INVESTIGATION OF SULFUR-TOLERANT CATALYSTS FOR SELECTIVE SYNTHESIS OF HYDROCARBON LIQUIDS FROM COAL-DERIVED GASES. ANNUAL TECHNICAL PROGRESS REPORT, SEPTEMBER 19, 1980-SEPTEMBER 18, 1981

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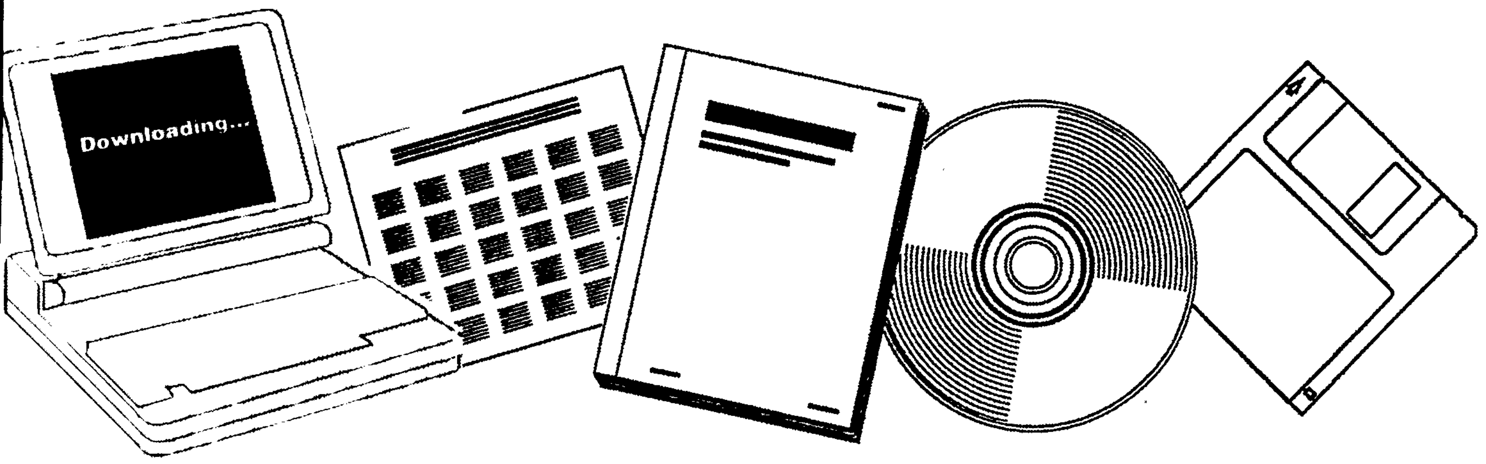

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INVESTIGATION OF SULFUR-TOLERANT CATALYSTS FOR SELECTIVE SYNTHESIS OF HYDROCARBON LIQUIDS FROM COAL-DERIVED GASES

Annual Technical Progress Report
For Period September 19, 1980 to September 18, 1981

Calvin H. Bartholomew
Brigham Young University
Provo, Utah 84602

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FOREWORD

This report summarizes technical progress during the second year (September 19, 1980 to September 18, 1981) 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: Duane M. Davis, Jeffery L. Rankin, Richard M. Bowman and Glen E. Witt. Mr. Rankin and Dr. Bartholomew were the principal authors. Laurie Witt provided typing services.

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ABSTRACT

During the past contract year, considerable progress was made in characterization and activity/selectivity testing of iron and cobalt catalysts. Preparation of boride promoted cobalt and iron catalysts was refined and nearly completed. H_2 and CO adsorption and oxygen titration measurements were performed on a number of supported and unsupported catalysts, especially several boride promoted cobalt and iron catalysts. Activity/selectivity tests of 3 and 15% Fe/SiO_2 and Co/SiO_2 and of 6 borided cobalt and iron catalysts were completed. The product distributions for iron and cobalt boride catalysts are unusual and interesting. Boron promoted iron is more active and stable than iron/silica; cobalt boride has an unusually high selectivity for alcohols. Tests to determine effects of H_2S poisoning on activity/selectivity properties of 15% Co/SiO_2 indicate that a significant loss of activity occurs over a period of 24-48 h in the presence of 10-20 ppm H_2S. Product selectivity to liquids increased through a maximum during the gradual addition of sulfur. Reactant CO and H_2S interact partially to form COS which is less toxic than H_2S. H_2 and CO adsorption data were obtained for 3, 6 and 9% Co/ZSM-5 catalysts prepared and reactor tested by PETC. The unusual and interesting results suggest that metal-support interactions may have an important influence on reactant adsorption properties. The PI and his students attended 7 meetings, presented 6 talks and seminars relating to the contract, while receiving 16 visitors.

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 desireable 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 diffusuional 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 in such proportions as to obtain a K/Fe ratio of 0.2 in the final product.

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

Table 1

Catalyst Preparation Plans[a] (Task 1)

Metal-Support Combination	Unpromoted	Promoted	Additive Pretreatments			No. Catalysts
		K_2O	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(3)[b]	x	x	8
Fe/Al_2O_3	x					1
Fe/ZSM-5	x	x	x[d]			3
Fe/Silicalite	x	x				2
				Total		27

[a] 15 wt.% metal unless otherwise noted; 0.5 to 3 wt.% K_2O.

[b] Promoted and unpromoted catalysts will be sulfided.

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

[d] Promoted catalyst will be sulfided.

different techniques including H_2 and CO chemisorption, chemical analysis, x-ray diffraction, thermal gravimetric analysis, and Moessbauer Spectroscopy. 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 oxygen titration and Moessbauer spectroscopy using equipment in our own laboratory. 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. 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 6-8 hours during which time chromatograph samples will be carried out intermittently. From previous 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 is 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 high pressure. It is also possible that some of the catalyst will have more desireable 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,

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, 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
	Effects of Sulfiding	Fe, Fe/SiO_2 (unpromoted and K_2O promoted); and Co/SiO_2
	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/ZSM-5, Fe/Al_2O_3
	Effects of metal	Co/SiO_2 and Fe/SiO_2
	Effects of metal loading	3 and 15% Fe/SiO_2
	Effects of Promoter	K_2O promoted Fe and Fe/SiO_2(sulfided and unsulfided)
	Effects of Sulfiding	Fe, Fe/SiO_2 (unpromoted and K_2O promoted), Fe/Al_2O_3, Co/SiO_2
	Effects of Nitriding, Boriding	Nitrided and Borided Fe,
	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.

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 has been fabricated. The reactor system will be modified by adding a trap for hydrocarbon liquids. Gaseous, liquid and aqueous phase hydrocarbons will be collected and analyzed using SP2100 and Carbosieve B columns.

Task 3: In situ H_2S Poisoning Measurements

Catalysts to be studied for sulfur resistance are listed in Table 2 (above) along with the reason for investigation. Activity measurement 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 500-2000 hr^{-1} with 10-20 ppm H_2S in the reactant mixture. The analysis of hydrocarbon products will be made using gas chromatography throughout the deactivation runs. During the majority of the tests, each catalyst sample will be housed in a Pyrex differential tubular reactor cell. Selected runs will be made using (i) a quartz mixed flow reactor at 1 atm and 500-550 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 presented in Figure 1 and accomplishments during the past year are summarized below. Figure 1 shows all tasks to be progressing on schedule.

Results are best summarized according to task:

Task 1:

Preparation of the proposed boride-promoted catalysts was nearly completed. H_2, CO, and CO_2 chemisorptions were performed on supported iron and cobalt catalysts. In addition, H_2 and CO chemisorption measurements were carried out for the boride promoted catalysts. O_2 titration measurements on Fe-S-102, Fe-S-103, FeK-S-100, Co-S-101, and Co-S-102 enabled calculations of percent reduction and dispersion to be made.

Task 2:

Reactor activity/selectivity tests of Fe-S-102, Fe-S-103, Co-S-101, Co-S-102, and six borided catalysts were completed. Product distributions were analyzed and CO turnover numbers determined, the results showing cobalt catalysts to be more active than iron catalysts. Selectivity data for iron and cobalt boride catalysts are unusual and interesting. Boron promoted iron is more active and stable than iron/silica; cobalt boride has an unusually high selectivity for alcohols. An analytical scheme using a new capillary column was adopted and is presently performing well.

Task 3:

The effects of H_2S poisoning on the activity/selectivity properties of 15% Co/SiO_2 were determined using a reactor system and suitable analytical techniques developed specially for this purpose. Reactant CO and H_2S were found to interact in the feed to give COS.

Misc.

H_2 and CO adsorption data were obtained for 3, 6 and 9% Co/ZSM-5 catalysts prepared by PETC using 2 different impregnation techniques. During the past year, the Principal Investigator and students working on the project attended 7 meetings and presented 4 papers or talks relating to the contract. The PI also visited 5 industrial and university laboratories presenting 2 additional seminars relating to this contract, while receiving 16 visitors.

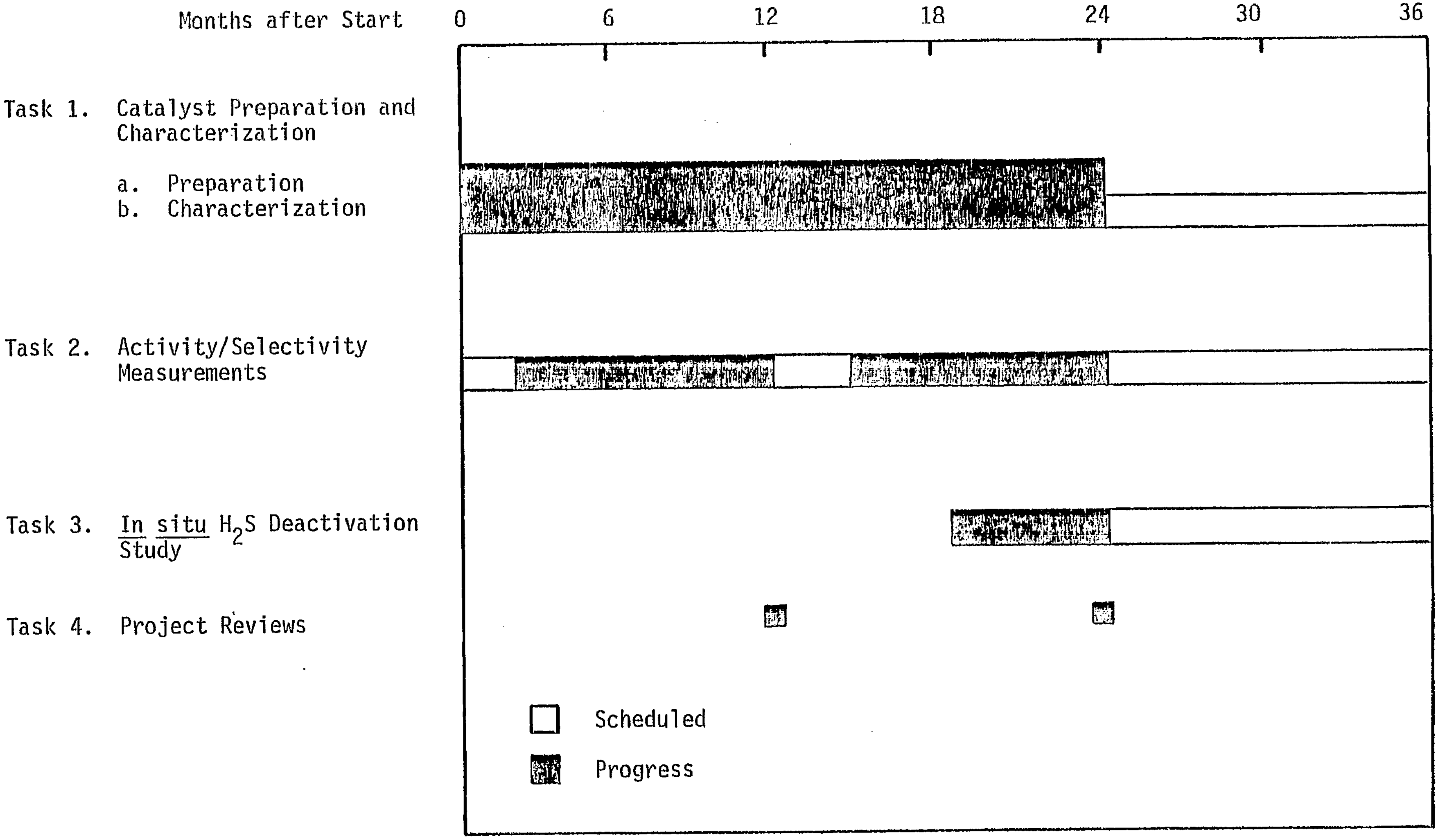


Figure 1. Schedule of Proposed Research Activities and Progress

III. DETAILED DESCRIPTION OF TECHNICAL PROGRESS

A. Task 1: Catalyst Preparation and Characterization

1. Catalysts Preparation

During the past year the preparation of most of the proposed boron-promoted catalysts was completed. Significant improvements in the preparation technique were made including the elimination of a series of decanting, mixing, and settling steps. The catalyst is presently filtered using a vacuum filter apparatus which results in less exposure to oxygen.

Additional improvements were made in the borohydride reduction procedure. An aqueous solution of $NaBH_4$ proved more efficient at attaching the metal boride to the support surface than the alcohol solution method used previously (1,2)

2. Catalyst Characterization

During the past year, samples of Co-S-101, Co-S-102, Fe-S-102, Fe-S-103, and FeK-S-100 were characterized by various adsorption techniques. Sample pretreatment included a reduction for 36 hours in flowing H_2 in order to ensure the maximum extent of reduction of the metal. Iron catalysts were reduced at 725 K while cobalt catalysts were reduced at 625 K. O_2 titration measurements at 673 K showed the percent of metal reduced to be adequate after the 36 h reduction. As shown in Table 3, the extent of reduction increased with metal loading as expected. However, the cobalt catalysts showed the opposite trend. This latter result is somewhat unexpected and is being rechecked.

H_2, CO, and CO_2 chemisorption data for the same catalysts are also shown in Table 3. CO/H ratios for the supported iron catalysts were near 0.7. The addition of the potassium promoter reduced this ratio to 0.3. In the case of the cobalt/silica catalysts it appears that the adsorption properties depend on metal loading since CO/H ratios of 0.9 and 0.4 were observed for the 3 and 15% catalysts respectively.

CO_2 chemisorption was used to measure the surface enrichment of potassium promoter, following the procedures developed by Emmett and Brunnauer (4). It was apparent that CO_2 adsorption was greatly enhanced by the addition of the potassium promoter. H_2 uptake decreased about 50% while CO adsorption decreased even more drastically. Assuming that the iron in the potassium-promoted catalyst accounts for the same amount of adsorption as the unpromoted catalyst, a surface concentration of potassium may be calculated as 87.5% for a 3% bulk potassium concentration.

Samples of Fe-S-102 and Fe-S-103 are currently being analyzed using our new Moessbauer spectrometer. Data will be gathered on the unreduced, reduced, and reactor tested samples to aid in determining changes in oxidation state and environment of the iron atoms on the support.

