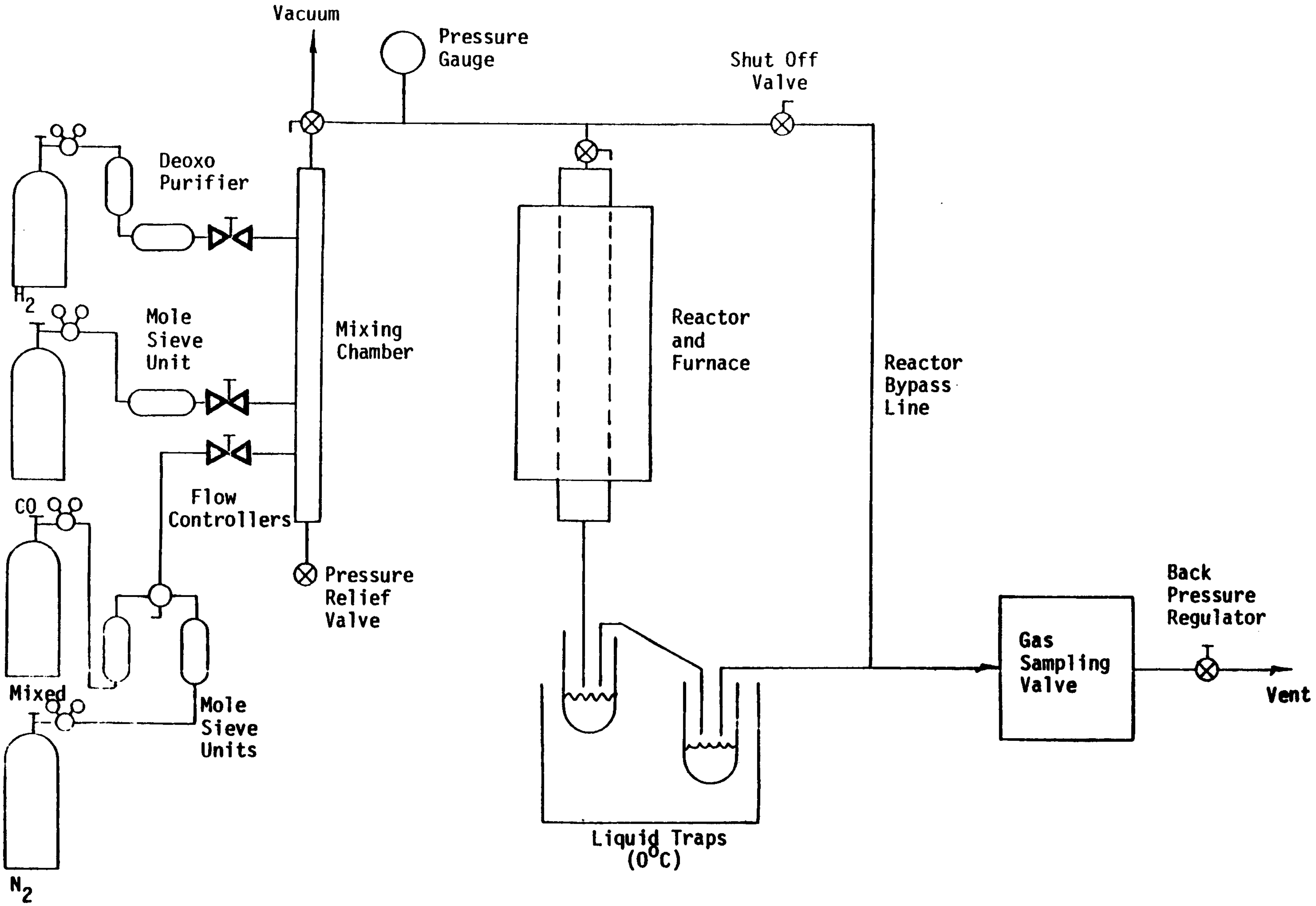

Figure 2. Fischer-Tropsch Reactor-System.

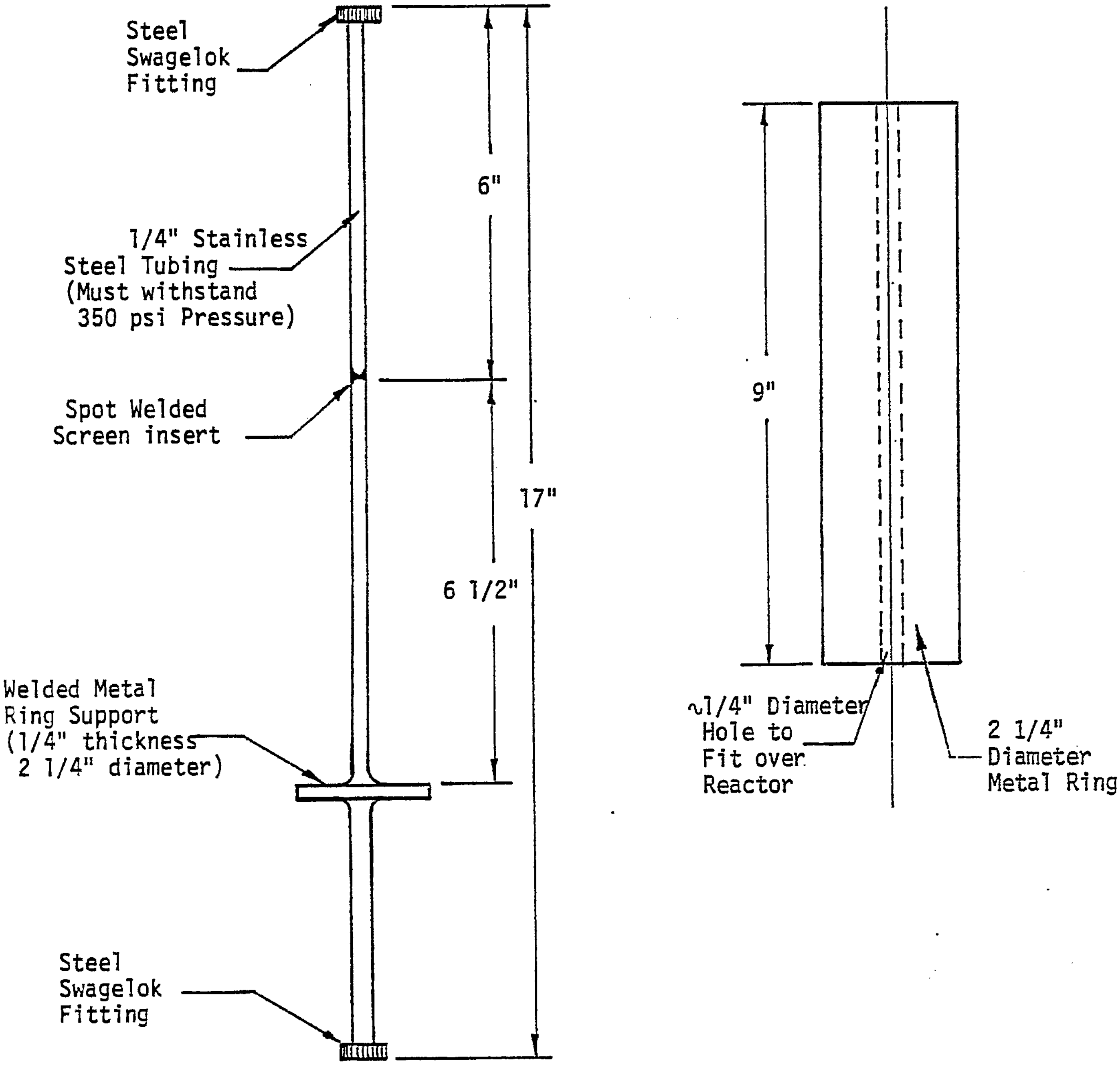

Figure 3. High Pressure Fischer-Tropsch Reactor.

Since liquid and wax products would probably cause reactor plugging or chromatograph fouling, two traps will be used at ice temperature. These are constructed of 1/2" stainless steel tubing and Swagelok fittings as shown in Figure 4. A small glass vial in each trap accumulates liquid and wax samples (24).

2. Chromatographic Analysis

Considerable, detailed discussion and planning were conducted regarding the chromatographic analysis of products. It was found that the use of capillary columns would be convenient for analysis but difficult and expensive to install in our existing system. Thus, packed columns will be used for hydrocarbon and gas product analysis.

A 30 feet by 1/8" packed column consisting of 10% SP2100 on Supelcoport is used for hydrocarbon analysis. By temperature programming from 0°C to 200°C, C_1, to C_{20} hydrocarbons may be separated and detected with a flame ionization detector.

Carbosieve B in a 10 ft by 1/8" packed column separates all fixed gases in a sample when temperature programmed from 50°C to 250°C. This analytical technique is unusual in that the separation of all components is accomplished with only one column. The components from this separation are analyzed by a thermal conductivity detector.

Figure 5 shows a diagram of the chromatograph internal arrangement. The temperature program-sampling scheme is shown in Figure 6. Two samples are served to the chromatograph and are analyzed over a two-hour period. Cooling is accomplished by a liquid N_2 cryogenic valve system. Figures 7 and 8 show typical chromatograms obtained for hydrocarbons and fixed gases. Peak identification was made by enhancement with pure samples obtained from Supelco, Incorporated. Alcohol peaks, though not shown, are also identifiable.

3. Experimental Measurements

Eight catalyst were tested in a Pyrex cell reactor at 1 atm pressure during the 4th quarter. Space velocities varied from 200 h^{-1} to 1000 h^{-1} to obtain CO conversions between 2% and 10%. Iron catalysts were tested at 495-500 K while cobalt catalysts were tested at 445-450 K. The following catalysts were run in a 2 to 1 H_2 to CO mixture:

1. Co-S-101
2. Co-S-102
3. Fe-S-100
4. Fe-S-102
5. Fe-ZSM-5

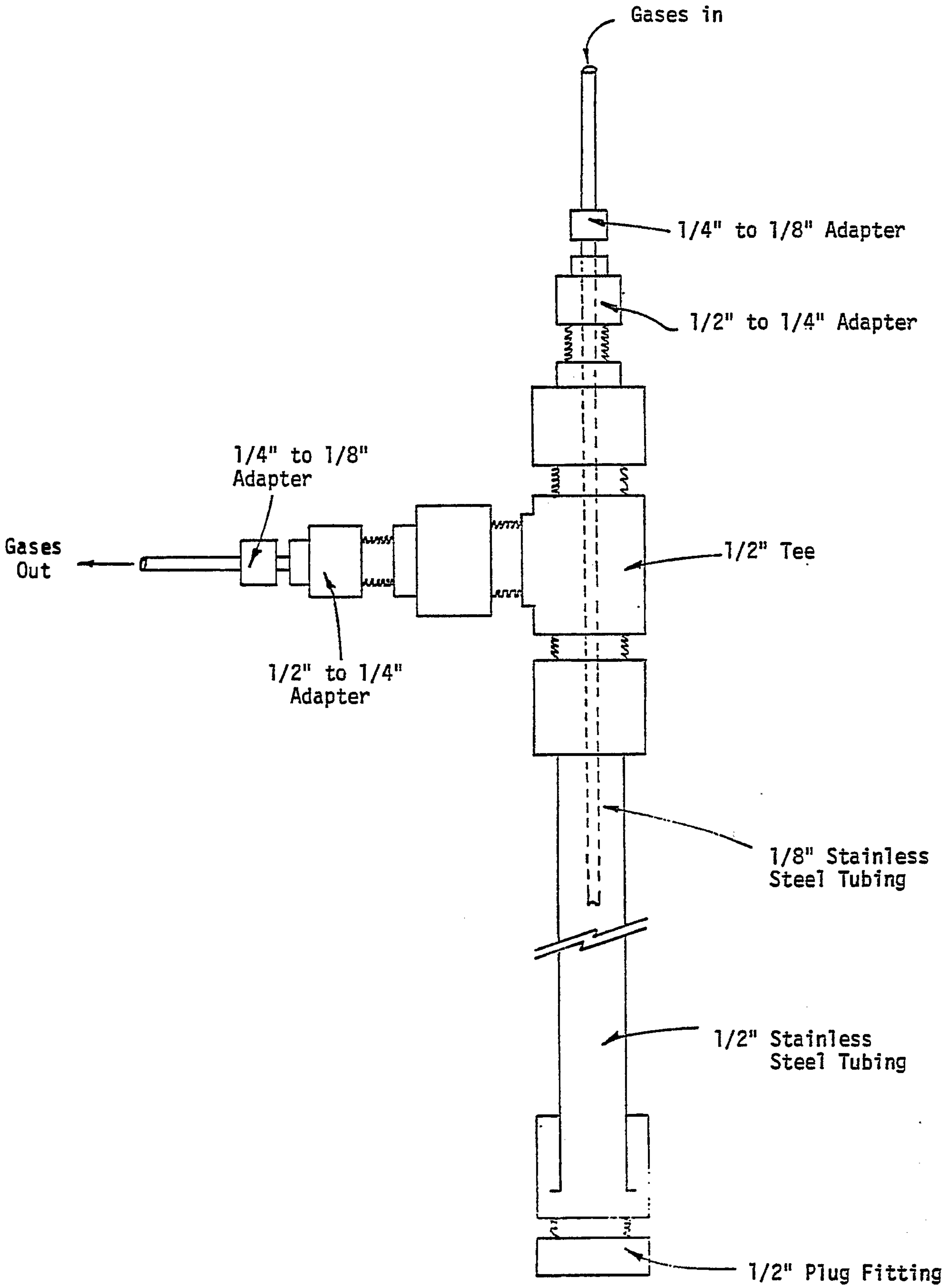

Figure 4. Liquid and Wax Trap.

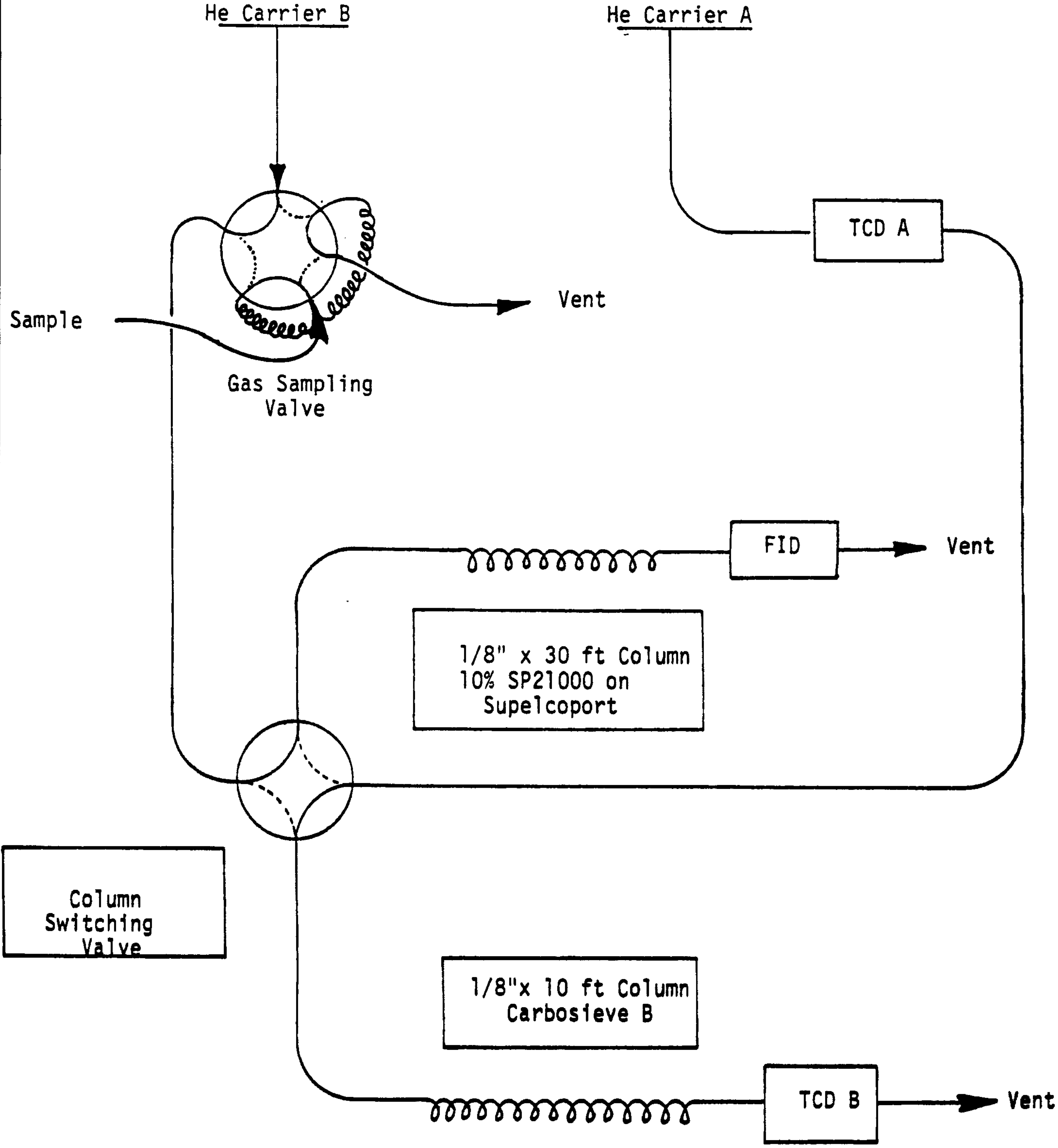

Figure 5. Chromatograph Internals.

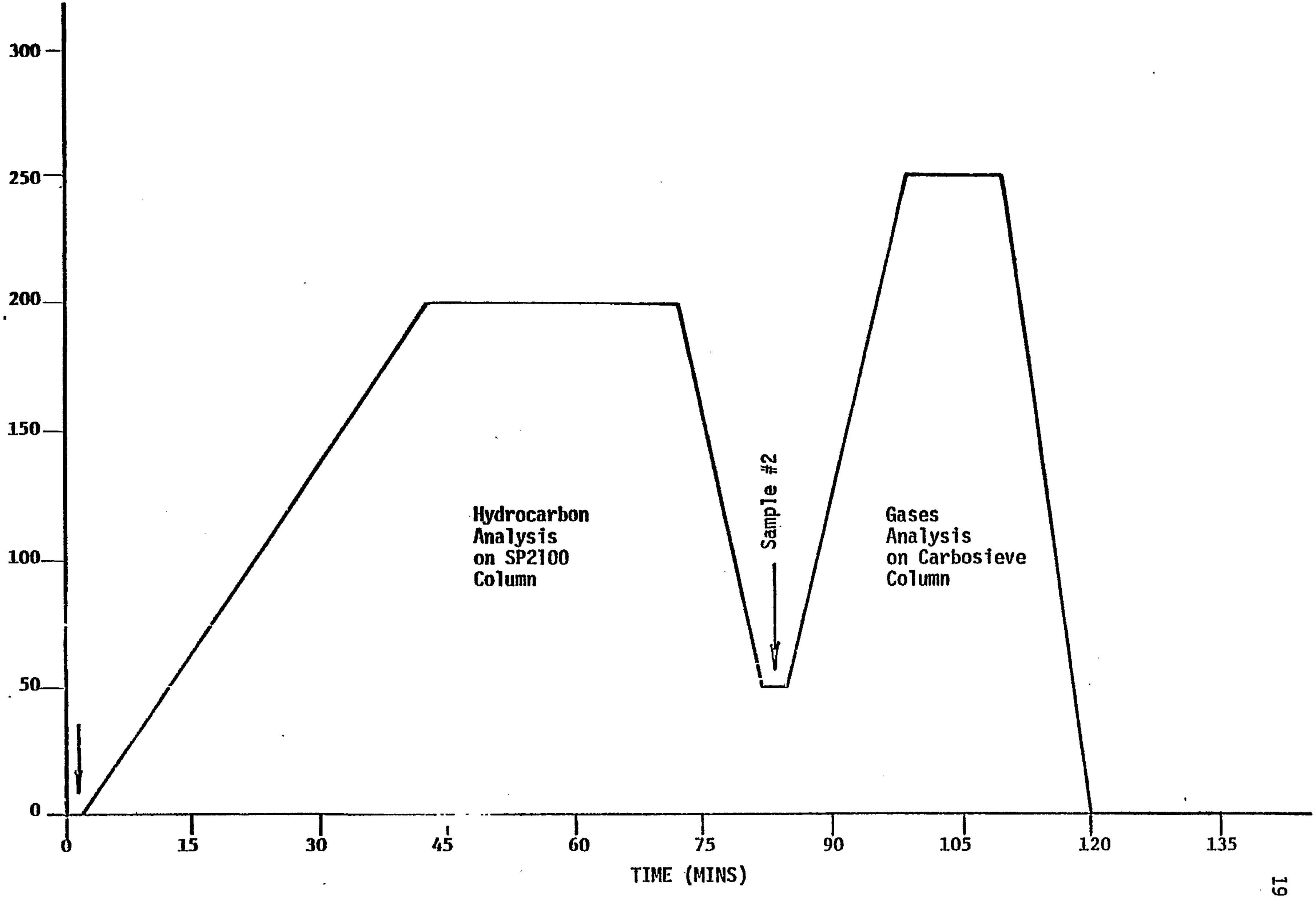

Figure 6. Temperature Program and Sampling Scheme for Chromatographic Analysis.