3. Future Plans

During the next quarter, preparation and chemisorption tests of nitrided

TABLE 3

H_2,CO, CO_2 and O_2 Uptakes on Iron and Cobalt Catalysts After 36-Hour Reductions in Hydrogen

Catalyst Code	% Metal Loading	H_2 Uptake[a] (*moles/g)	CO Uptake[b] (*moles/g)	CO_2 Uptake[c] (*moles/g)	O_2 Uptake[d] (*moles/g)	%[e] Reduction	% D[j]
Fe-S-102[f]	15	20.19	3.52	--	--	--	--
Fe-S-102	15	17.10	24.80	1.16	1622	80.5	1.7
Fe-S-103	3	3.10	4.82	--	50.16	12.5	9.4
FeK-S-100[g]	15	9.11	4.94	6.56	856	42.5	1.7
FeB-S-101[h]	10	6.37	--	--	--	--	--
Co-S-101	3	13.24	24.80	--	242	71.2	7.2
Co-S-102	15	35.95	31.93	3.79	656	38.6	7.3
CoB-102[b]	10	47.5	32.6	--	--	--	--
CoB-S-100[i]		6.20	4.11	--	--	--	--
FeB-102		4.13	1.85	--	--	--	--

---

[a] At 298 K
[b] At 298 K
[c] At 373 K
[d] At 673 K
[e] Based on Fe_2O_3 or Co_3O_4 stoichiometry
[f] After 20 hour reduction in H_2
[g] Containing 3% K_2O promoter
[h] Containing Boride promoter
[i] After 12 hour reduction in H_2
[j] Percent dispersion or perent exposed

iron catalysts and silicalite-supported iron catalysts is planned. Moessbauer studies of the supported iron catalysts for which adsorption data are available will also be initiated on samples of Fe-S-102, and FeK-S-100.

B. Task 2: Activity/Selectivity Measurements

1. Chromatographic Analysis

Installation of a new capillary inlet system for the HP5834A gas chromatograph was completed during the past quarter. It has been fully calibrated and is currently fully operational. The following advantages over packed column techniques have been noted:

1. Separation of alcohols and other oxygenates is quantitative
2. Analysis time is reduced by a factor of more than two (from two hours to less than one hour).
3. Extremely good resolution of most isomers.
4. No baseline drift even when operating to high temperatures (270°C).
5. More accurate splitting of olefin/paraffin peaks for analysis.

Methane and C_2 hydrocarbons are analyzed on the light gas column of carbosieve B. The capillary column receives a gas sample from an on-line gas sampling valve using a split ratio of approximately 75. To our knowledge, this is the first time a gas sampling system has been used directly with a capillary column for analysis of Fischer-Tropsch products. No peak broadening has been detected. Elution of the hydrocarbons of a specific carbon number occurs in the following time sequence:

$$\text{alkene} < \text{alkane} < \text{aldehyde, ketone} < \text{alcohol} < \text{acid}$$

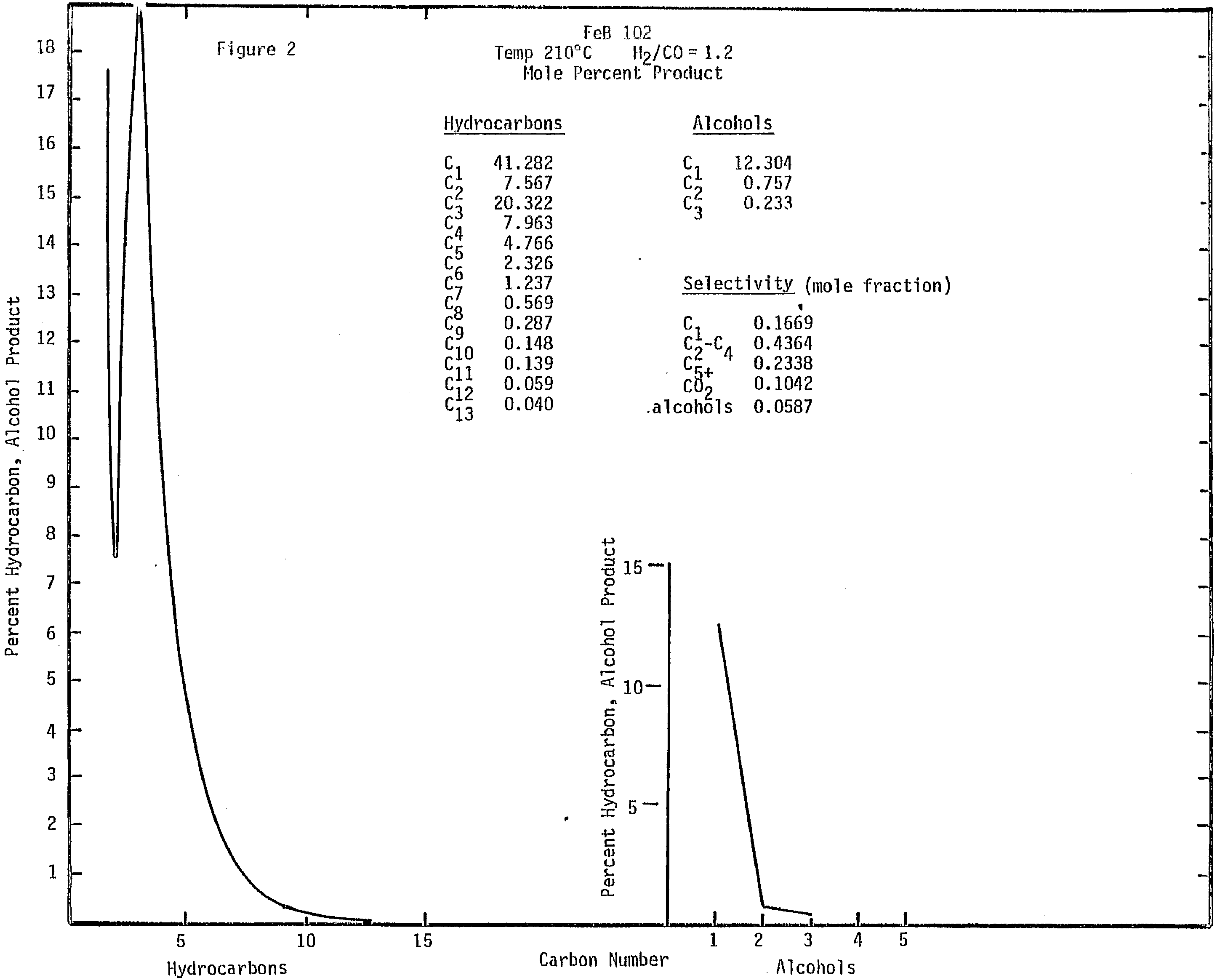
A correlation of retention time data for different hydrocarbons is presently being worked out and will be included in the next report.

2. Experimental Measurements

During the past quarter, reactor activity/selectivity tests of FeB-102, CoB-103, and CoB-S-100 were completed. Reactor runs on unsupported iron boride were done at five different temperatures. The product selectivity of this catalyst was particularly interesting, i.e., the most abundant products were in the C_2-C_4 range. As the temperature was increased from 210°C to 250°C this selectivity shifted somewhat from the C_2-C_4 range to C_1 and C_5^+ hydrocarbons. Production of CO_2 was quite low and that of alcohols was comparable to the alcohols produced on 15% $FeSiO_2$ (see Figures 2-6 for specifics). The most notable characteristic of this catalyst was its apparent lack of deactivation at high temperatures. This suggests a resistance to deactivation by carbonaceous deposits or by formation of inactive carbide forms.

In tests of 15% cobalt boride on silica at 230 and 250°C (Figs. 7 and 8) the product selectivity for CO_2 was exceptionally low, while nearly equal fractions (0.25-0.3) of C_1, C_2-C_4, and C_5^+ products were observed. Some alcohols (4-6%) were also produced. Reaction runs for an unsupported cobalt boride at 458, 470, and 485 K (Figs 9-11) yielded some interesting, unexpected results. Selectivity towards higher alcohols (up to C_8) and towards CO_2 was unusually high considering that conventional cobalt catalysts produce little

Figure 2



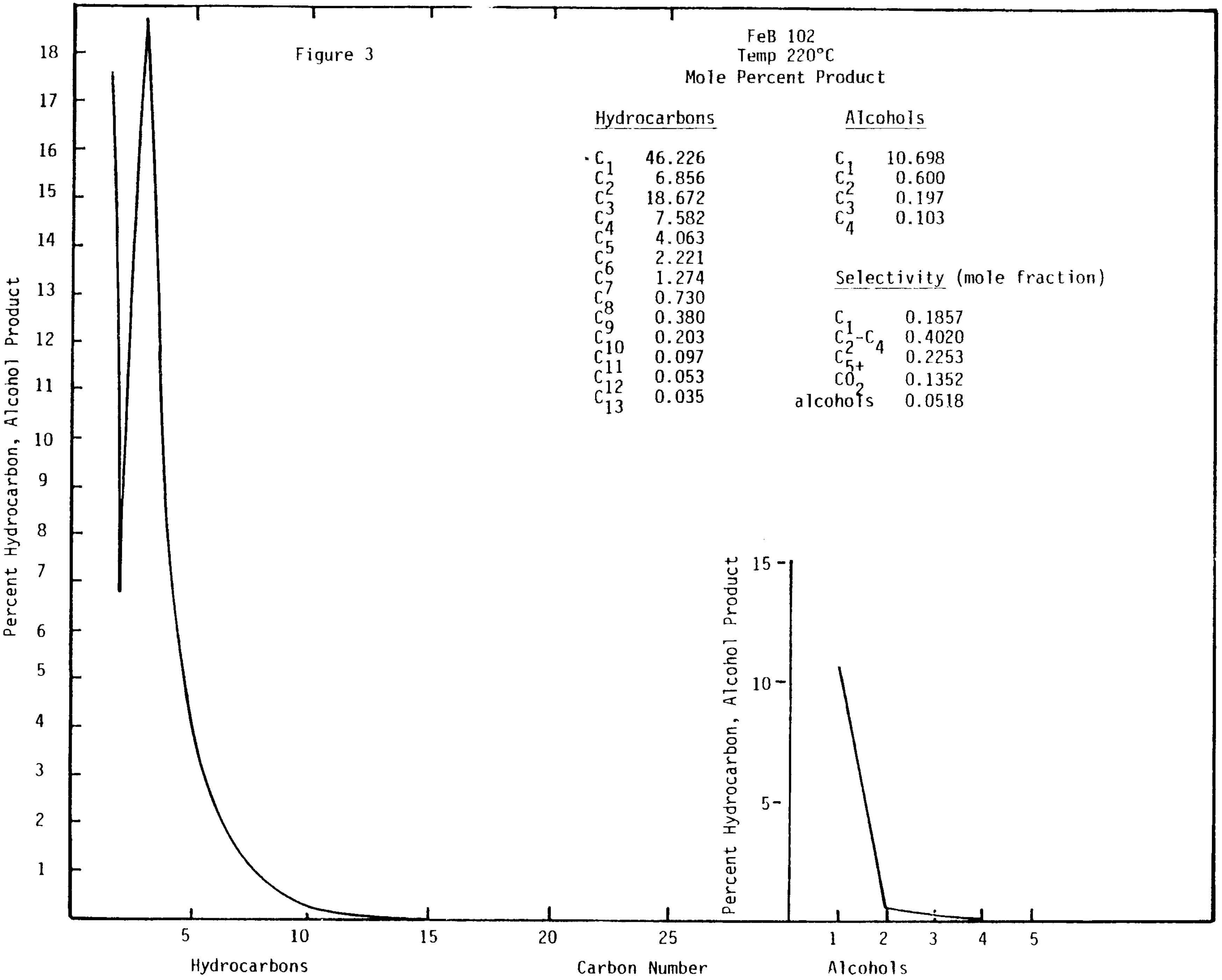
FeB 102
Temp 210°C $H_2/CO = 1.2$
Mole Percent Product

Hydrocarbons	
C_1	41.282
C_2	7.567
C_3	20.322
C_4	7.963
C_5	4.766
C_6	2.326
C_7	1.237
C_8	0.569
C_9	0.287
C_{10}	0.148
C_{11}	0.139
C_{12}	0.059
C_{13}	0.040

Alcohols	
C_1	12.304
C_2	0.757
C_3	0.233

Selectivity (mole fraction)	
C_1	0.1669
C_2-C_4	0.4364
C_{5+}	0.2338
CO_2	0.1042
alcohols	0.0587

Figure 3



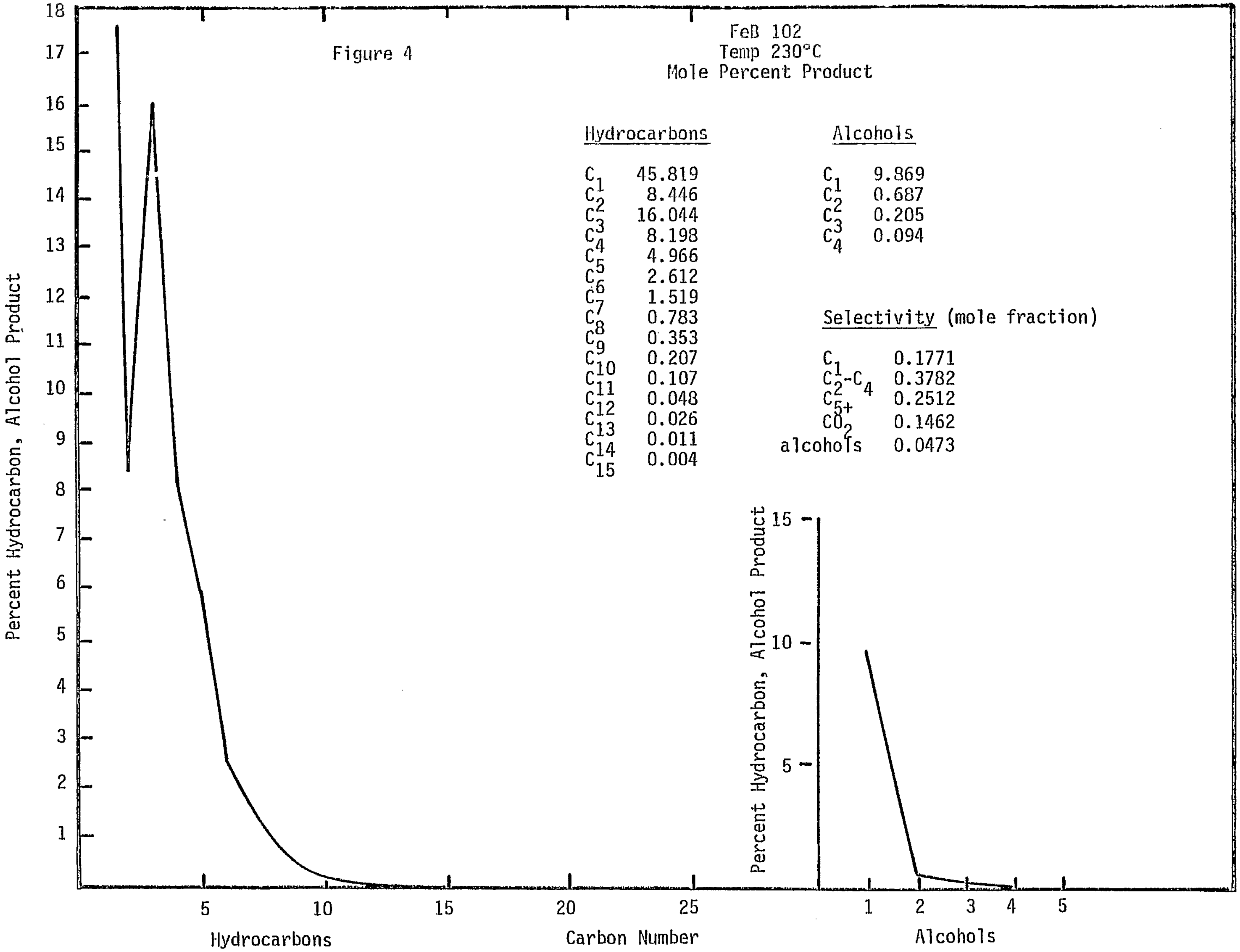
FeB 102
Temp 220°C
Mole Percent Product

Hydrocarbons	
C_1	46.226
C_2	6.856
C_3	18.672
C_4	7.582
C_5	4.063
C_6	2.221
C_7	1.274
C_8	0.730
C_9	0.380
C_{10}	0.203
C_{11}	0.097
C_{12}	0.053
C_{13}	0.035

Alcohols	
C_1	10.698
C_2	0.600
C_3	0.197
C_4	0.103

Selectivity (mole fraction)	
C_1	0.1857
C_2-C_4	0.4020
C_{5+}	0.2253
CO_2	0.1352
alcohols	0.0518

Figure 4



FeB 102
Temp 230°C
Mole Percent Product

Hydrocarbons	
C_1	45.819
C_2	8.446
C_3	16.044
C_4	8.198
C_5	4.966
C_6	2.612
C_7	1.519
C_8	0.783
C_9	0.353
C_{10}	0.207
C_{11}	0.107
C_{12}	0.048
C_{13}	0.026
C_{14}	0.011
C_{15}	0.004

Alcohols	
C_1	9.869
C_2	0.687
C_3	0.205
C_4	0.094

Selectivity (mole fraction)	
C_1	0.1771
C_2-C_4	0.3782
C_{5+}	0.2512
CO_2	0.1462
alcohols	0.0473

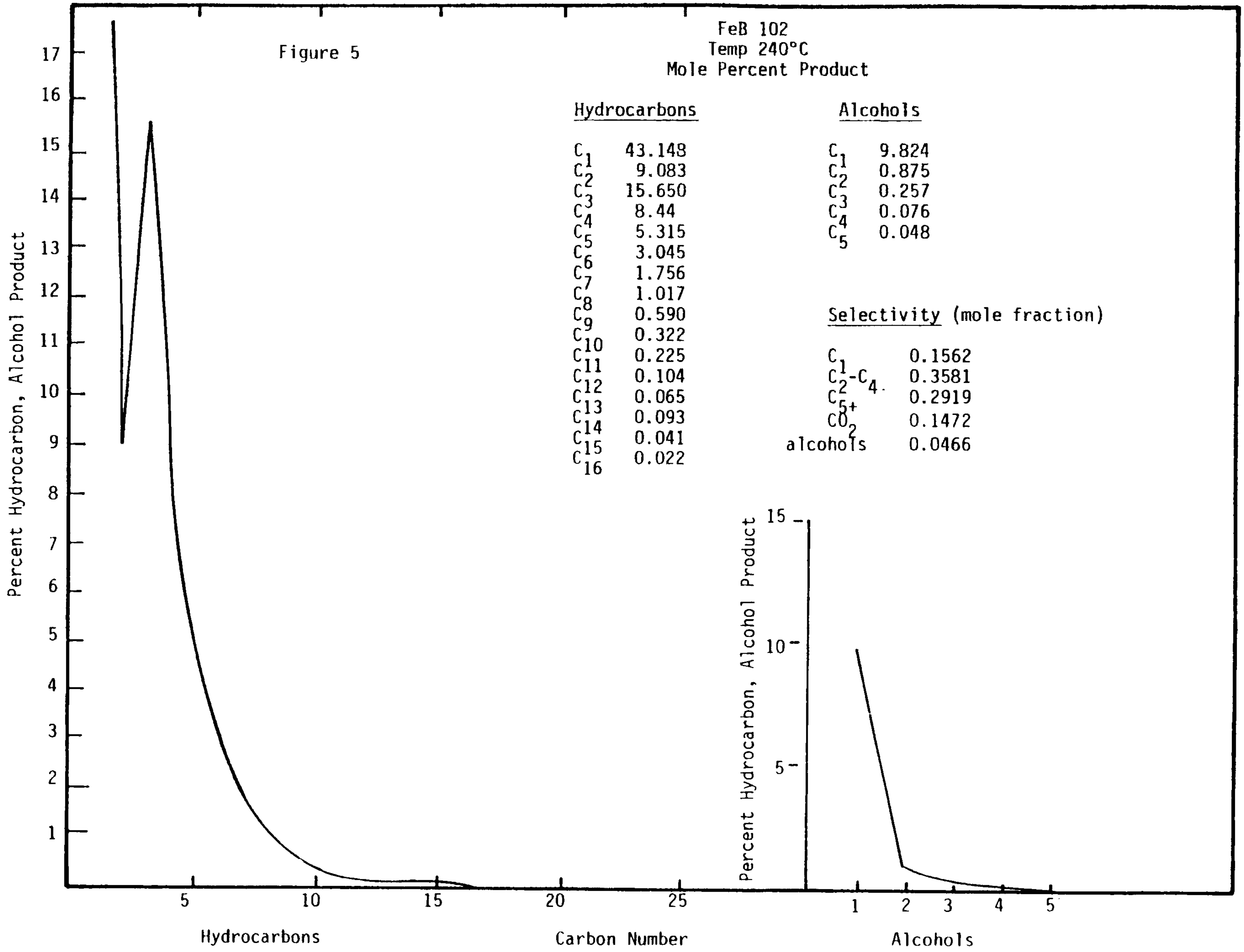


Figure 5

FeB 102
Temp 240°C
Mole Percent Product

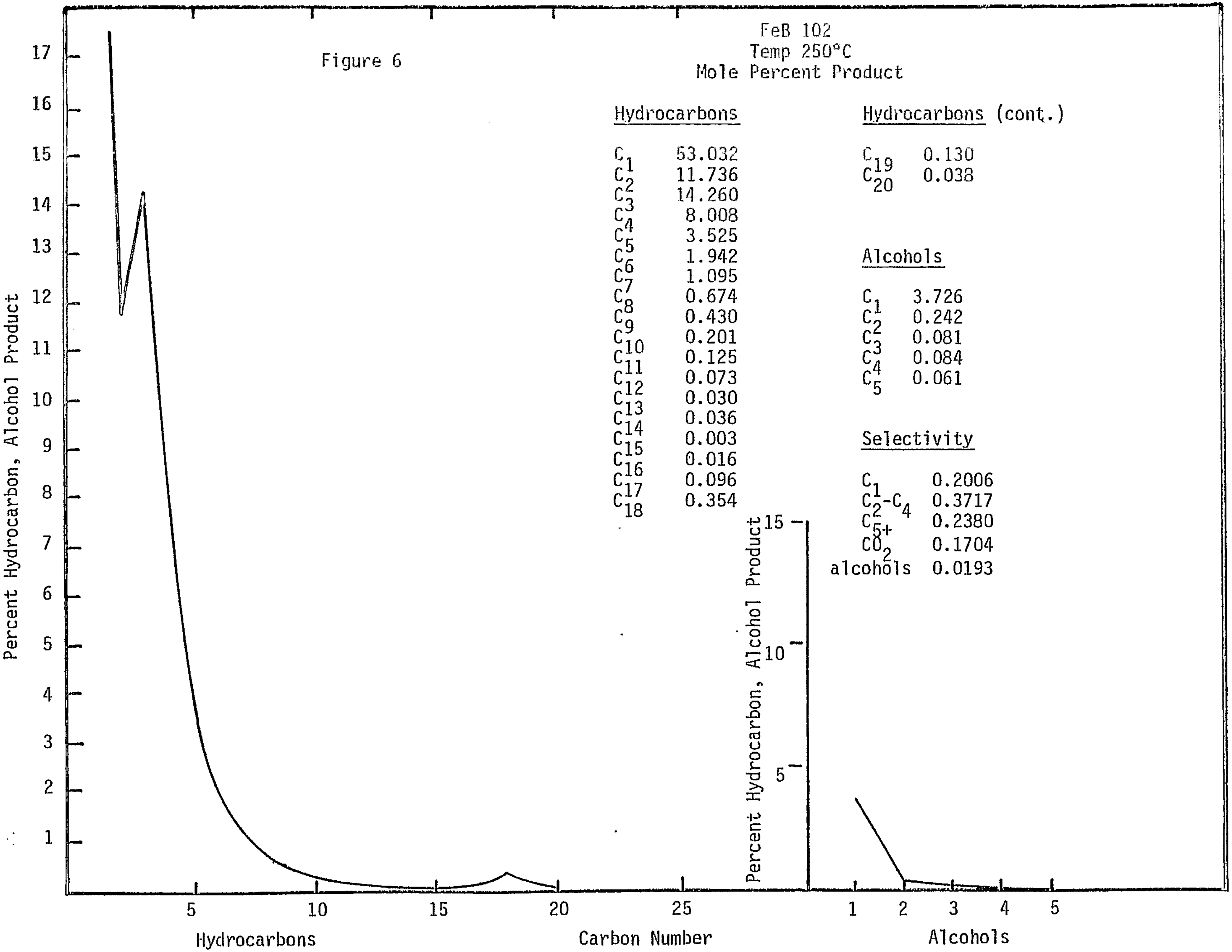
Hydrocarbons	
C_1	43.148
C_2	9.083
C_3	15.650
C_4	8.44
C_5	5.315
C_6	3.045
C_7	1.756
C_8	1.017
C_9	0.590
C_{10}	0.322
C_{11}	0.225
C_{12}	0.104
C_{13}	0.065
C_{14}	0.093
C_{15}	0.041
C_{16}	0.022

Alcohols	
C_1	9.824
C_2	0.875
C_3	0.257
C_4	0.076
C_5	0.048

Selectivity (mole fraction)	
C_1	0.1562
C_2-C_4	0.3581
C_{5+}	0.2919
CO_2	0.1472
alcohols	0.0466

Figure 6

FeB 102
Temp 250°C
Mole Percent Product



Hydrocarbons

C_1	53.032
C_2	11.736
C_3	14.260
C_4	8.008
C_5	3.525
C_6	1.942
C_7	1.095
C_8	0.674
C_9	0.430
C_{10}	0.201
C_{11}	0.125
C_{12}	0.073
C_{13}	0.030
C_{14}	0.036
C_{15}	0.003
C_{16}	0.016
C_{17}	0.096
C_{18}	0.354

Hydrocarbons (cont.)

C_{19}	0.130
C_{20}	0.038

Alcohols

C_1	3.726
C_2	0.242
C_3	0.081
C_4	0.084
C_5	0.061

Selectivity

C_1	0.2006
C_2-C_4	0.3717
C_{5+}	0.2380
CO_2	0.1704
alcohols	0.0193

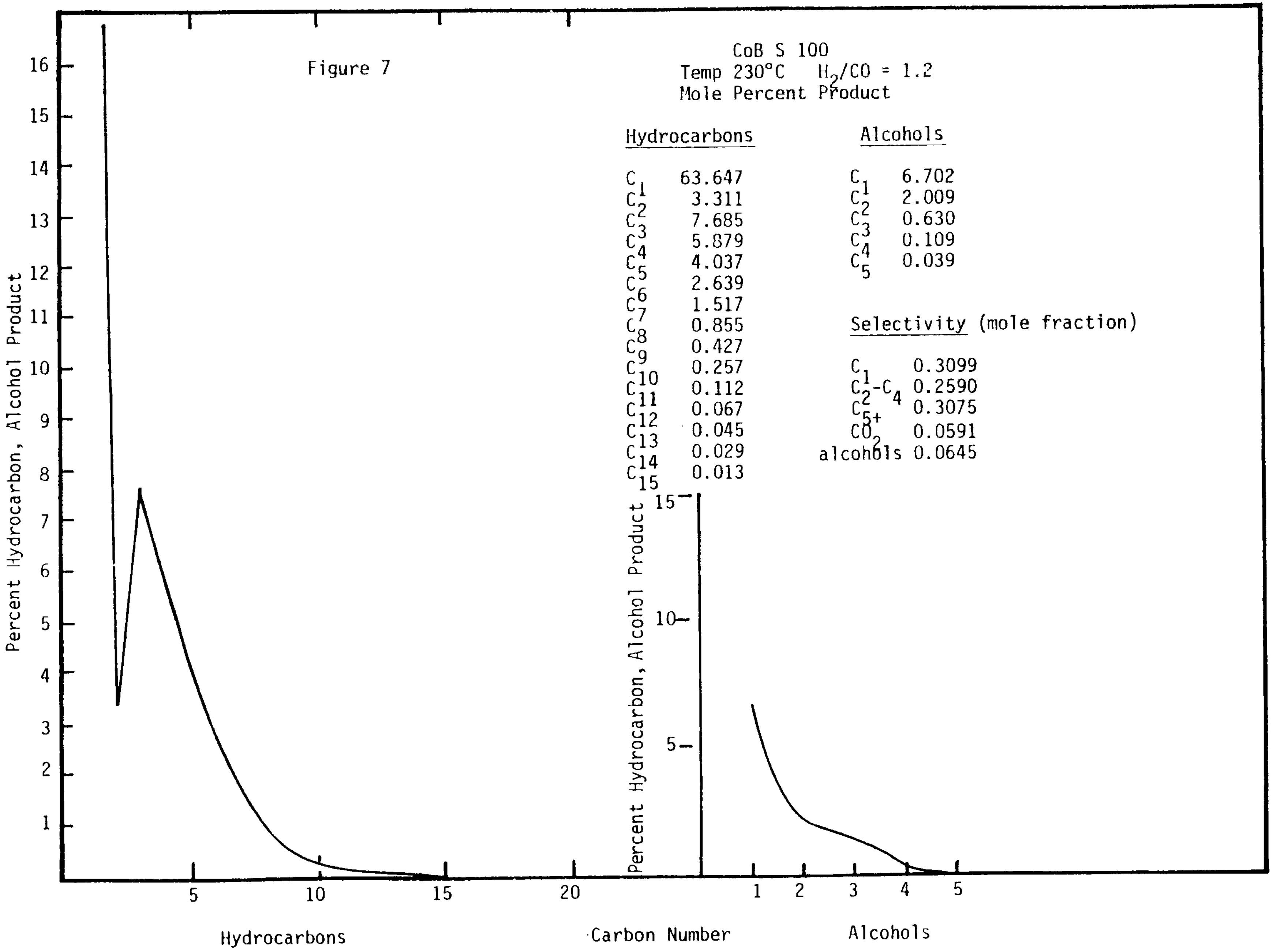


Figure 7

CoB S 100
Temp 230°C $H_2/CO = 1.2$
Mole Percent Product

Hydrocarbons	
C_1	63.647
C_2	3.311
C_3	7.685
C_4	5.879
C_5	4.037
C_6	2.639
C_7	1.517
C_8	0.855
C_9	0.427
C_{10}	0.257
C_{11}	0.112
C_{12}	0.067
C_{13}	0.045
C_{14}	0.029
C_{15}	0.013

Alcohols	
C_1	6.702
C_2	2.009
C_3	0.630
C_4	0.109
C_5	0.039

Selectivity (mole fraction)	
C_1	0.3099
C_2-C_4	0.2590
C_{5+}	0.3075
CO_2	0.0591
alcohols	0.0645