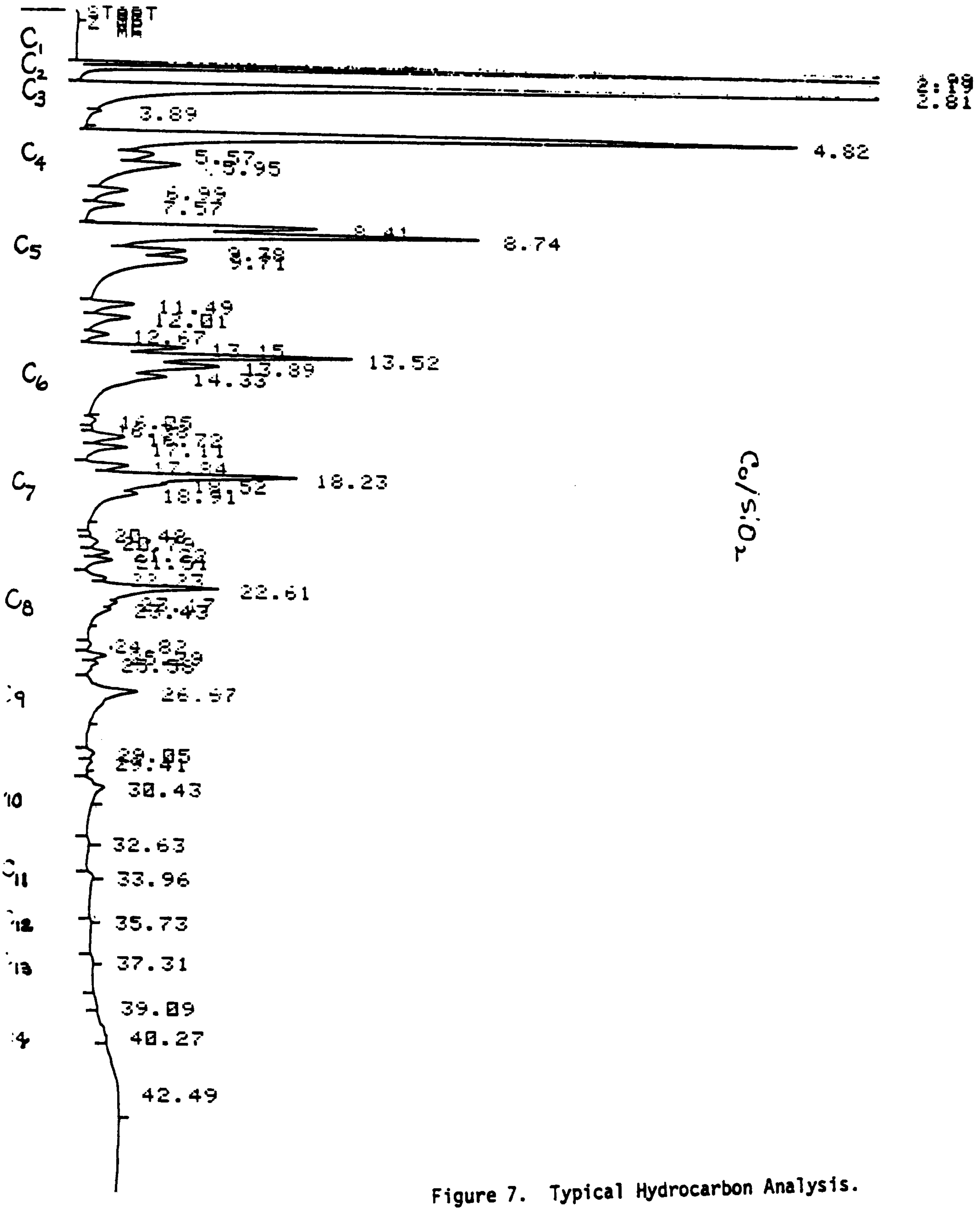

Figure 7. Typical Hydrocarbon Analysis.

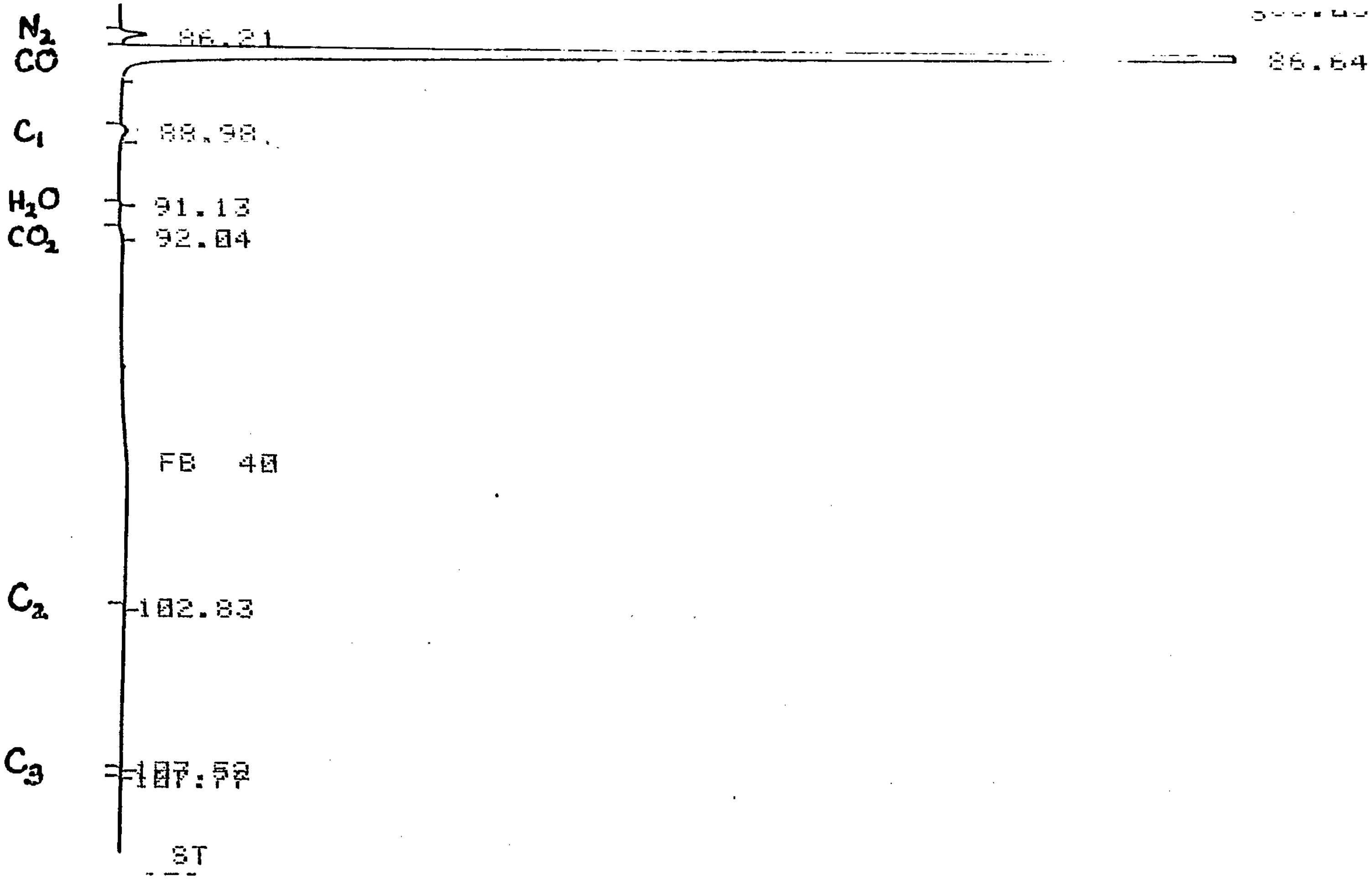

Figure 8. Typical Fixed Gases Analysis.

6. Fe-Silicalite

7. Co-B-A-101

8. Co-B-S-101

As shown by Figure 9 conversion of CO reached steady state after approximately 15 hours for a 15% Co/SiO$_2$ catalyst. A similar pattern was also observed in tests of other unpromoted catalysts. The cobalt boride catalyst required longer conditioning in the synthesis gas to achieve steady state. A graph of conversion versus time for Co-B-A-101 is shown in Figure 10 (24).

CO turnover numbers calculated on the basis of metal surface areas as measured by H$_2$ chemisorption are listed in Table 5. Metal loading significantly affects activity of iron and cobalt catalysts. In the case of iron CO turnover number increased from 0.09 x 10^{-3} molecules/site-sec to 12 x 10^{-3} molecules/site-sec as loading increased from 3% to 15%. The opposite trend occurred with cobalt catalysts. Fe/ZSM-5 and Fe/Silicalite showed relatively poor activity for Fischer-Tropsch synthesis. These results are presented diagrammatically in Figure 11.

Conversion over Co-B-A-101 was measured at 4 temperatures in the range of 460 to 550 K and an activation energy plot was made by plotting logrithm of the CO turnover numbers versus inverse temperature as shown in Figure 12 (24). An activation energy ranging from 68 to 79 kJ/mol was obtained by linear regression. These values are in good agreement with the value of 63 kJ/mol reported previously for unsupported borided cobalt (1,2).

Figures 13 through 18 present the product distribution curves for each catalyst tested. It should be noted that the iron catalysts produced many more isomers and oxygenates than cobalt. This hindered analysis, especially in the C$_2$ to C$_3$ range, and caused errors in the product distribution curves. However, Fe/ZSM-5, Fe/Silicalite, and apparently Co-B/Silica catalysts show distinctly unusual distributions with second peaks at heavier weight hydrocarbons. The result for cobalt boride is presently being checked.

Table 6 lists selectivity data for the catalysts tested. The Fe catalysts produce greater amounts of olefins, increasing the olefin/paraffin ratio. No olefins were detected from the Co/SiO$_2$ catalyst runs. It is also apparent that the iron catalysts tend to produce more oxygenated compounds as evidenced by the alcohol content of the products. At 1 atm pressure, the cobalt catalysts produce higher molecular weight products than any of the iron catalysts. Higher operating pressures may be required to minimize CH$_4$ formation on Fe.

4. Transport Limitation Calculations

During the second quarter (24), criteria for avoiding mass and heat transfer limitations in reactors of the fixed bed type were examined, including the following areas:

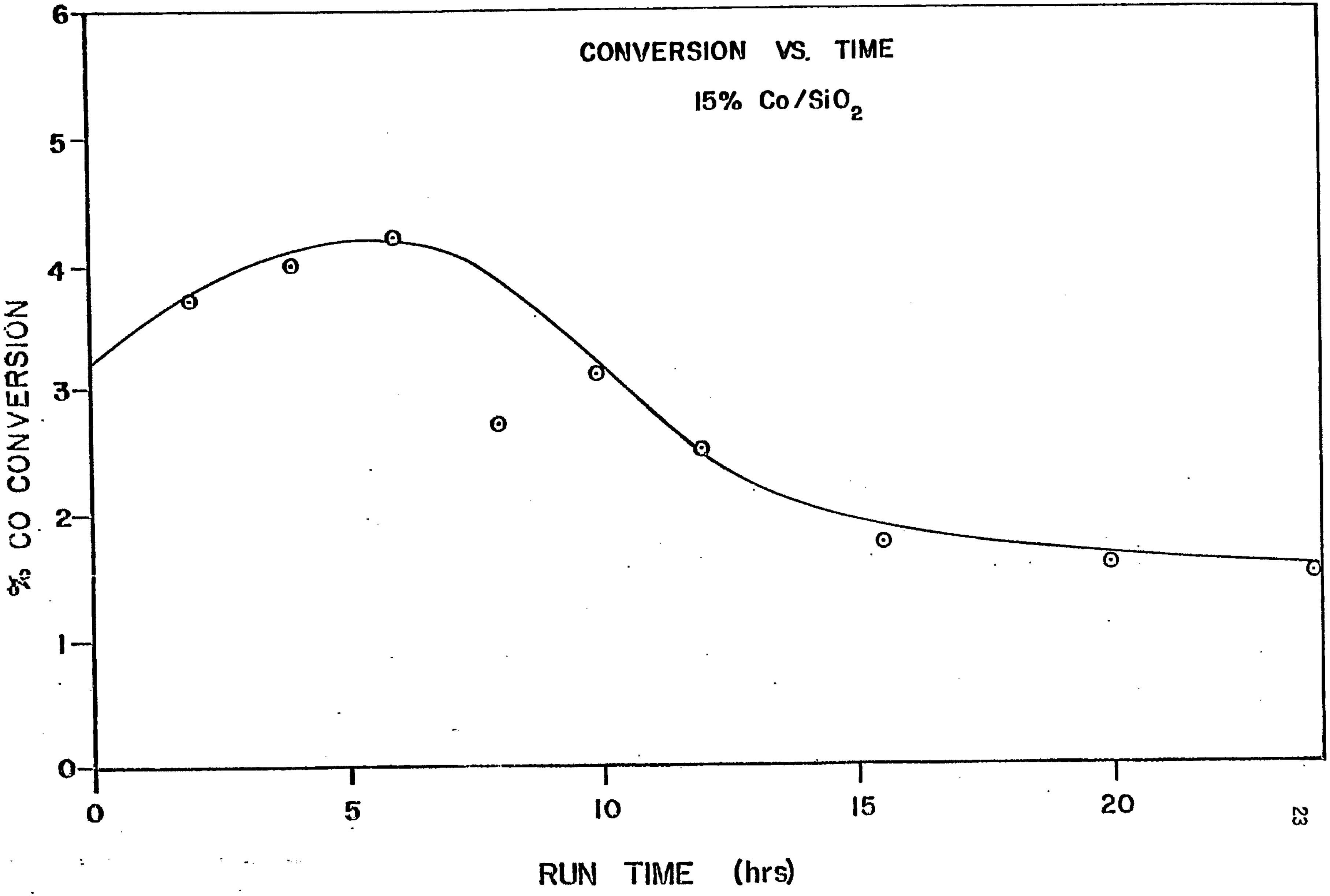

Figure 9. Percent CO Conversion vs. Reaction Time for Co-S-102.

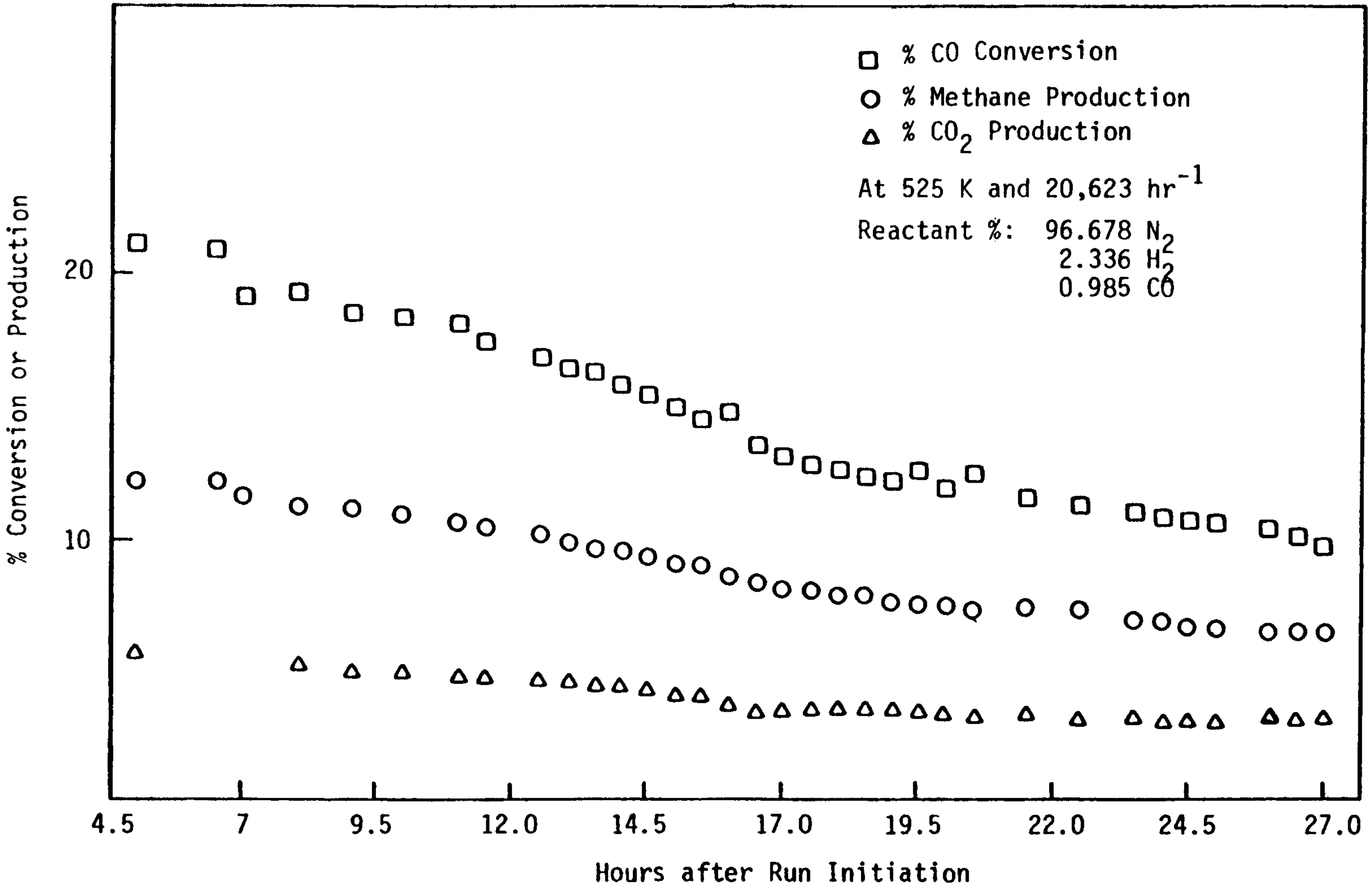

Figure 10. Percent CO Conversion, Percent CH_4 and CO_2 Production vs. Reaction Time for Co-B-A-101.

TABLE 5

CO Turnover Numbers

Catalyst Code	Temperature (K)	CO Turnover Numbers (molecules/site-sec)
Co-S-101	450	3.0×10^{-3}
Co-S-102	450	6.4×10^{-4}
Fe-S-100	500	9.4×10^{-5}
Fe-S-102	500	1.2×10^{-2}
Fe-ZSM-5	500	4.5×10^{-4}
Fe-Silicalite	500	2.4×10^{-4}
Co-B-A-101	460	4.4×10^{-4}
Co-B-A-101	500	1.4×10^{-3}
Co-B-A-101	525	3.4×10^{-3}
Co-B-A-101	550	7.8×10^{-3}

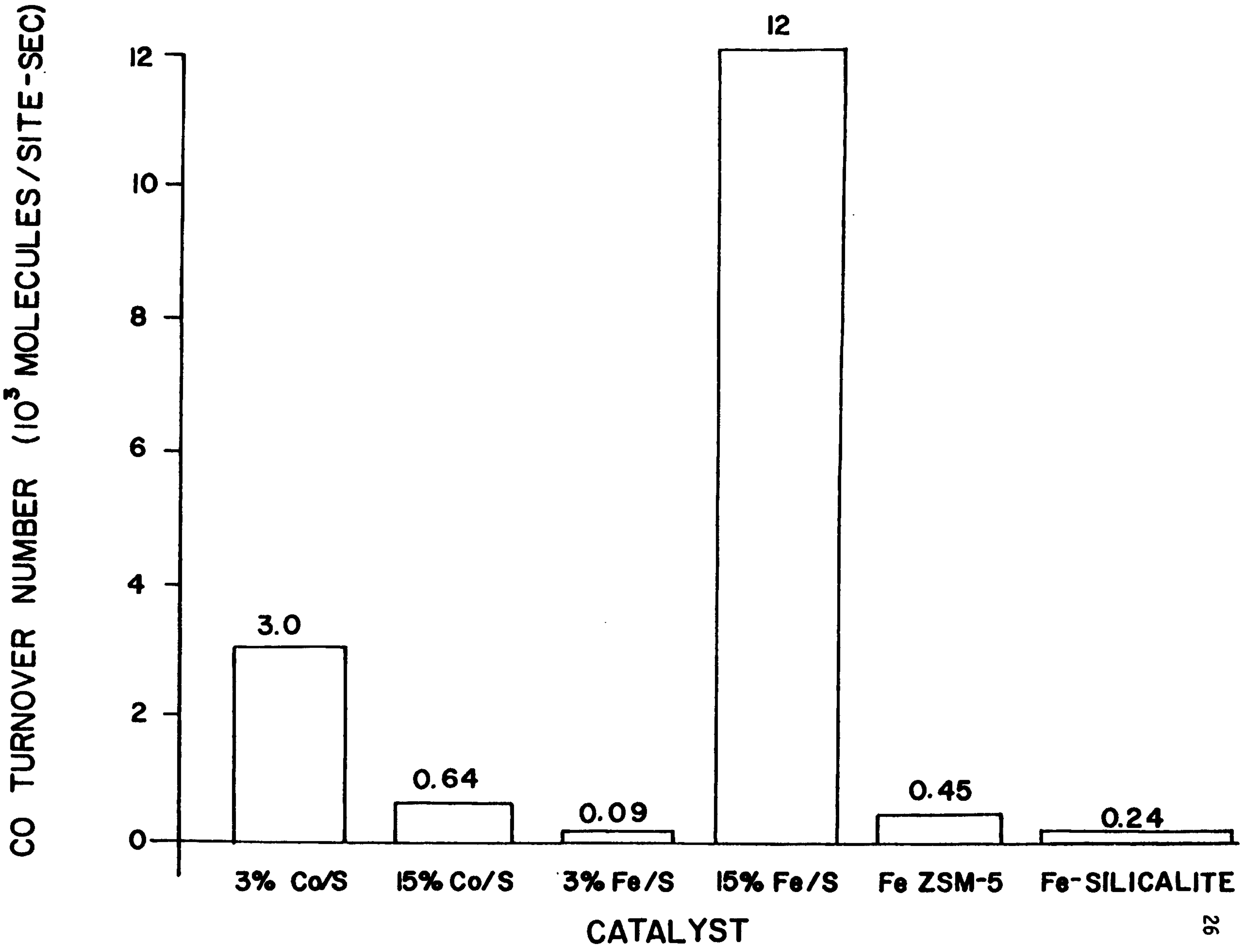

Figure 11. CO Turnover Numbers for Iron and Cobalt Catalysts.