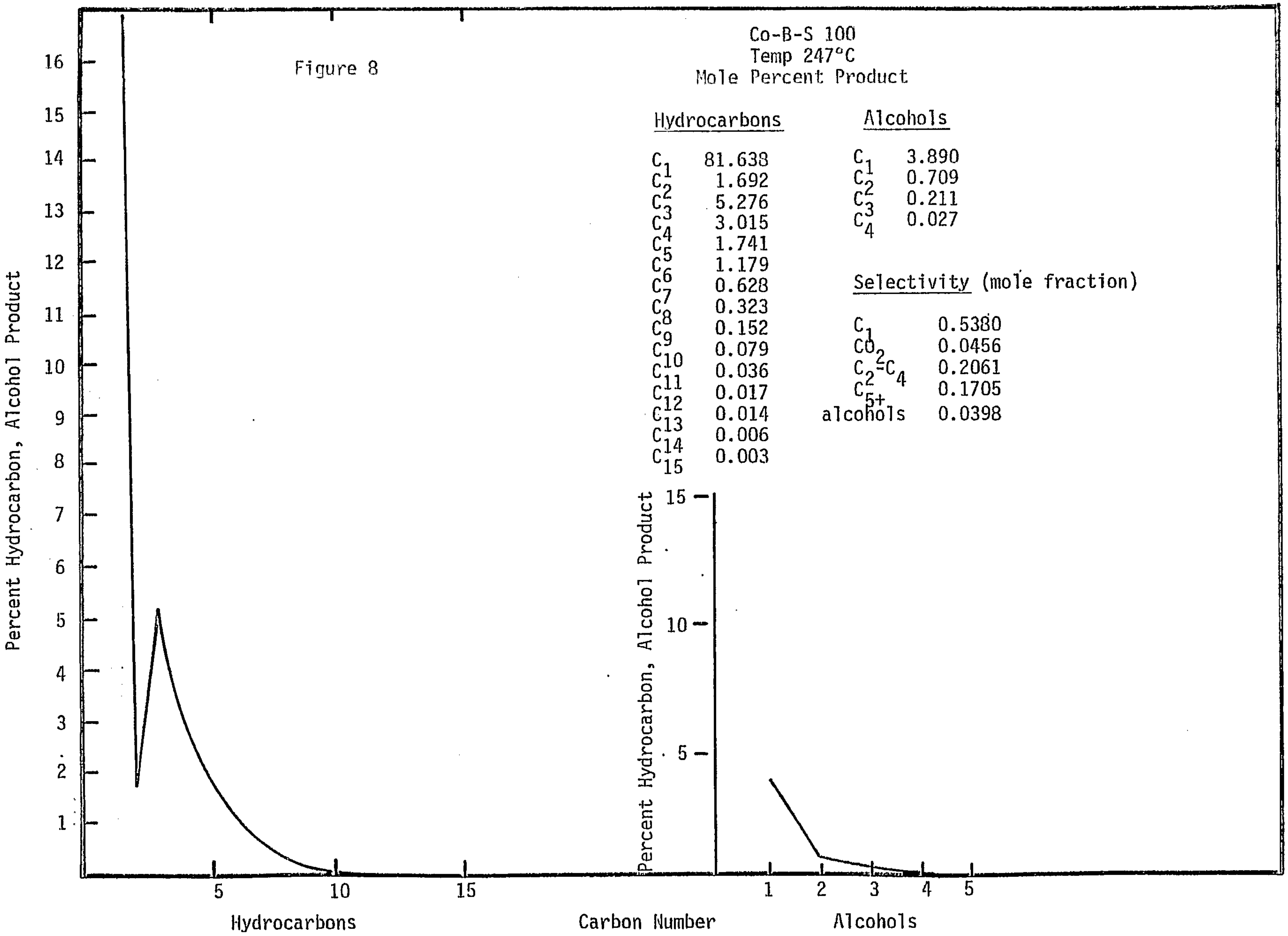


Figure 8

Co-B-S 100
Temp 247°C
Mole Percent Product

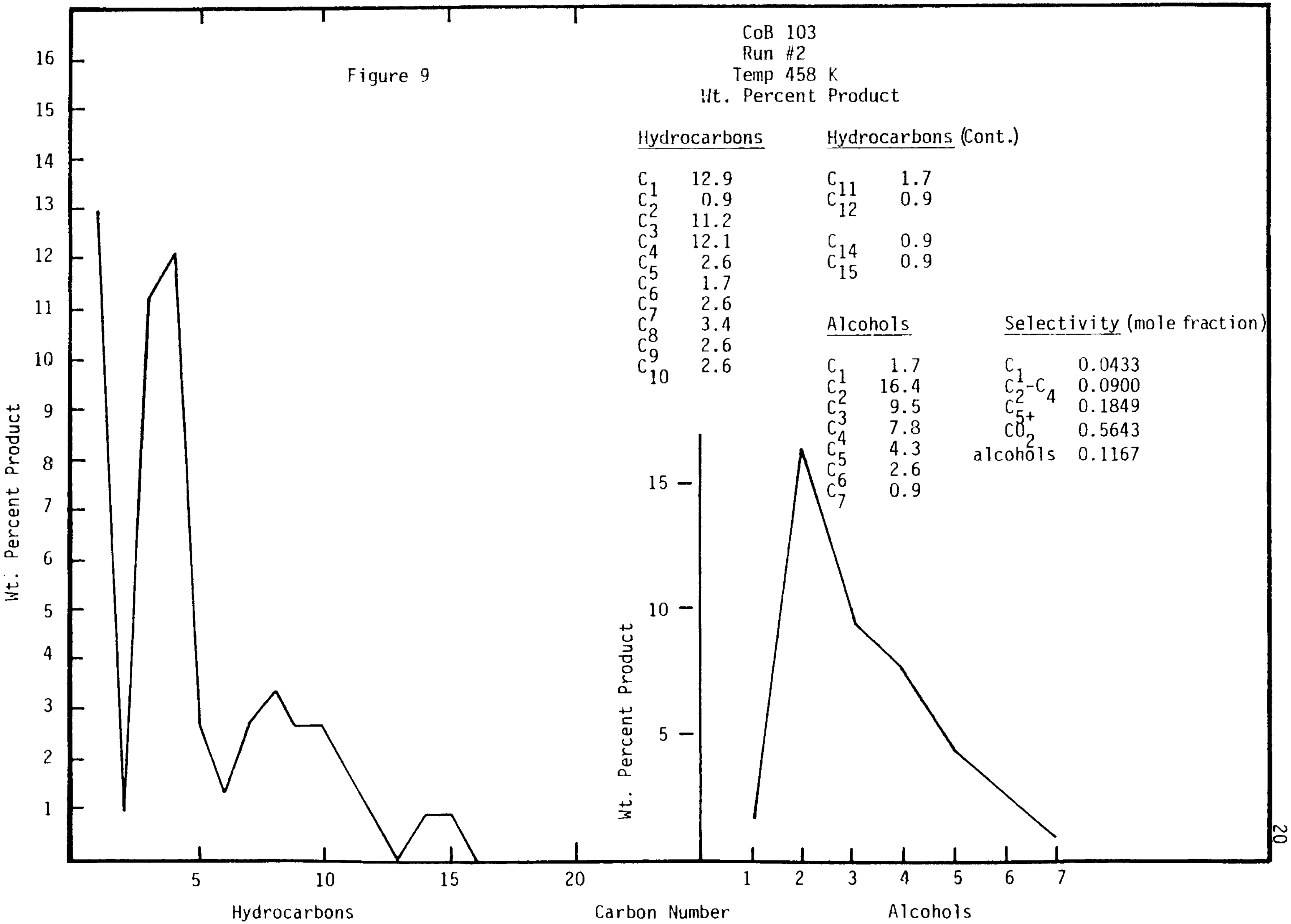
Hydrocarbons	
C_1	81.638
C_2	1.692
C_3	5.276
C_4	3.015
C_5	1.741
C_6	1.179
C_7	0.628
C_8	0.323
C_9	0.152
C_{10}	0.079
C_{11}	0.036
C_{12}	0.017
C_{13}	0.014
C_{14}	0.006
C_{15}	0.003

Alcohols	
C_1	3.890
C_2	0.709
C_3	0.211
C_4	0.027

Selectivity (mole fraction)	
C_1	0.5380
CO_2	0.0456
C_2-C_4	0.2061
C_{5+}	0.1705
alcohols	0.0398

Figure 9

CoB 103
Run #2
Temp 458 K
Wt. Percent Product



Hydrocarbons	
C_1	12.9
C_2	0.9
C_3	11.2
C_4	12.1
C_5	2.6
C_6	1.7
C_7	2.6
C_8	3.4
C_9	2.6
C_{10}	2.6

Hydrocarbons (Cont.)	
C_{11}	1.7
C_{12}	0.9
C_{14}	0.9
C_{15}	0.9

Alcohols	
C_1	1.7
C_2	16.4
C_3	9.5
C_4	7.8
C_5	4.3
C_6	2.6
C_7	0.9

Selectivity (mole fraction)	
C_1	0.0433
C_2-C_4	0.0900
C_{5+}	0.1849
CO_2	0.5643
alcohols	0.1167

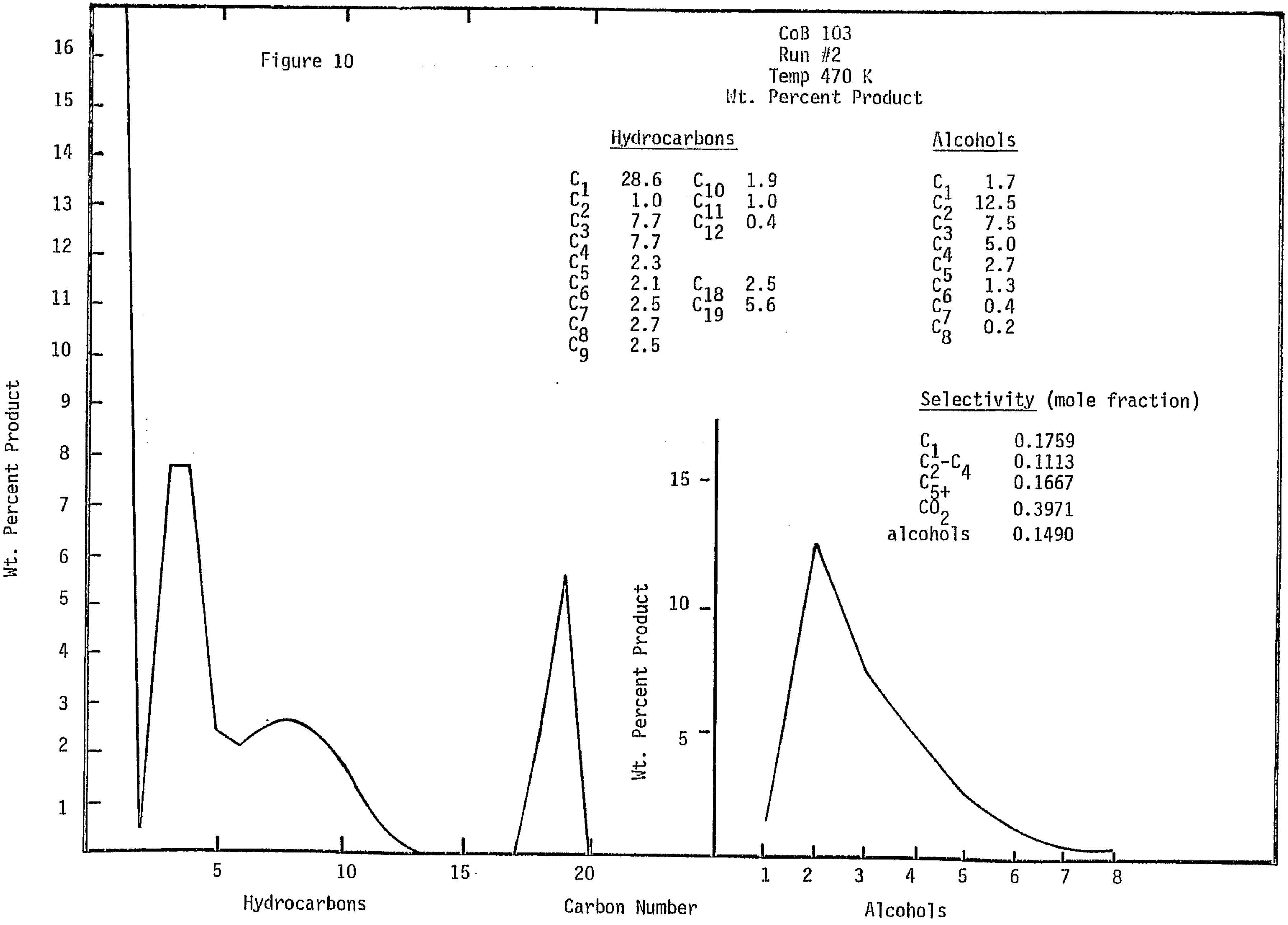


Figure 10

CoB 103
Run #2
Temp 470 K
Wt. Percent Product

Hydrocarbons

C_1	28.6	C_{10}	1.9
C_2	1.0	C_{11}	1.0
C_3	7.7	C_{12}	0.4
C_4	7.7		
C_5	2.3		
C_6	2.1	C_{18}	2.5
C_7	2.5	C_{19}	5.6
C_8	2.7		
C_9	2.5		

Alcohols

C_1	1.7
C_2	12.5
C_3	7.5
C_4	5.0
C_5	2.7
C_6	1.3
C_7	0.4
C_8	0.2

Selectivity (mole fraction)

C_1	0.1759
C_2-C_4	0.1113
C_{5+}	0.1667
CO_2	0.3971
alcohols	0.1490

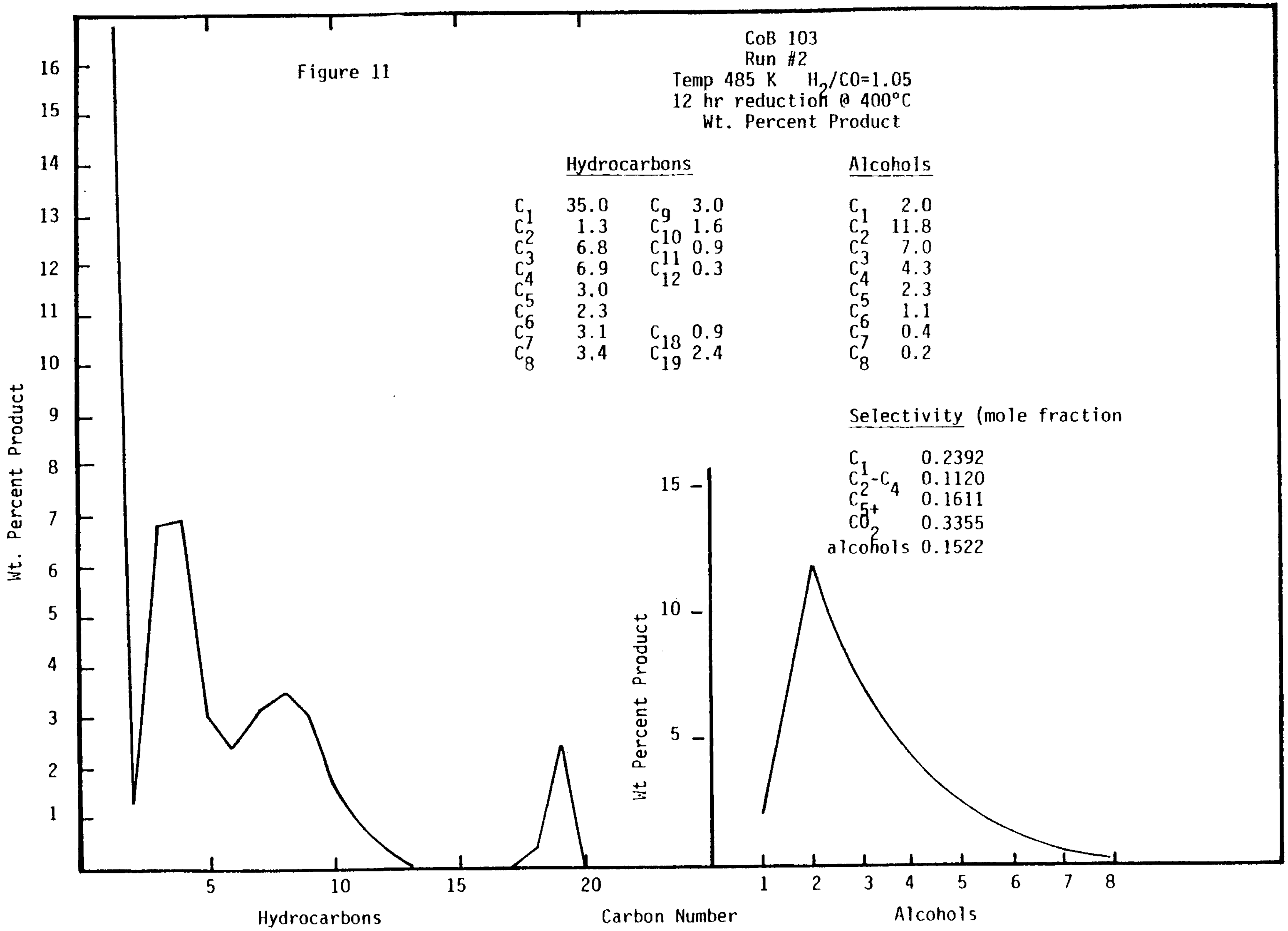


Figure 11

CoB 103
Run #2
Temp 485 K $H_2/CO=1.05$
12 hr reduction @ 400°C
Wt. Percent Product

Hydrocarbons				Alcohols	
C_1	35.0	C_9	3.0	C_1	2.0
C_2	1.3	C_{10}	1.6	C_2	11.8
C_3	6.8	C_{11}	0.9	C_3	7.0
C_4	6.9	C_{12}	0.3	C_4	4.3
C_5	3.0			C_5	2.3
C_6	2.3			C_6	1.1
C_7	3.1	C_{18}	0.9	C_7	0.4
C_8	3.4	C_{19}	2.4	C_8	0.2

Selectivity (mole fraction

C_1	0.2392
C_2-C_4	0.1120
C_{5+}	0.1611
CO_2	0.3355
alcohols	0.1522

CO_2 and no alcohols. The product distribution for the hydrocarbon product was also very interesting with maxima occurring at both C_4 and C_8. Also Arrhenius plots of the turnover numbers vs. 1/T yielded an activation energy of ~140 KJ/mole which agrees with the previously reported value of ~150 KJ/mole but is nearly double the value of 80-85 KJ/mole obtained for silica suported cobalt and iron catalysts and unsupported iron boride. This suggests that a different rate determining step or even different mechanism operates in this catalyst compared to the other borides and the silica supported cobalt and iron. The unusually high production of alcohols on the CoB catalyst is analogous to that of Fe_2N catalysts; moreover the propect of developing CoB and FeB catalysts with greater chemical/thermal stability than Fe_2N appears promising.

Activity/selectivity tests occupied much of the work effort during the second year of the project. Specific activities in the form of turnover numbers for CO conversion and product selectivities are summarized in Tables 4 and 5 for the catalysts testing during the past year. It should be emphasized that very few activity/selectivity data are available in literature for cobalt and iron catalysts, which were clearly determined in the absence of heat and mass transport influences using properly conditioned catalysts. Our results to date show that without exception cobalt/silica catalysts produce higher molecular weight products than iron/silica catalyst of similar loading (Table 5) and that cobalt catalysts are more active on a per site basis than iron Fischer-Tropsch catalysts (Table 4). Also evident is-the typical low yield of CO_2 from cobalt catalysts as compared to iron catalysts (Table 5). As can be seen, the cobalt boride catalyst was less active than the silica-supported cobalt catalyst but equally as active as Fe/SiO_2. However its product was of much higher molecular weight than Co/SiO_2. This hydrocarbon product distribution is presented in Figure 13 and Table 5.

The effects of H_2/CO ratio on activity and selectivity of Fe/SiO_2 were also examined (Tables 4 and 5). As H_2/CO ratio decreased, methane production decreased. More CO_2 was generated, and the average molecular weight of the hydrocarbon product increased as expected. The high levels of C_2 hydrocarbon production over the iron catalysts (Figure 12) is interesting. In comparison, cobalt catalysts appear to have much lower selectivities to C_2 hydrocarbons.

The effects of metal loading on product distribution are also evident from comparison of the selectivity of Fe-S-103, 3% metal catalyst, with that of Fe-S-102, a 15% metal catalyst. Fe-S-103 produced much greater amounts of methane (nearly double), a significantly higher fraction of C_2-C_4 hydrocarbons and less CO_2. The product molecular weight decreased accordingly.

The potassium-promoted catalyst, though slightly less active, produced a higher molecular weight product. It's product distribution is also shown graphically on Figure 12 to contrast it to that of the unpromoted catalyst of the same loading. A shift from methane to C_2-C_4 and higher hydrocarbons is evident. Table 5 shows that CO_2 make is also increased by potassium.

3. Future Plans

Activity/selectivity tests will continue in the next year, focusing on the unsupported iron, nitrided iron, borided iron, and zeolite-supported iron catalysts. The present analytical scheme is working well, and no further

TABLE 4

CO Turnover Numbers for Supported Iron and Cobalt Catalysts

Catalyst Code	H_2/CO Ratio	Temperature (K)	Turnover Number (N_{CO} x 10^3)	Activation Energy (kJ/g mole)
Fe-S-102	2	460	0.64	92.5
	2	483	2.5	
	2	498	3.9	
	1	449	0.19	99.3
	1	483	1.4	
	1	498	2.5	
Fe-S-103	2	448	0.72	82.8
	2	483	3.2	
	2	498	7.0	
	1	448	0.79	80.8
	1	473	2.3	
	1	498	7.0	
FeK-S-100	2	498	6.6	--
FeB-S-101	2	498	0.33	--
Co-S-101	2	463	5.9	
CoB-102	2	453	0.31	151.6
	2	473	1.7	--
CoB-102	1	458	.28	139.6
	1	470	.64	
	1	485	1.55	
CoB-S-100	1	504	16.49	79.1
	1	520	29.46	
FeB-102	1	483	8.05	81.4
	1	493	14.58	
	1	503	22.92	
	1	513	25.42	
	1	523	42.24	

TABLE 5

Product Selevtivities for Supported Iron Catalysts at 498 K and Cobalt Catalysts at 473 K

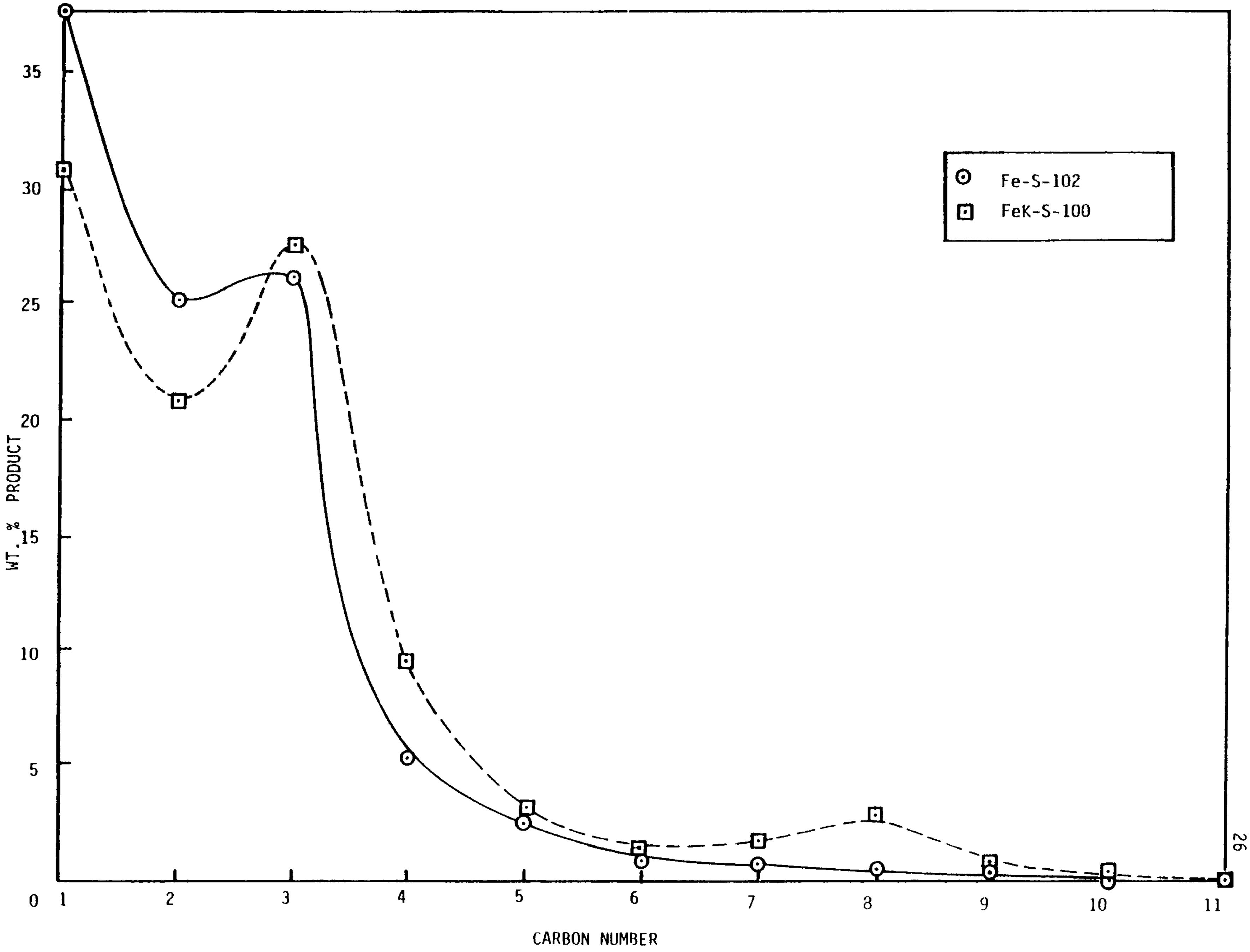
Catalyst Code			Selectivity			Ave. Molecular Weight Hydrocarbon Product
	CH_4	C_2-C_4	C_5+	CO_2	Alcohols	
Fe-S-102[a]	0.16	0.27	0.03	0.47	0.07	27.77
Fe-S-102[b]	0.12	0.23	0.02	0.56	0.07	28.68
Fe-S-103[a]	0.25	0.33	0.04	0.30	0.08	26.27
Fe-S-103[b]	0.20	0.31	0.03	0.36	0.10	27.54
FeK-S-100[a]	0.08	0.19	0.03	0.65	0.05	30.26
FeB-S-100[a]	0.26	0.19	0	0.55	0	20.25
Co-S-101[a]	0.27	0.24	0.34	0.04	0.11	31.21
CoB-S-102[a]	0.15	0.24	0.50	0.07	0.04	40.25
FeB-102[b]	0.17	0.44	0.23	0.10	0.06	--
CoB-S-100[b]	0.31	0.26	0.31	0.06	0.06	--
CoB-103[b]	0.18	0.11	0.17	0.40	0.15	--

---

[a] $H_2/CO = 2$

[b] $H_2/CO = 1$

Figure 12. PRODUCT DISTRIBUTIONS FOR Fe-S-102 AND FeK-S-100



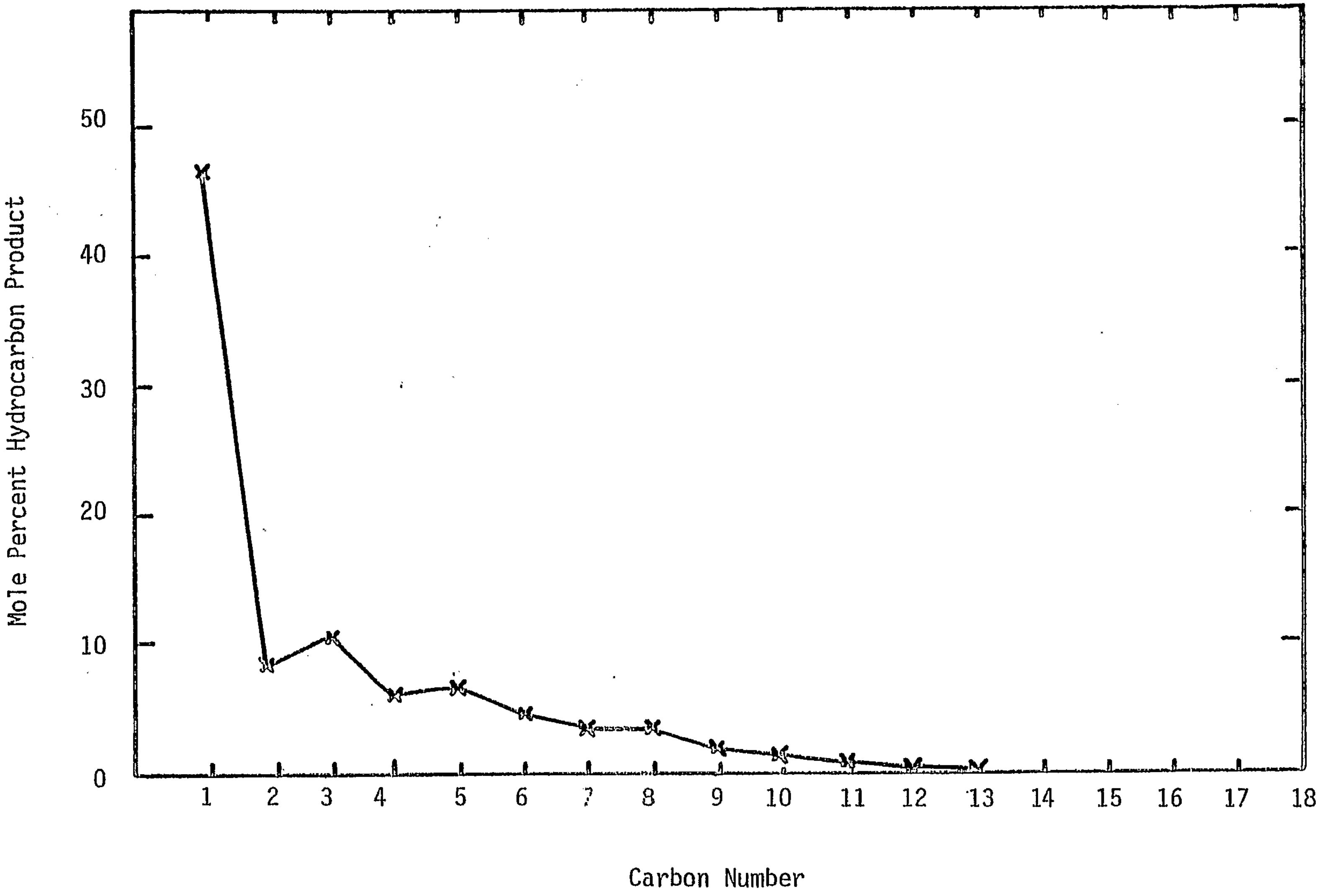


Figure 13. Product Distribution for CoB-102 at 473 K, H_2/CO=2.

changes are anticipated.

C. Task 3: In Situ H_2S Poisoning Measurements

During the past 6 months development of a sulfur-poisoning reaction system was completed. The resulting reactor flow system is shown in Figure 14. It is essentially the same as the one in use for activity/selectivity measurements, with certain modifications necessary to allow use with low levels of H_2S. To avoid in-line adsorption of H_2S, Teflon tubing and valves are used where necessary throughout the system. Pyrex is used for a portion of the heated exit line for the same reason.

Analyses of fixed gases, hydrocarbon products and H_2S concentrations are performed simultaneously using a gas chromatograph equipped with gas sampling and switching valves as shown in Figure 15. A 5' x 1/8" carbosieve B column and a thermal conductivity detector are used for analysis of both feed and product fixed gases. 30' of 1/8" 10% SP2100 in series with 10' of 1/8" SP2100 with 0.1% Carbowax and a flame ionization detector are used for hydrocarbon product analysis. Both columns are temperature programed from 40°C to 100°C at 10°C/min. H_2S levels of both feed product streams are measured using Chromosil 310 in an 8' x 1/8" teflon tubing column at ambient temperature and a flame photometric detector.

The FPD has been calibrated from 66 ppm to 0.2 ppm H_2S. As shown in Figure 16 response below 10 ppm is approximately linear. It has also been observed that addition of 3-5 ppm H_2S to the CO/H_2 feed mixture results in the formation of 0.2 to 0.5 ppm COS with a corresponding decrease in H_2S concentration. The COS formed appears not to affect catalyst activity.

A FORTRAN computer program has also been written to aid in deactivation data analysis. The program reduces product peak areas and flow rates to turnover numbers, selectivities, and deactivation rates.