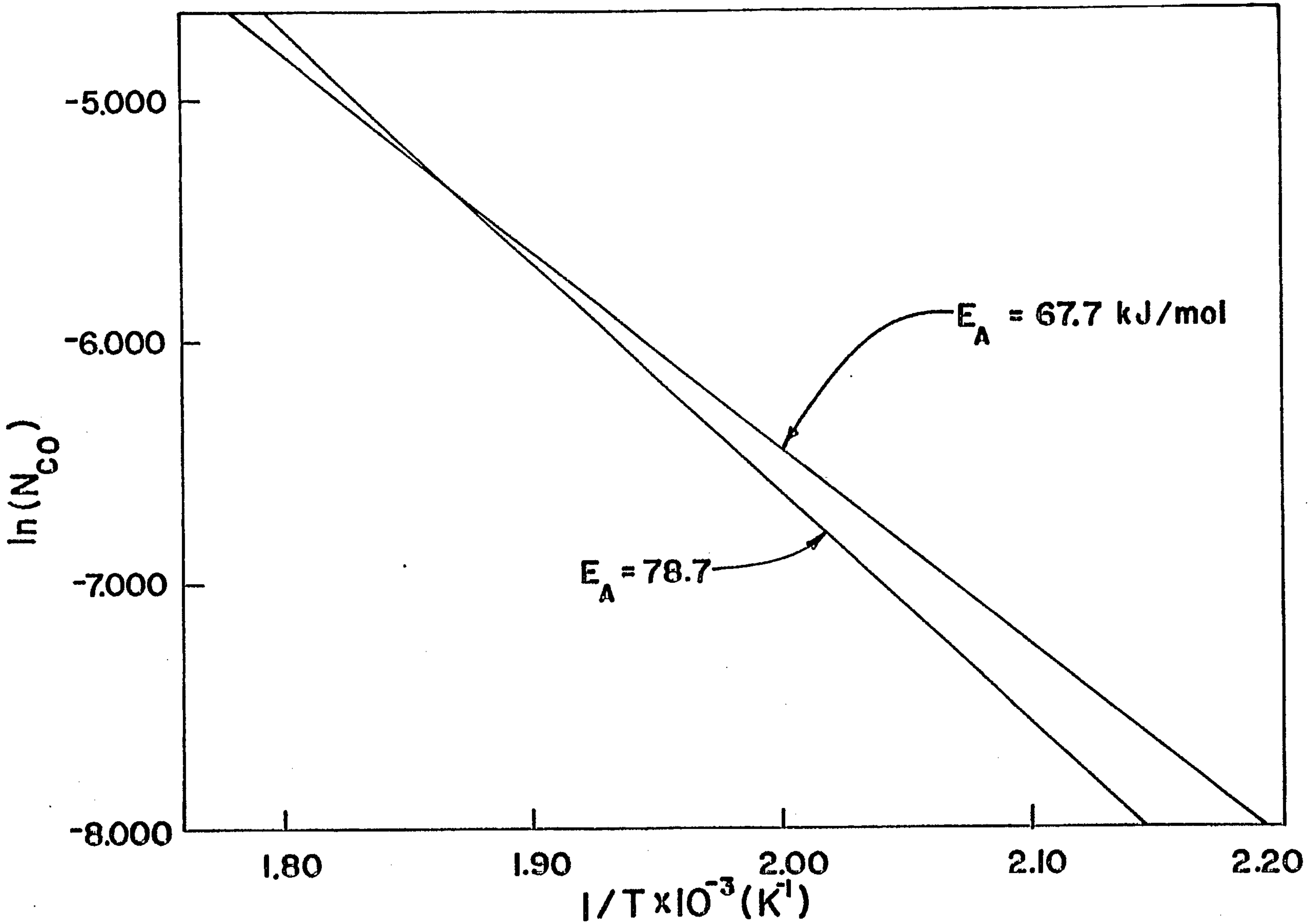

Figure 12. Activation Energy Plot for Co-B-A-101.

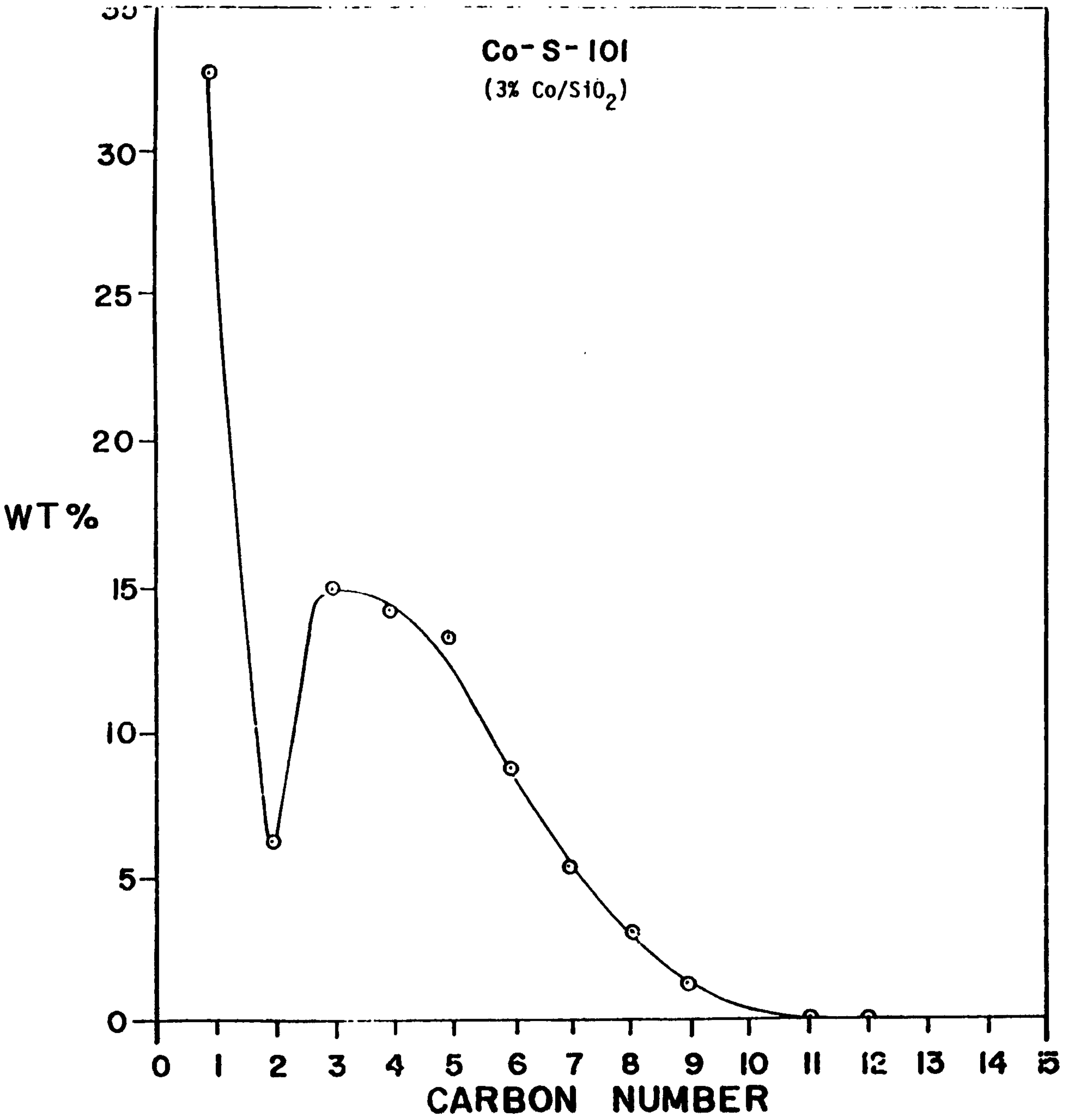

Figure 13. Product distribution for Co-S-101.

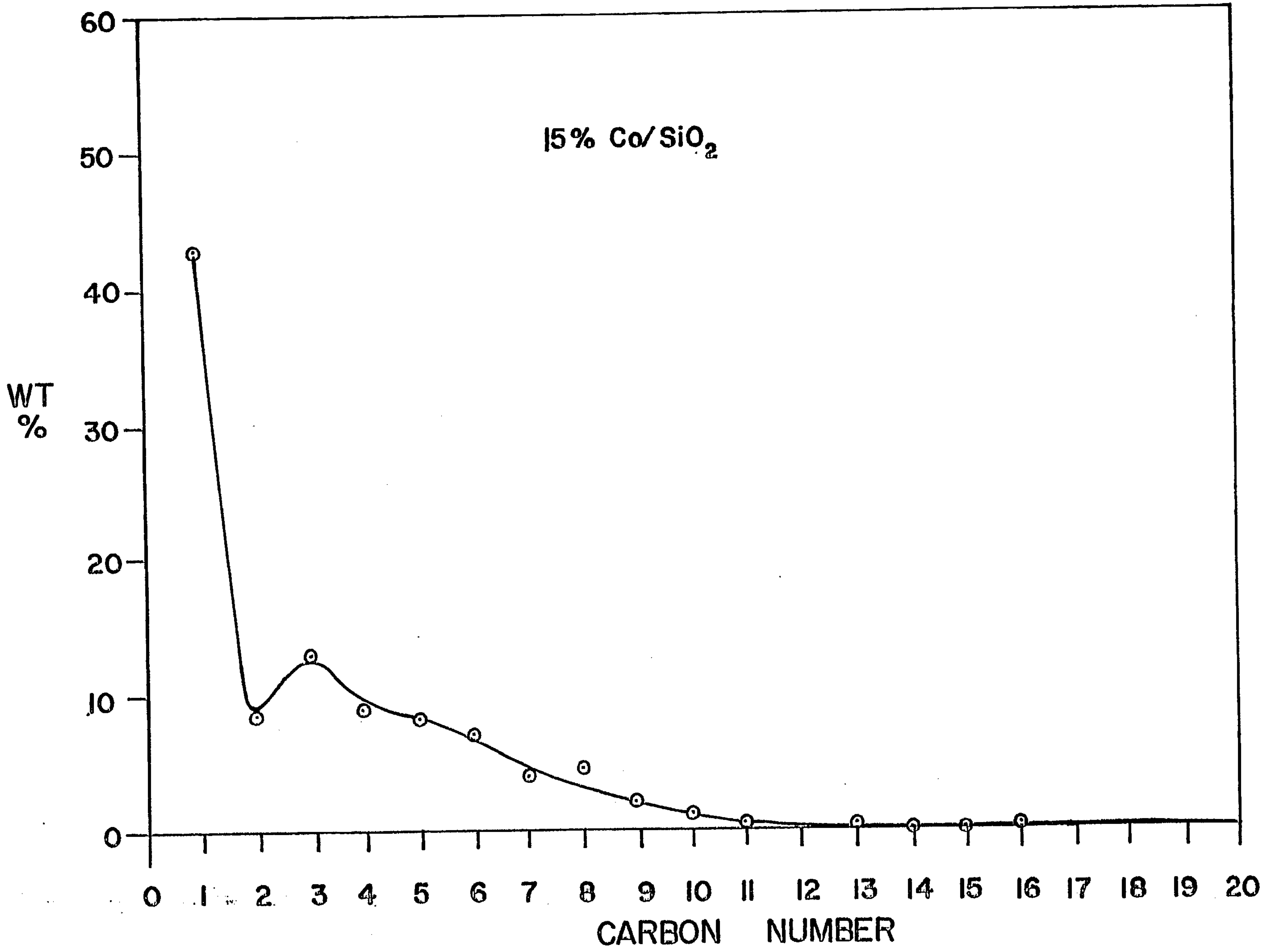

Figure 14. Product Distribution for Co-S-102

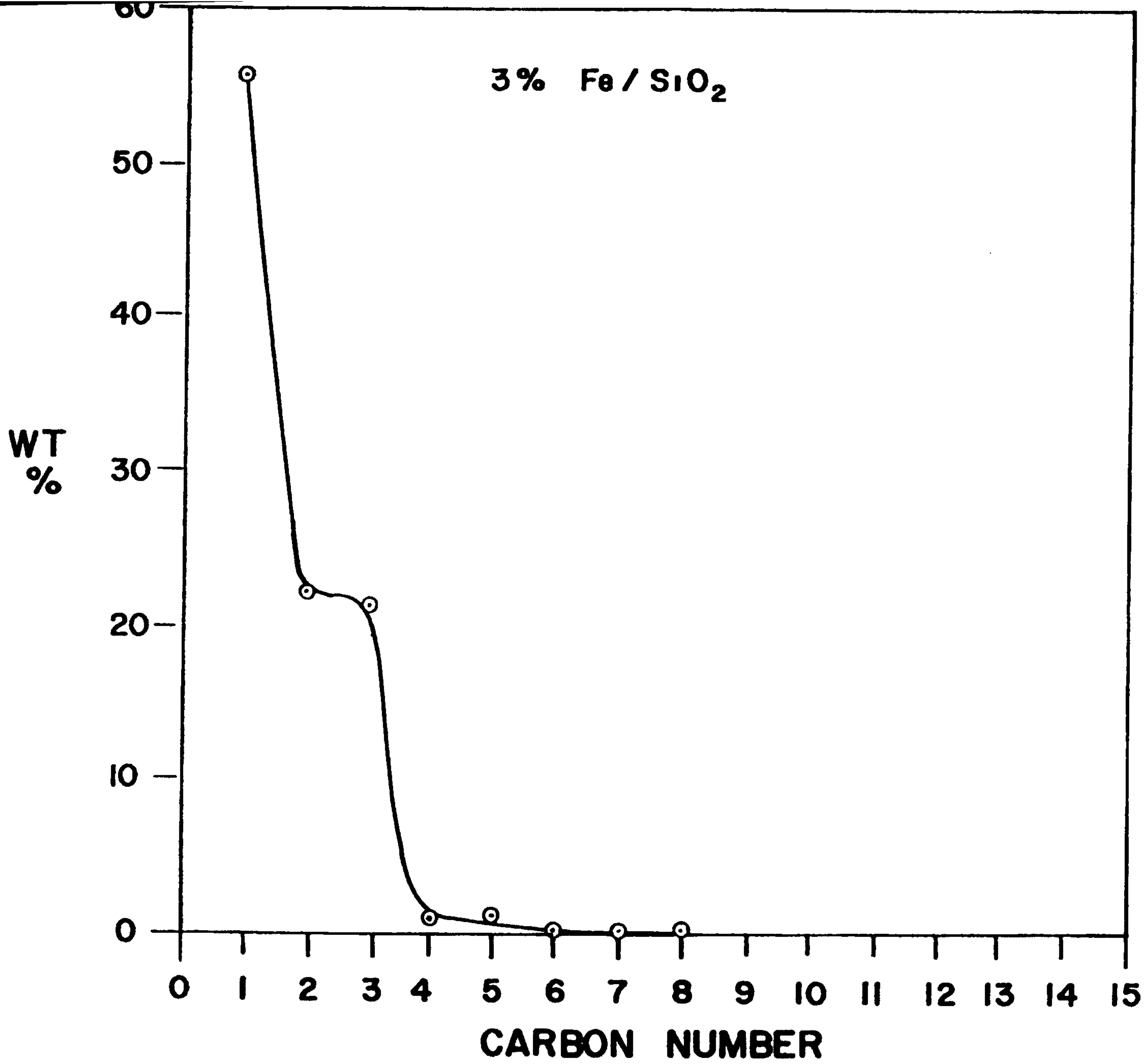

Figure 15. Product Distribution for Fe-S-100.

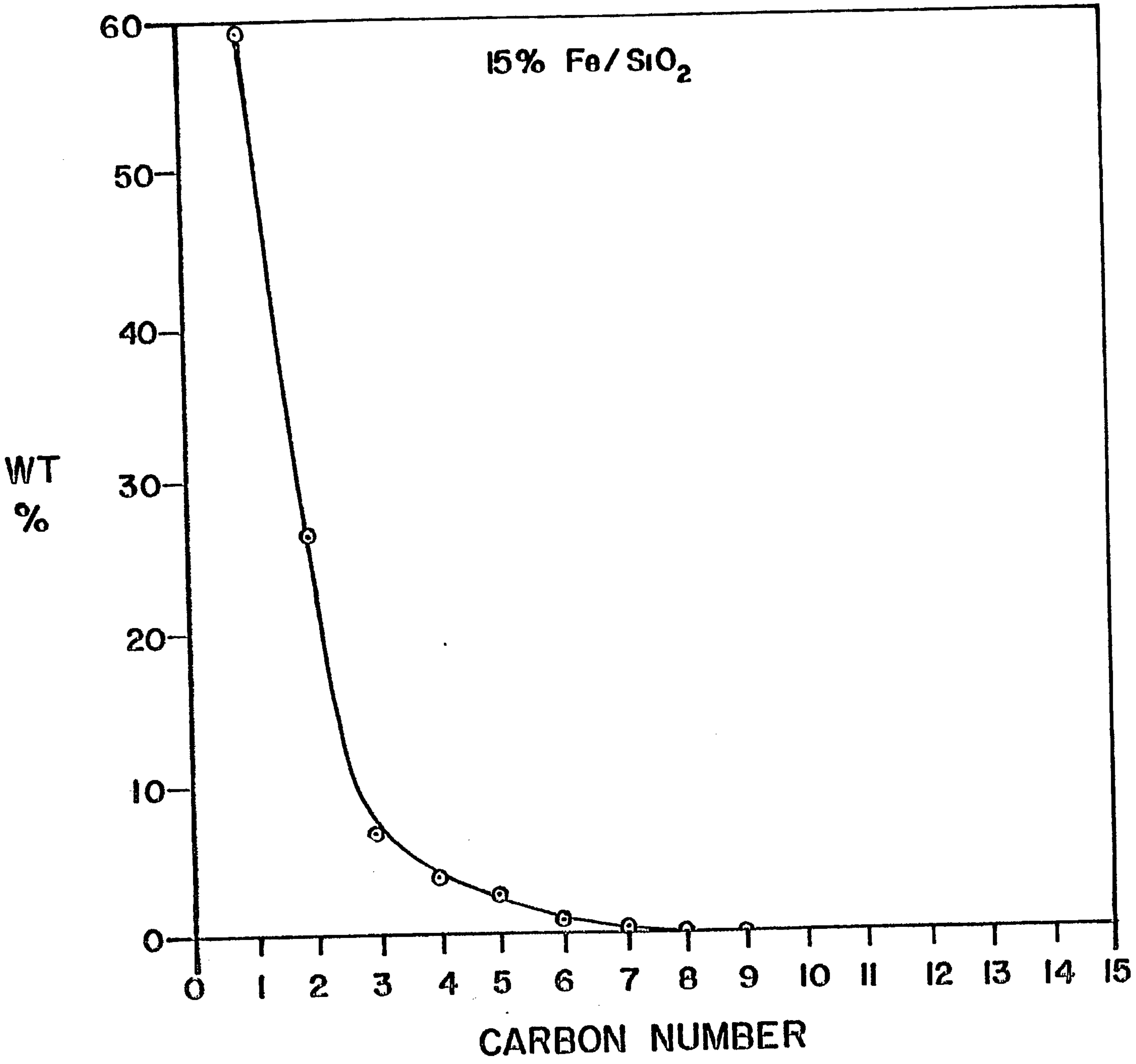

Figure 16. Product Distribution for Fe-S-102.

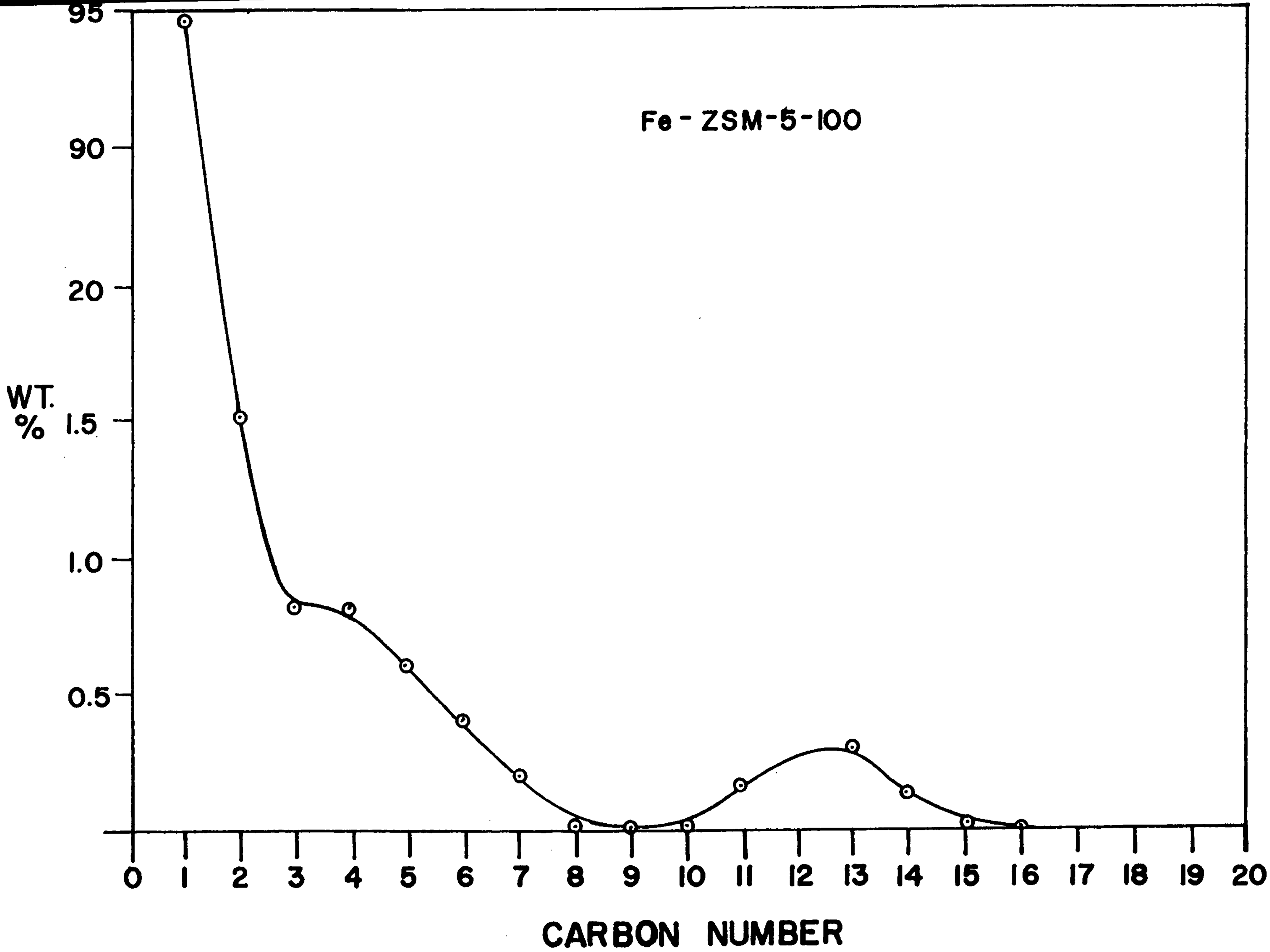

Figure 17. Product Distribution for Fe-ZSM-5-100.