Tests were run of 15% Co/SiO_2 at 495 K, 1 atm and a space velocity of 1500 hr^{-1}. CO conversion varied from 4-30%. As H_2S was added to the feed stream, total activity declined to less than one fifth of the original value after 60 hrs of operation. As poisoning occurred, the product selectivity was altered, with higher molecular weight hydrocarbons being favored (Figure 17). This effect passed through a maximum as the catalyst was partially poisoned, and declined as complete poisoning occurred. Breakthrough of H_2S occurred after 58 hours of running.

Similar tests were made with 15% Fe/SiO_2, however, failure of the gas sampling valve forced the run to be aborted. The valve was returned to the manufacturer for repair, reinstalled and is presently ready for operation.

Quantitative deactivation tests will continue during the next quarter. These will be performed at 250°C and a H_2 to CO ratio of 2:1. Space velocities will be varied from 200-1000 h^{-1} in order to maintain CO conversions between 2 and 10%. After steady state has been reached 10-20 ppm of H_2S will be added to the feed stream and catalyst activity monitored for 24-48 hrs. These conditions were determined to be optimum in preliminary tests using 15% Fe and Co Catalysts.

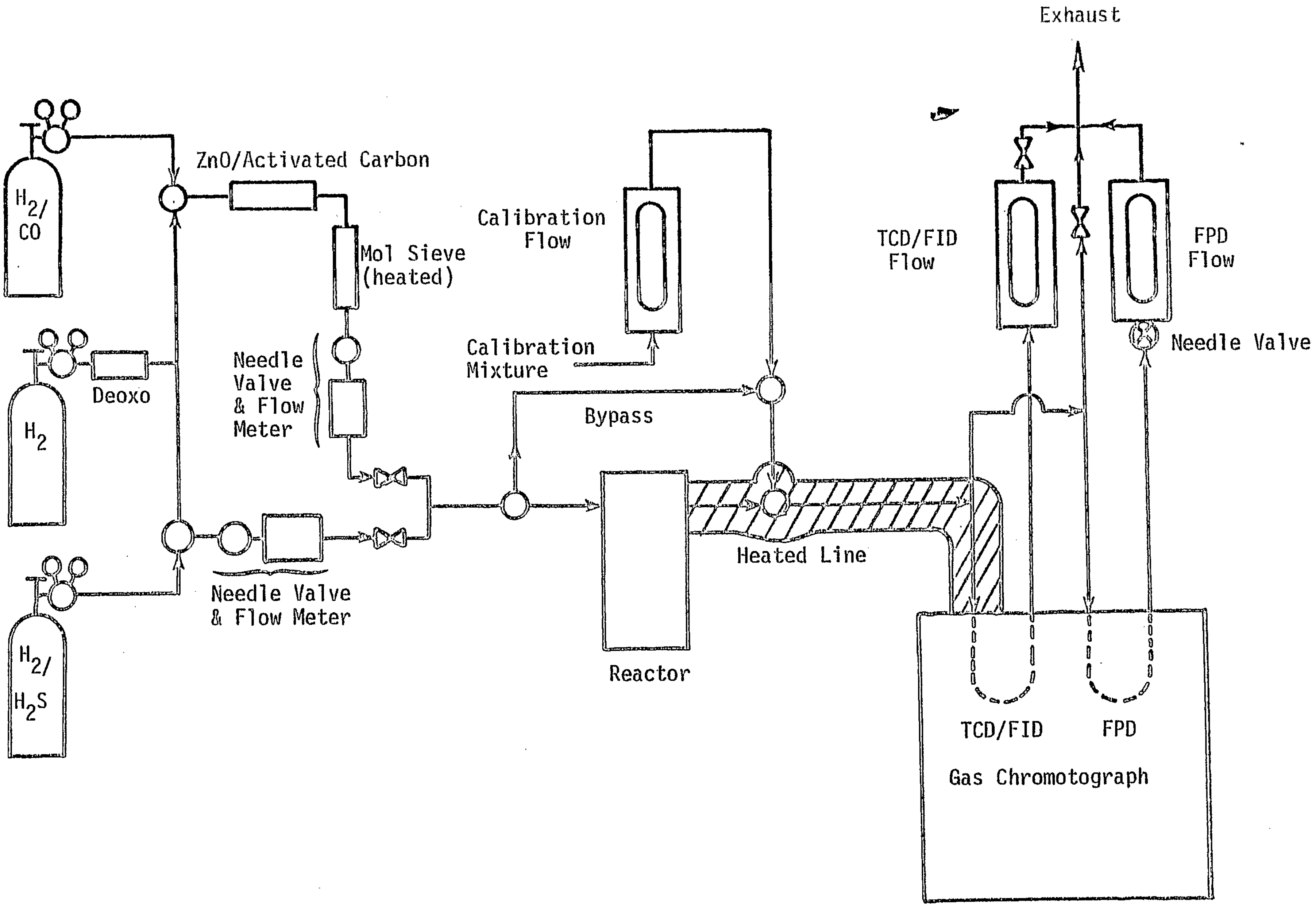


Figure 14. Fischer Tropsch Sulfur Deactivation System

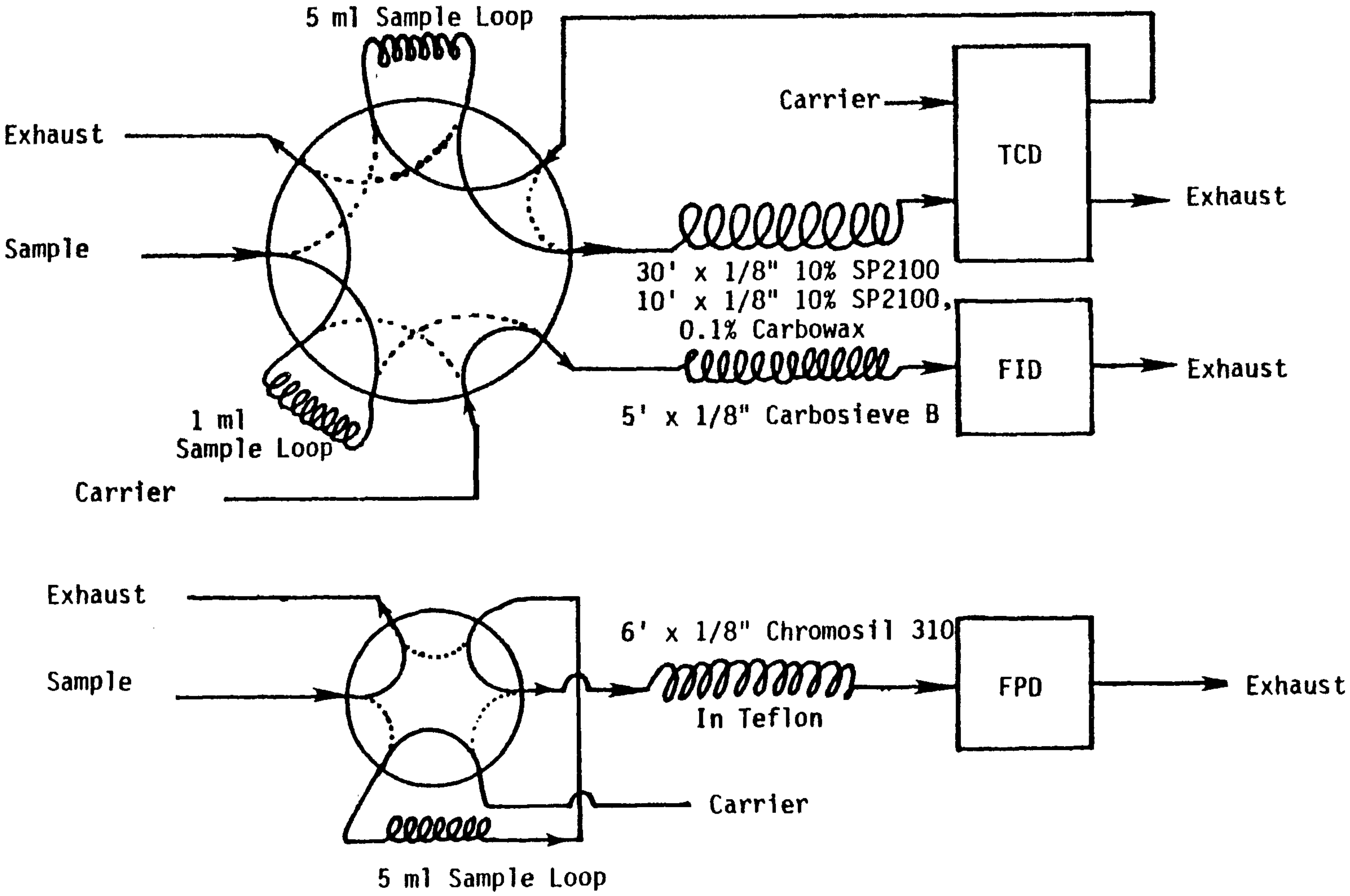


Figure 15. Gas Chromatograph Schematic for H_2S Deactivation Studies

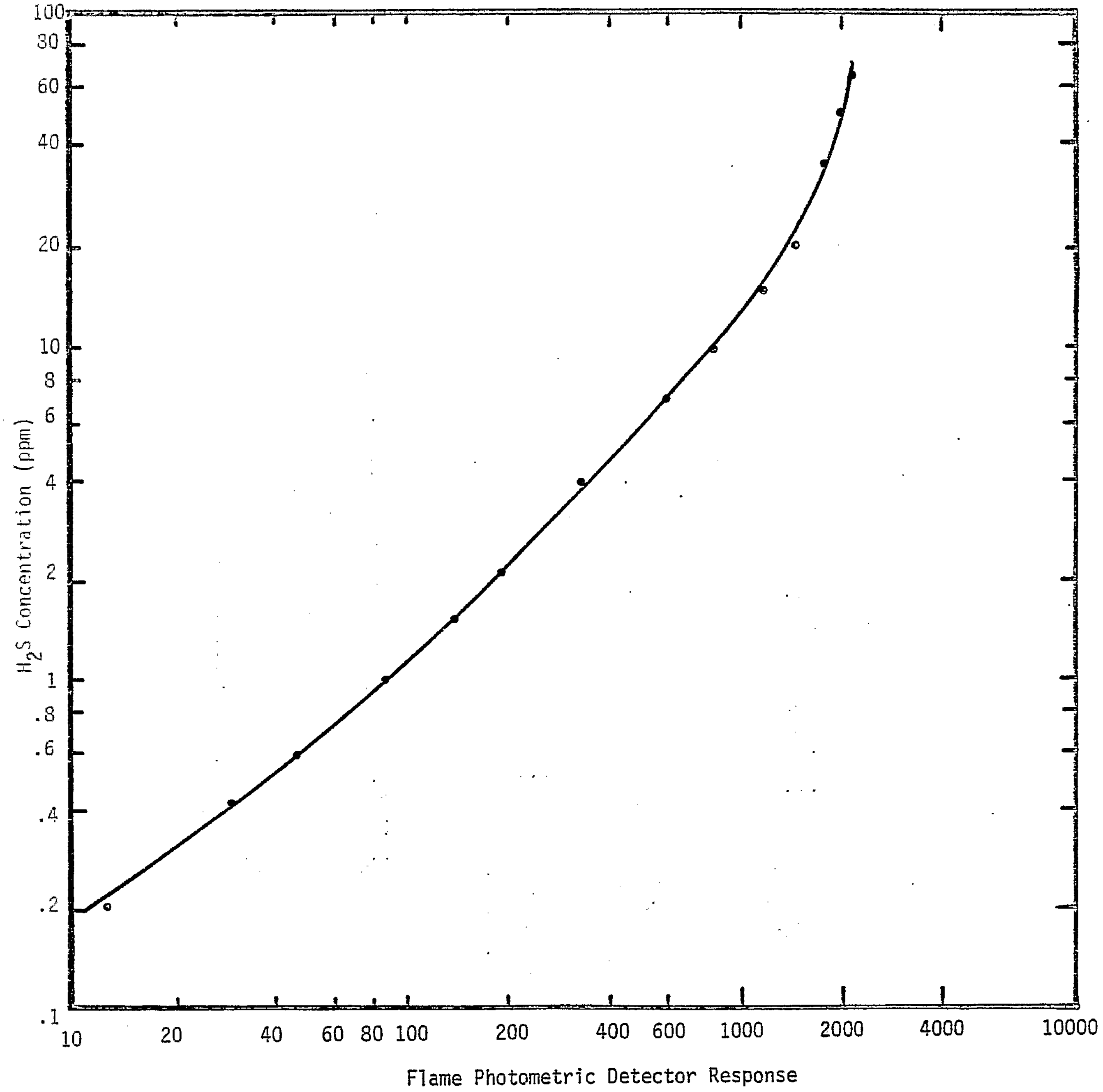


Figure 16. Flame Photometric Detector Calibration Curve

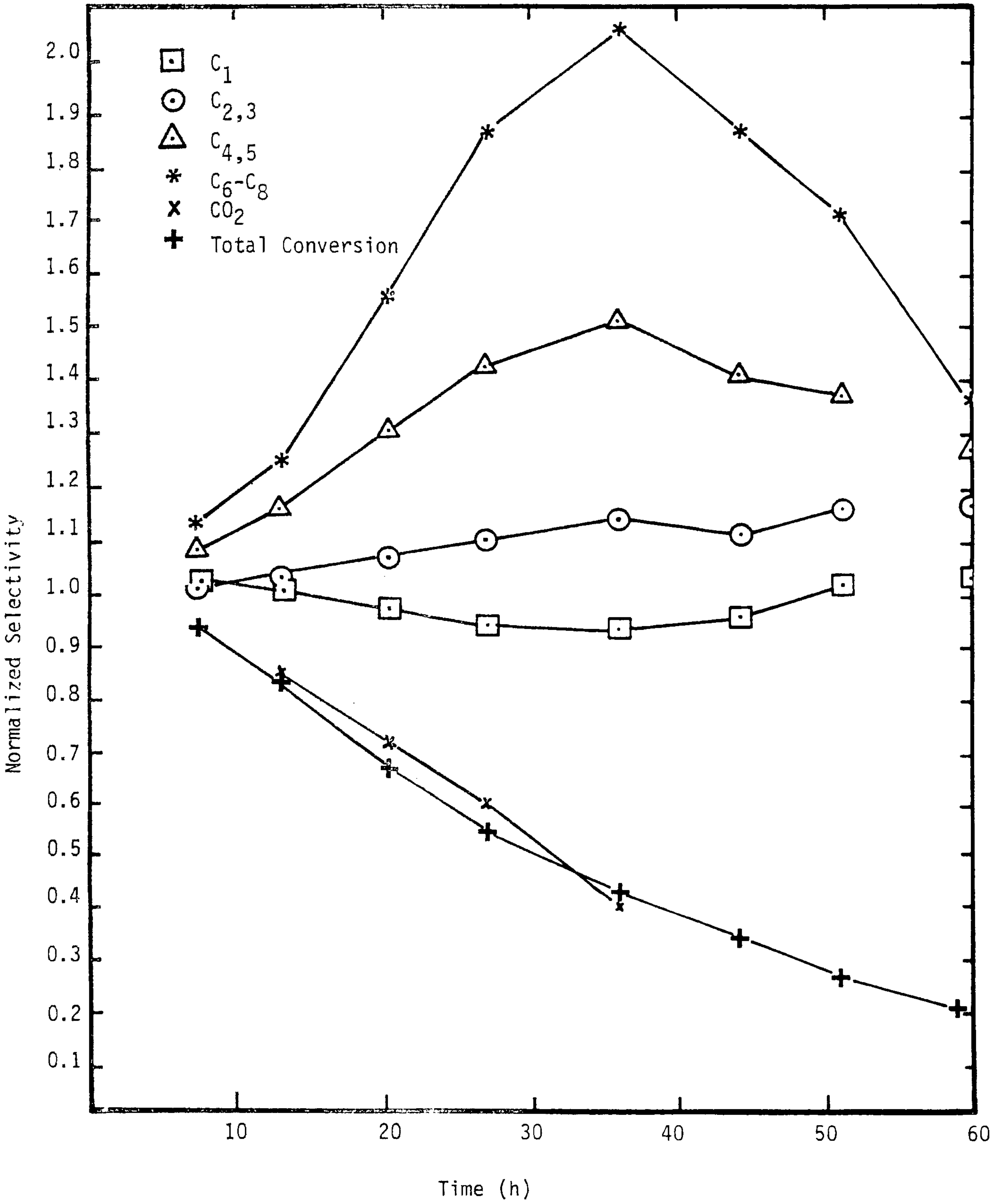


Figure 17. Product Selectivity as a Function of Time of Exposure to H_2S.