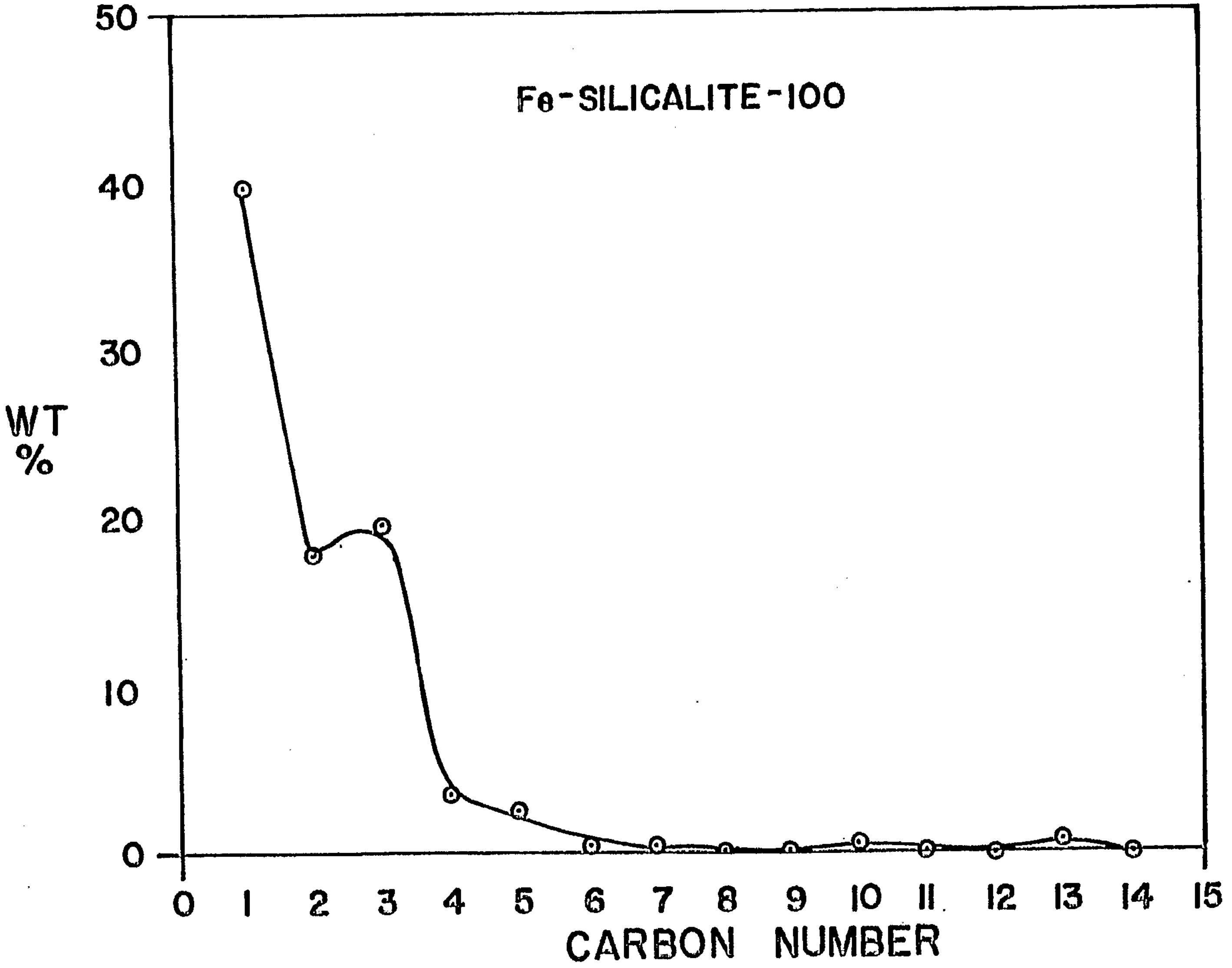

Figure 18. Product Distribution for Fe-Silicalite-100.

TABLE 6

Selectivity Data for Fe and Co Supported Catalysts

Catalyst Code	Selectivity (%)[a]					(Olefin)[a] / (Paraffin)
	CH_4	C_2-C_4	C_5+	CO_2	Alcohols	
Co-S-101	31	36	33	0.4	0	0
Co-S-102	40	31	28	0.4	0	0
Fe-S-100	51	44	0.8	4.6	0	0.31
Fe-S-102	55	38	4.1	0.4	2.8	0.33
Fe-ZSM-5	94	2.7	3.4	0	0	0.013
Fe-Silicalite	27	51	4.4	8.6	9.0	0.66
Co-B-A-101	34	66	-	0	0	0
Co-B-S-101	30	49	7.8	8.3	4.6	0
Co-B-S-101[b]	57	14	0	0	29	0

[a] 185-225° C, 90 kPa, $H_2/CO = 2$; mole %

[b] 195° C, 90 kPa, $H_2/CO = 1$, exposed to O_2

1. Intraparticle mass transfer (pore diffusion)
2. Intraparticle heat transfer
3. Interparticle mass transfer (film diffusion)
4. Interparticle heat transfer
5. Wall effects
6. Radial mass transfer
7. Radial heat transfer
8. Axial mass transfer
9. Axial heat transfer

These criteria were applied to typical powders and reaction conditions encountered in the proposed reactor tests. These calculations, summarized in Appendix A, show that the measurement of intrinsic rates is not influenced by any of these phenomena with the possible exception of axial temperature gradients in the reactor bed. From the literature examined, it appears this effect, if it does exist, will be minor.

5. Computer Analysis of Data

The analysis of reaction and analytical data is now performed by computer. A calculation program has been written and coded in FORTRAN which reduces chromatographic data to usable turnover numbers, product distributions, selectivities, and conversions.

6. Future Plans

Reactor testing of catalysts prepared next quarter will be undertaken. Plans include testing each of the catalysts at H_2/CO ratios of 1 and 2 to determine any changes due to synthesis gas composition.

C. Task 3: In Situ H_2S Deactivation Study

Experimental work on this task is not scheduled to begin till March 1981.

D. Miscellaneous Accomplishments and Technical Communication

During the first year of the contract, a significant effort was undertaken to establish and maintain communications with other laboratories involved in similar research. Names of some of the scientists and engineers with whom we maintain communication are listed in Appendix B. The principal investigtor also visited 6 laboratories and companies (Table 7) while hosting 6 visitors (Table 8).

Another important aspect of the contract work was the education and training of three chemical engineering students: Mr. Jeffery Rankin (Ph.D. Candidate), Mr. Glenn Davis (M.S. Candidate) and Mr. Glen Witt (B.S. Candidate).

Table 7 Laboratories Visited by Principal Investigator During Contract Period

	Laboratory Visited	Hosts(s)	Date Visited
1.	Process Sciences & Engineering Div. Pittsburgh Energy Technology Center	Dr. Richard Schehl	Oct. 31, 1979
2.	Cornell University	Prof. Robert Merrill	Feb. 14, 1980
3.	Dept. of Chem. Eng. Univ. of Delaware	Dr. Glen Schraeder Dr. James Katzer	April 9-12, 1980
4.	Catalytica Associates	Dr. Robert Garten Dr. Ralph Dalla Belta Dr. Richard Levy	April 15, 1980
5.	Lawrence Berkeley Lab Univ. of California	Dr. Heinz Heinemin	April 16, 1980
6.	Refinery Research Science & Technology Union Oil Research Brea, California	Dr. Kess Alley Dr. Dennis McArthur Dr. David Mears	Summer 1980

Table 8. Visitors and Speakers, BYU Catalysis Laboratory, During Contract Period.

Dr. Robert Ference Technical Specialist	Catalyst Development Climax Molybdenum Co. of Michigan	Oct. 1-2, 1979
Prof. M. Albert Vannice Associate Professor	Dept. of Chemical Eng. Penn. State University	Oct. 2, 1979
Professor Robert Merrill	Dept. of Chemical Eng. Cornell University	Oct. 8, 1979
Dr. P. Govind Menon	Laboratory for Petrochem. Eng. State University of Ghent, Belgium	Oct. 26, 1979
Dr. Perry Maxfield	Department of Chemistry Brigham Young University	Nov. 6, 1979
Dr. Richard Pannell	Catalysis Research Gulf Res. & Dev. Co.	Feb. 26, 1980

IV. Conclusions

1. Using techniques developed in a previous investigation (1,2) it is possible to prepare a well-dispersed cobalt boride on alumina. The boron apparently acts as a promoter for increasing the metal dispersion of cobalt on the alumina.

2. Silica-supported cobalt and iron evidence relatively poor metal dispersion and require long H_2 reduction periods to obtain adequate metal surface areas.

3. Calcination of Fe/SiO_2 catalysts in air before H_2 reduction increases metal dispersion as measured by CO and H_2 chemisorption.

4. The CO/H adsorption ratios varied from 0.28 to 1.36 in the K-promoted and unpromoted Fe catalysts. The very low value (0.28) is probably an effect of the K promoter. The CO/H adsorption ratios of Fe/ZSM-5 and Fe/Silicalite catalysts were 4 to 8 times lower than was typical for Fe supported on slica. This may be a result of a strong interaction between iron and the support.

5. A sufficient chromatographic analysis for C_1 to C_{20} hydrocarbons and fixed gases may be obtained on two columns, one of SP2100 supported on Sulpelcoport, and the other of Carbosieve B. Temperature programming from subambient to 250°C aids peak analysis.

6. The apparent activation energy of 68-79 kJ/mol observed for CO hydrogenation over $Co\text{-}B/Al_2O_3$ is about the same as the value of 63 kJ/mol for unsupported cobalt boride.