D. Miscellaneous Accomplishments and Technical Communication

1. Investigation of H_2 and CO Adsorption on Co/ZSM-5

During the past six months we determined H_2 and CO adsorption uptakes for a series of Co/ZSM-5 catalysts prepared by PETC personnel using two different impregnation techniques. Although these measurements were not part of the proposed contract work, the data are within the scope of interest of this project and are therefore reported here.

Catalyst compositions and preparations are summarized in Table 6. The Co/ZSM-5 catalyst series included 3, 6 and 9 wt.% cobalt catalysts, umpromoted and promoted with ThO_2 and prepared by either aqueous or acetone impregnation of cobalt nitrate. The catalysts prepared from acetone solution were found to produce more aromatics in activity/selectivity tests at PETC. ThO_2 was found to increase liquid hydrocarbon yields and to effect a larger fraction of branched paraffins and of olefins.

Catalysts were pretreated according to the reduction and evacuation schedules shown in Table 7. During reduction the water-impregnated catalysts evolved copious quantites of water and brownish gas (probably NO_2), while acetone-impregnated catalysts did not evolve a brownish gas to any observable degree (decomposition to NO ?). All reduced catalysts appeared to have a low metallic content; that is, colors ranged from blue to light grey in contrast to the black color observed for Co/SiO_2 Catalysts of corresponding loadings. The acetone-impregnated catalysts were fluffy in texture, while the water-impregnated catalysts formed a compact, hard mass upon reduction.

Adsorption measurements were carried out in a volumetric, vacuum adsorption system previously described (5) using the same techniques as in the previous adsorption measurements in this contract. During adsorption of CO there was considerable drift, suggesting a slow approach to equilibrium. Measurements were repeated every few minutes until the rate of drift slowed significantly.

In order to determine the quantity of either H_2 or CO adsorbed on the cobalt metal surface of each catalyst it was necessary to first determine the quantity adsorbed on the support. The adsorption data for two different ZSM-5 samples pretreated in the same manner as the Co/ZSM-5 catalysts (see Table 8) show that generally negligible quantities of H_2 and CO are adsorbed on the support at 25-200°. The negative adsorption values of -3.8 and -7.4 in µmoles/g are probably the result of a small leak, out gassing, or inaccurate extrapolation due to data scatter, since a negative uptake has no physical meaning. All of the other uptake values (except the +7.2 µmoles H_2/g at 200°C) are essentially zero within the experimental precision estimated to be ±1 µmole/g. In other words, no correction for adsorption on the support (particularly at 25 and 100°C) is necessary.

H_2 and CO uptakes for 9% Co/ZSM-5 catalyst (acetone impregnation) are shown as a function of temperature in Table 9. Negligible amount of H_2 is adsorbed on the catalyst at 25°C. This behavior is highly unusual considering that H_2 adsorption occurs with essentially monolayer coverage on unsupported cobalt at 25°C (6). At 100°C the total H_2 uptake was 123 µmoles/g suggesting that H_2 adsorption is activated between 25 and 100°C; at 200°C the H2

TABLE 6

Cobalt/ZSM-5 Catalysts:

Composition and Preparation

Sample	wt.%		Impregnation Medium
	Co	Th	
B0	0		
B7	0		
B2	9		Aqueous Cobalt Nitrate
B3	6		" "
B4	3		" "
B1	9		Acetone Soln Cobalt Nitrate
B5	6		" " " "
B6	3		" " " "
B8	9	1.4	Acetone Soln
B9	6	0.9	" "
B10	3	0.5	" "
B11	9	1.4	Aqueous soln
B12	6	0.9	" "
B13	3	0.5	" "

Notes:

1. Catalyst prepared with acetone produce more aromatics.
2. ThO_2 increases liquid HC yield; results in branched paraffins and olefins.

TABLE 7

CONDITIONS FOR PRETREATMENTS of Co/ZSM-5 CATALYSTS

Reduction in 60 ml/min H_2

25-200°C	at	2°C/min
200°C		2 hrs.
200-350°C	at	2°C/min
350°C		16-17 hrs

Evacuate at 350°C 1-2 hrs.

TABLE 8

H_2 and CO Adsorptions on ZSM-5 (NH_4^+ form) Supports

	H_2 Uptake (μmoles/g)[a]			CO Uptake (μmoles/g)		
Support	25°C	100°C	200°C	25°C	100°C	200°C
B0	-0.3	0.4	7.2	-3.8	1.3[b] -1.1	-0.6
B7		-7.4			-0.7[b] -0.5	

---

[a] Total uptake

[b] Total uptake; other data for CO refer to irreversible uptake

TABLE 9

H_2 and CO Adsorption on Co/ZSM-5

Effects of Temperature

	H_2 Uptake (moles/g)[b]			CO Uptake (moles/g)		
Catalysts	25°C	100°C	200°C	25°C	100°C	200°C
9% Co/ZSM-5 Acetone Prepn	-1.6	123	48.5	47.5[b] -1.1[c]	23.5[b] 1.1[c]	15.8[b] -2.4[c]
		98[a]				

---

[a] Repeat run

[b] Total uptake

[c] Irreversible Uptake

adsorption dropped to 48.5 moles. Since the H_2 uptake was maximum at 100°C this temperature was chosen for the remainder of the measurements. Note that a repeat of the H_2 adsorption at 100°C yielded 98 moles/g in reasonably good agreement with the previous measurement, considering the estimated experimental accuracy to be ±10%.

The total CO adsorption uptake (Table 9) was highest at 25°C and decreased with increasing temperature. However, irreversible CO adsorption (the difference in adsorption isotherms after evacuation at 350°C and the adsorption temperature respectively) was negligible at all three temperatures. In other words, CO is relatively weakly adsorbed on ZSM-5 supported cobalt even at 25°C. This behavior is anomolous, since CO is typically strongly bound to cobalt/silica or cobalt/alumina at 25°C (7).

Typical adsorption isotherms for H_2 and CO adsorption at 100°C on 9% Co/ZSM-5 prepared by either water or acetone impregnation are shown in Figs. 18-21. All of the isotherms have a positive slope suggestive of physical or weak chemical adsorption on the metal and illustrative of the need to extrapolate the data to zero pressure. The two isotherms for 9% Co/ZSM-5 prepared by acetone impregnation (Fig. 20) are nearly coincidental and thus the quantity of irreversible (strong) adsorption determined from the difference in the two isotherms is negligible. On the other hand the data for 9% Co/ZSM-5 prepared by aqueous impregnation indicates that about 30% of the total adsorption is irreversible or strong.

Table 10 summarizes H_2 and CO uptake data for 3, 6 and 9% Co/ZSM-5 catalysts prepared by either aqueous or acetone impregnation and illustrates the effects of loading and preparation on the adsorption behavior. Comparison of the data for catalysts of different loadings prepared from aqueous solution (AQ) reveals large variations in total H_2 adsorption uptakes while total CO uptakes are nearly the same within experimental accuracy. The negligibly low uptake for the 3% Co/ZSM-5 (AQ) suggests that H_2 adsorption is altogether suppressed, an indication of a very strong metal-support interaction (3).

The relatively large H_2 uptake for the 9% Co catalyst prepared by acetone (AC) suggests it is more highly dispersed than the corresponding Co/ZSM-5 (AQ). On the other hand the 6% Co (AQ) has significantly higher uptake than the 6% Co (AC). Moreover the CO uptakes for all of the AC catalysts is significantly lower and more reversible compared to the AQ catalysts. This apparent weakening and suppression of CO adsorption is suggestive of a strong metal-support interaction in the AC catalysts. Thus it is not clear from the adsorption data which of the two preparations results in the more highly dispersed catalysts. Before accurate estimates of dispersion can be made from the adsorption data, extents of reduction to cobalt metal are needed; complementary data from TEM and XRD are also needed to determine adsorption stoichiometries and to provide independent measures of crystallite size.

Effects of the thoria promoter on H_2 and CO adsorption at 100°C are illustrated by the data listed in Table 11. The 9% Co promoted with ThO_2 takes up less H_2 but more CO. Perhaps, its larger CO/H adsorption ratio is related to the ability of the ThO_2 promoted catalyst to produce a greater fraction of hydrogen poor products (i.e. liquids, olefins and branched hydrocarbons).

TABLE 10

H_2 and CO Adsorptions on Co/ZSM-5

Effects of Loading and Preparation

Catalyst	Prepn	H_2 Uptake[a] (moles/g)	H/Co_T	CO Uptake[b] (moles/g)	CO/Co_T	CO/H
B2, 9% Co	H_2O	11.2	0.015	68.0[b]	0.044	3.0
				22.4[c]	0.015	1.0
B3, 6% Co	"	51.3	0.10	80.0	0.0785	0.79
				12.6	0.012	0.12
B4, 3% Co	"	0.4	0.0016	72.3	0.142	89
				19.7	0.039	24
B1, 9% Co	Acetone	110±10	0.14	23.5[b]	0.0154	0.11
				1.1	7.2×10^{-4}	0.005
B5, 6% Co	"	12.3	0.023	27.5	0.027	1.17
				5.7	5.6×10^{-3}	0.24
B6, 3% Co	"	11.0	0.043	16.5	0.032	0.75
				1.7	3.3×10^{-3}	0.07

---

[a] Total H_2 uptake at 100°C

[b] Total CO uptake at 100°C

[c] Irreversible CO uptake at 100°C

TABLE 11

H_2 and CO Adsorptions on Co/ZSM-5

Effects of Thoria

Catalyst	Prepn	H_2 Uptake[a] (moles/g)	H/Co	CO Uptake[a] (moles/g)	CO/Co	CO/H
B1, 9% Co	Acetone	110	0.14	23.5	0.0154	0.11
B8, 9% Co, 1.4% Th	Acetone	13.7	0.018	38.3	0.025	1.4

---

[a] Total uptake at 100°C

Figure 18. H_2 Adsorption on Sample B2
(9 wt.% Co via H_2O soln.)

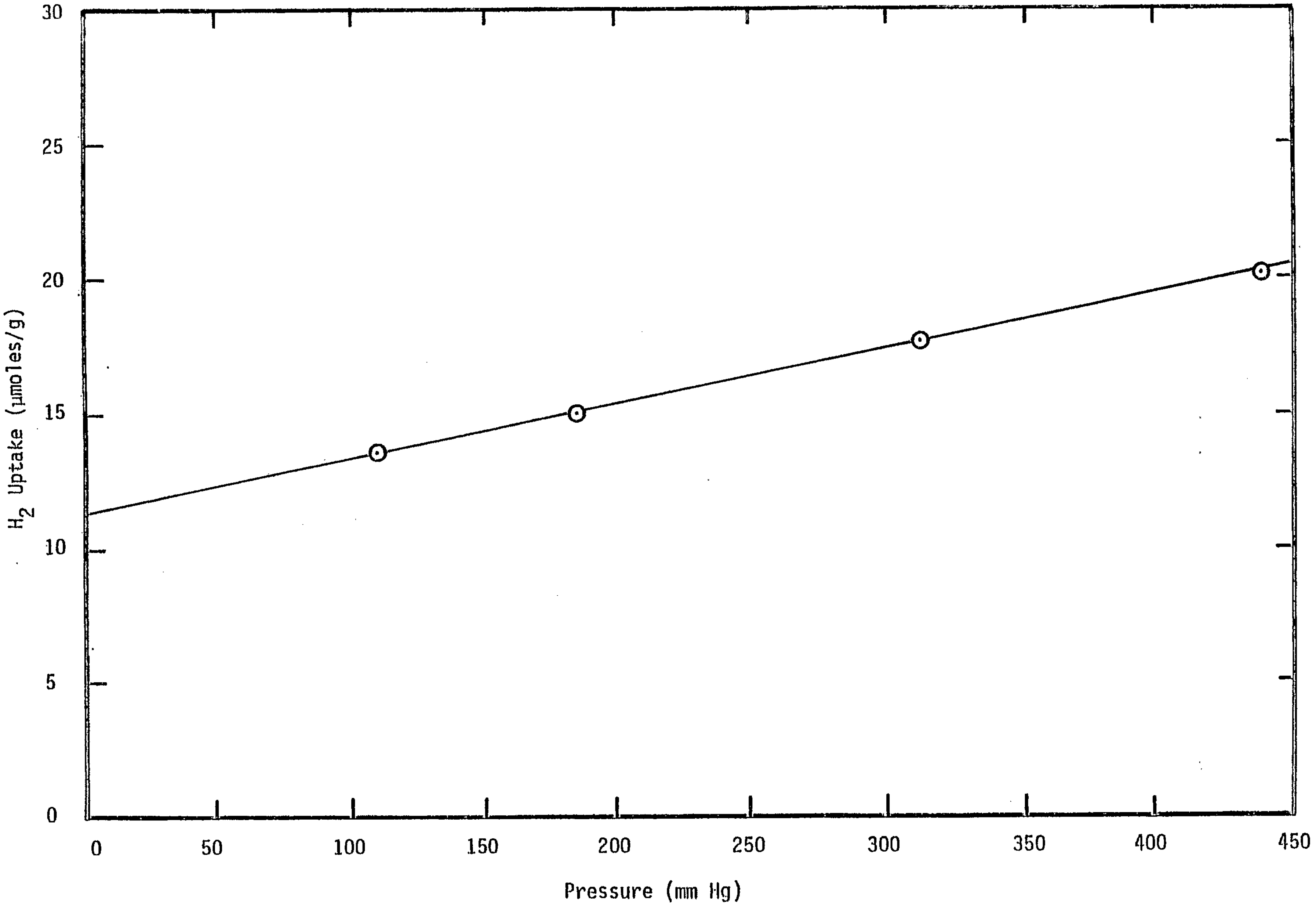


Figure 19. H_2 Adsorption on Sample B1
(9 wt.% Co via acetone soln)