7. Metal loading has significant effect on iron and cobalt supported metal activity. As metal loading increases, Fe activity increases. The opposite trend is observed for cobalt.

8. Fe/ZSM-5 and Fe/Silicalite alter product distributions to include a second peak at higher molecular weight hydrocarbons. At 1 atm, this occurs at C_{12} or C_{13}.

9. Fe catalysts produce greater amounts of olefins than do the supported cobalt catalysts. No olefins are detected during cobalt catalyst trials.

10. Alcohols and other oxygenated compounds are produced over supported iron catalysts. No alcohols are detected over cobalt observations are generally in line with previously reported literature.

11. At 90 kPa pressure, cobalt catalysts produce a higher molecular weight product than supported iron catalysts, also consistent with previous literature.

12. Transport limitations on intrinsic rate measurement may be avoided during Fischer-Tropsch synthesis if finely crushed powders are used and the catalysts are tested at lower temperatures and low CO conversions.

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APPENDIX A

TRANSPORT LIMITATION CALCULATIONS

I. Internal Effects

A. Intraparticle Mass Transfer (Pore Diffusion)

1. Weisz - Prater Criterion (4)

$$\frac{r^2 R_V}{D_e C_s} < 1$$

where r = particle radius
R_V = reaction rate per unit volume
D_e = effective mass diffusivity
C_s = surface reactant concentration

2. Calculation of D_e using Wilkie-Chang Equation (5)

a. $$D = (7.4 \times 10^{-8}) \frac{T M_s^{1/2}}{\mu_M V_{CO}^{0.6}}$$

where D = bulk mass diffusivity in cm^2/s
T = absolute temperature in K
M_3 = molecular weight of solvent
μ_M = viscosity of mixture in cp
V_{CO} = molar volume of solute (CO) at normal boiling point in $cm^3/gmole$

b. Data used:

T = 473.15 K
M_s = 422.826 g/gmole for n-C_{30} as solvent in pores
μ_M = 0.12 cp for liquid hydrocarbon (6)
V_{CO} = 30.7 $cm^3/gmole$ (7)

3. Data used:

$C_s = 1.43 \times 10^{-5}$ gmole/cm^3 for CO at 1 atm (8)
$R_V = 3 \times 10^{-6}$ gmole/s-cm^3 from preliminary runs

4. Conclusion - since the powders being used have $r < 0.005$ cm, the criterion is obeyed.

B. Intraparticle Heat Transfer

1. Anderson Criterion (9)

$$\frac{q R_V r^2}{T k_p} < \frac{3 T R}{4 E}$$

where q = heat of reaction
R_V = reaction rate per unit volume

r = particle radius
T = absolute temperature at particle surface
k_p = thermal conductivity of the catalyst particle
R = gas constant
E = activation energy of the reaction

2. Data used:

$q = 209{,}000$ J/gmole (10)
$R_V = 3 \times 10^{-6}$ gmole/s-cm^3
$T = 473.15$ K
$k_p = 4.184 \times 10^{-4}$ J/s-cm-K (11)
$R = 8.31$ J/gmole-K
$E = 100{,}416$ J/gmole (12)

3. Conclusion - For powders being used with $r < 0.005$ cm, the criterion is obeyed.

II. External Effects

A. Interparticle Mass Transfer (Film Diffusion)

1. Hudgins Criterion (13)

$$\frac{2R_V r}{k_m} \cdot \frac{R_V'(C)}{R_V(C)} < 0.3$$

where $R_V(C)$ = reaction rate per unit volume as a function of concentration
r = particle radius
k_m = interphase mass transfer coefficient

2. Calculation of k_m using Chilton-Colburn analysis (14)

a. $$\left(\frac{k_m}{v}\right)\left(\frac{\mu}{\rho D}\right)^{2/3} = 0.91\ Re^{-0.51}\ \psi$$

where k_m = interphase mass transfer coefficient
v = gas velocity
μ = gas mixture viscosity
ρ = gas misture density
D = gas mixture binary diffusion coefficient
Re = Reynolds number
ψ = shape factor

b. Calculation of D by Gilliland correlation (15)

1. $$D = \frac{(0.0043)T^{3/2}\ (1/M_A + 1/M_B)^{1/2}}{(V_A^{1/3} + V_B^{1/3})^2\ P}$$

where T = absolute temperature in K

M_A, M_B = molecular weights
V_A, V_B = molar volumes at normal boiling points in cm^3/gmole
P = pressure in atm

2. Data used:

$T = 473.15$ K
$M_{CO} = 28.01$ g/gmole
$M_{H_2} = 2.016$ g/gmole
$V_{CO} = 30.7$ cm^3/gmole (7)
$V_{H_2} = 14.3$ cm^3/gmole (7)
$P = 1$ atm

c. Data used:

$v = 0.66$ cm/s for space velocity of 250 hr^{-1}
$\rho = 2.75 \times 10^{-4}$ g/cm^3
$\mu = 0.01633$ cp for $H_2/CO = 2$ (6)
$\psi = 1.0$ for spherical particles

3. Data used:

$R_V(C) = 3 \times 10^{-6}$ gmole/s-cm^3

$\frac{R_V(C)}{R_V'(C)} = C_{CO}$ for first order in CO

$C_{CO} = 8.5907903 \times 10^{-6}$ gmole/cm^3

4. Conclusion - For powders with $r < 0.005$ cm the criterion is obeyed.

B. Interparticle Heat Transfer

1. Mears Criterion (16)

$$\frac{q\, R_V r}{h\, T_b} < \frac{0.15\, RT_b}{E}$$

where q = heat of reaction
R_V = reaction rate per unit volume
r = particle radius
h = heat transfer coefficient
T_b = bulk gas temperature
R = gas constant
E = activation energy of reaction

2. Calculation of h using Chilton-Colburn analysis (14)

a. $$\left(\frac{h}{\rho C_p v}\right)\left(\frac{C_p \mu}{k}\right)^{2/3} = 0.91\, Re^{-0.51}\, \psi$$

where h = interphase heat transfer coefficient
ρ = gas mixture density
C_p = gas mixture heat capacity
V = gas velocity
μ = gas mixture viscosity
k = gas mixture thermal conductivity
Re = Reynolds number
ψ = shape factor

b. Data used:

$\rho = 2.75 \times 10^{-4}$ g/cm^3
C_p = 29.41 J/gmole-K (17)
V = 0.66 cm/s for space velocity of 250 hr^{-1}
μ = 0.01633 cp for $H_2/CO = 2$ (6)
k = 0.00183 J/cm-s-K for $H_2/CO = 2$ (7)
ψ = 1.0 for spherical particles

3. Data used:

q = 209,000 J/gmole (10)
$R_V = 3 \times 10^{-6}$ gmole/s-cm^3
T_b = 473.15 K
R = 8.31 J/gmole-K
E = 100,416 J/gmole (12)

4. Conclusion - For powders with $r < 0.005$ cm the criterion is obeyed.

III. Fixed Bed Effects

A. Wall Effects

1. Mears Criterion (18)

$$\frac{d_r}{d_p} > 10$$

where d_r = reactor diameter
d_p = particle diameter

2. Conclusion - For 1/4" reactor and powders with $r < 0.005$ cm, the criterion is obeyed.

B. Radial Heat Transfer

This limitation is always negligible (19,20)

C. Radial Heat Transfer

1. Mears Criterion (16)

$$\frac{q\, R_V(1- \ )r_o^2}{k_e T_w (1-b)} \qquad \frac{0.4\ RT_w/E}{\left[1 + \frac{4k_e}{h_w r_o}\right]}$$

where q = heat of reaction
R_V = reaction rate per unit volume
ε = bed void fraction
r_o = reactor radius
k_e = effective radial thermal conductivity
T_w = reactor wall absolute temperature
δ = reactor wall absolute temperature
R = gas constant
E = reaction activation energy
h_w = wall heat transfer coefficient

2. Calculation of k_e

a. $k_e/k = 8.6$ (21)

b. $k = 0.00183$ J/cm-s-K for $H_2/CO = 2$ (7)

3. Calculation of h_w (21)

a.
$$\left(\frac{2h_w r}{k}\right) = \left(\frac{2h_w^o r}{k}\right) + 0.054\ PrRe \qquad (21)$$

where h_w = wall heat transfer coefficient
r = particle radius
k = gas thermal conductivity
h_w^o = wall heat transfer coefficient at zero flow
Pr = Prandtl number
Re = Reynolds number

b. Data used:

$k = 0.00183$ J/cm-s-K for $H_2/CO = 2$ (7)
$$\left(\frac{2h_w^o r}{k}\right) = 1.2 \qquad (21)$$
$Pr = 0.1506$
$Re = 0.0111$

4. Data used:

q = 209,000 J/gmole (10)
$R_V = 3 \times 10^{-6}$ gmole/s-cm^3
$\varepsilon = 0.5$
$r_o = 0.3175$ cm
$T_w = 473.15$ K
$\delta = 0$ (nondiluted bed)
$R = 8.31$ J/gmole-K
E = 100,416 J/gmole (12)

5. Conclusion - For powders with $r < 0.005$ cm, the criterion is obeyed.

D. Axial Mass Transfer

1. Mears Criterion (16)

$$\frac{L}{2r} > \frac{20n}{Pe_a} \ln \frac{C_o}{C_f}$$

where L = bed length
r = particle radius
n = power exponent in rate law
C_o = initial reactant concentration
C_f = final reactant concentration
Pe_a = axial Peclet number = $\frac{2rv}{D_a}$
v = gas velocity
D_a = axial mass diffusivity

2. Data used:

$n = 1$ for CO first order reaction
$C_f = (0.8)\ C_o$ for 20% conversion
$v = 0.66$ cm/s
$D_a = D = 1.044\ \text{cm}^2/\text{s}$

3. Conclusion - For powders with $r < 0.005$ cm, the criterion is met if at least 0.50 g of catalyst are used.

E. Axial Heat Transfer

1. Young and Finlayson Criterion (22)

$$\frac{2qR_v r}{(T_i - T_w) v\rho\ C_p Pe_a} < 1$$

where q = heat of reaction
R_v = reaction rate per unit volume
r = particle radius
T_i = initial reactant temperature
T_w = reactor wall absolute temperature
v = gas velocity
ρ = gas mixture density
C_p = gas mixture heat capacity
Pe_a = axial Peclet number = $\frac{2vC_p r\rho}{ke_z}$
k_{ez} = effective axial thermal conductivity

2. Data used:

$q = 209{,}000$ J/gmole (10)
$R_v = 3 \times 10^{-6}$ gmole/s-cm^3
$T_i = 300$ K
$T_w = 473.15$ K
$\rho = 2.75 \times 10^{-4}\ \text{g/cm}^3$
$C_p = 29.41$ J/gmole-K (17)

k_{ez} = 0.0157 J/cm-s-K

3. Conclusion - For particles with r = 0.005 cm, gas velocity must exceed 0.76 cm/s to meet the criterion. This is slightly higher than the 0.66 cm/s in the average conditions used. Thus, some hot spots may develop. However, a survey of the literature shows these hot spots seldom exceed 10 K over isothermal bed operation.

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