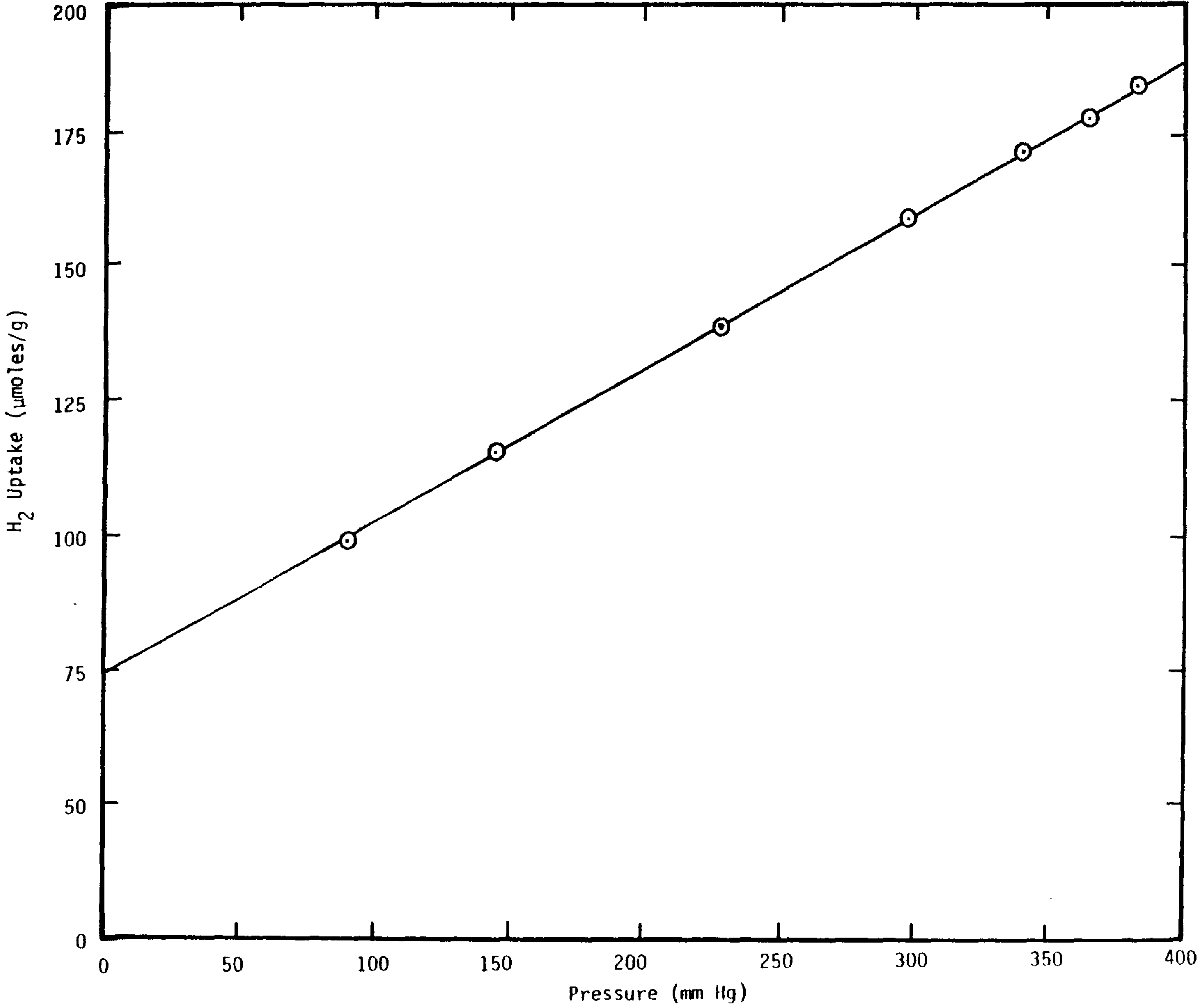


Figure 20. CO Adsorption on Sample B1
(9 wt.% Co via acetone soln.)

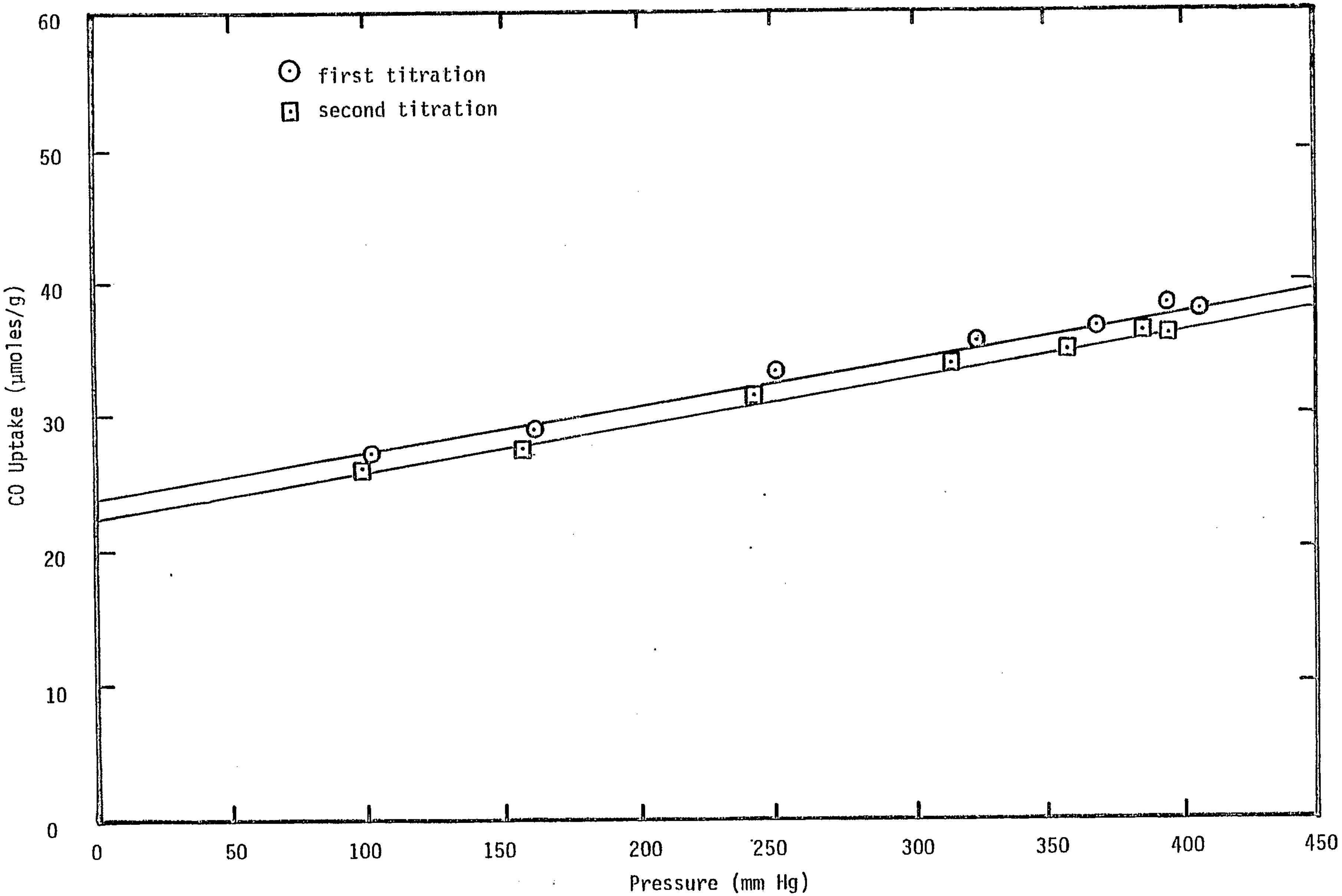
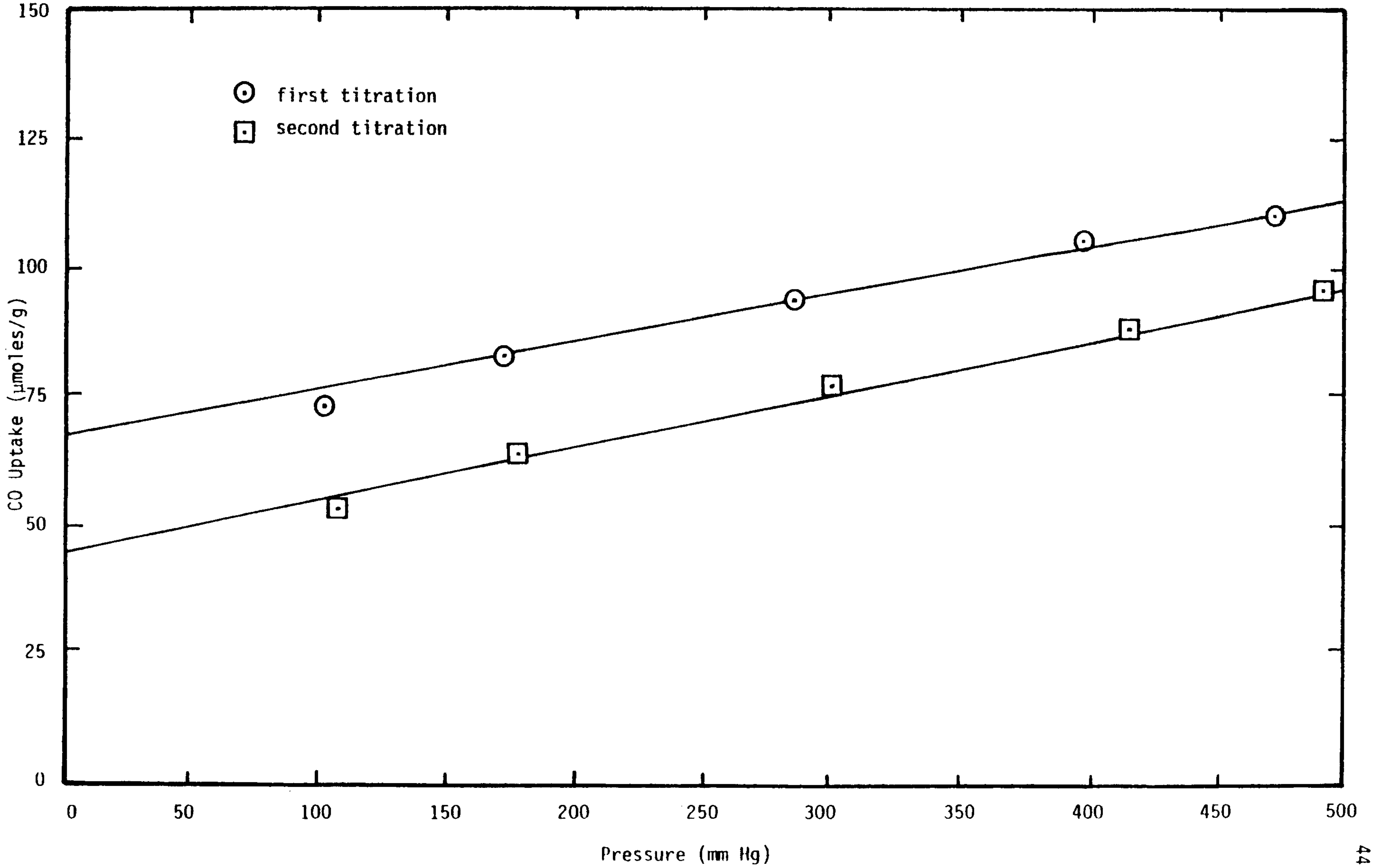


Figure 21. CO Adsorption on Sample B2

(9 wt.% Co via H_2O soln.)



Although somewhat preliminary, the results of the H_2 and CO adsorption measurements are sufficiently unusual and merit further investigation. The need for a careful, systematic 1-2 year investigation involving repetition of the measurements, temperature-programmed-desorption measurements, and additional characterization of the catalyst by temperature-programmed-reduction and TEM is clear.

2. Technical Communication

During the past year the principal investigator, Calvin H. Bartholomew, and his students attended seven different regional and national meetings (see Table 12) where they presented 4 papers or talks on sulfur poisoning, metal borides and similar topics related to this contract. In addition the PI visited five industrial and University laboratories and presented two additional seminars related to this contract (see Tables 13 and 14), while receiving 16 visitors to our laboratory (Table 15). These meetings and visits provided useful scientific interchanges and feedback relating to our present work.

TABLE 12

Meetings Attended and Papers Presented during 1980-81 Contract Year

1.[a] C.H. Bartholomew and J.R. Katzer, "Sulfur Poisoning of Nickel in CO Hydrogenation," presented at the International Conference on Catalyst Deactivation, Antwerp, Belgium, Oct. 13-15, 1980.

2.[a] C.H. Bartholomew, "Investigation of Catalysts for Selective Synthesis of Hydrocarbon Liquids from Coal-Derived Gases," Presented at the DOE University Contractors Conference on Coal Liquification, Oct 21-22, 1980.

3. C.H. Bartholomew, "Crystallite Size and Support Effects in CO Hydrogenation," Annual Meeting of the Materials Research Society, Boston, Nov. 17-18, 1980.

4. E.L. Sughrue and C.H. Bartholomew, "Kinetics of CO Methanation on Nickel Monolithic Catalysts," 73rd National Meeting of the AIChE, Chicago, Ill., Nov. 16-20, 1980.

5. G.D. Weatherbee and C.H. Bartholomew, "Specific Activity and Kinetics of Carbon Dioxide Hydrogenation on Nickel," The Sixth Symposium of the Rocky Mountain Fuel Society, Salt Lake City, Feb. 19-20, 1981.

6.[a] J.L. Rankin and C.H. Bartholomew, "Investigation of Sulfur-Tolerant Catalysts for Selective Synthesis of Hydrocarbon Liquids from Coal-Derived Gases," DOE Contractors Conference on Indirect Liquification," Pittsburgh, May 20, 1981

7.[a] C.H. Bartholomew, "Sulfur Poisoning of Nickel," GRI Workshop on Catalysis and Surface Chemistry," Chicago, June 15 and 16, 1981.

8. Calvin H. Bartholomew and Gordon D. Weatherbee, "Specific Activity and Kinetics of CO_2 Hydrogenation on Nickel," Seventh North American Meeting of the Catalysis Society, Boston, Oct 11-15, 1981.

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[a] Paper presentation related to this contract.

TABLE 13

Seminars Presented by Calvin H. Bartholomew during 1980-81 Contract year

1. C.H. Bartholomew, "Nickel-Support Interactions in CO Hydrogenation" Presented at the Department of Fuels Engineering, University of Utah, Dec. 11, 1980.
2. C.H. Bartholomew, "Future of Catalysis" Civil Engineering Department, BYU, February 17, 1981.
3. C.H. Bartholomew, "Metal Boride Catalysts in CO Hydrogenation," Department of Chemistry, University of Utah, May 19, 1981.
4. C.H. Bartholomew, "H_2 and CO Adsorption on Co-ZSM-5 Catalysts," Presented to the Process Science and Engineering Division; Pittsburgh Energy Technology Center, Oct. 9, 1981.

TABLE 14

Laboratories Visited by

Calvin H. Bartholomew

during 1980-81 Contract year

Laboratory Visited	Host(s)	Date
Petrochemical Institute of Technology University of Ghent	Prof. G.F. Froment Dr. P. Govind Menon	Oct. 16, 1980
Institute of Physical Chemistry University of Munich	Prof. H. Knoezinger	Oct. 17, 1980
Laboratory of Coal Science, Synthetic Fuels and Catalysis University of Utah	Prof. Francis Hanson	Dec. 11, 1980
Department of Chemistry Laboratories University of Utah	Prof. Edward Eyring	May 19, 1981
Harvey Technical Center ARCO Petroleum Co. Harvey, IL	Dr. John Mooy	Aug. 12, 1981
Process Sciences and Engineering Division,	Dr. Udaya Rao	Oct. 9, 1981

TABLE 15
Visitors to the BYU Catalysis Laboratory during 1980-81 Contract Year

Visitors	Affiliation	Date
Dr. Howard Evans	IBM Corp Boulder, Colorado	Feb. 27, 1981
Prof. John Falconer	Univ. Colorado	Mar. 12, 1981
Dr. Tony Perotta	Catalysis Research Gulf Res. & Dev.	Mar. 26, 1981
Dr. Richard Pannell	Catalysis Research Gulf Res. & Dev.	April 2, 1981
Mr. Peter Hughes Ms. Nellie Arsilla Mr. Charles Davis Ms. Linda Hook	Advanced Reactor Systems Department General Electric	March 5, 1981
Dr. Dennis Broderick	Chevron Res.	April 31, 1981
Dr. William Hecker	Chevron/Berkeley UC.	April 23, 1981
Dr. Russell Collins	University of Texas	April 24, 1981
Mr. Thomas Clough Dr. John Sibert Mr. Gary Myers	ARCO	May 13, 1981
Dr. Jaques Coenen	Kathlieke Universiteit	June 29, 1981
Dr. Jens Rostrup-Nielsen	Haldor Topsoe	Aug. 25, 1981

IV. CONCLUSIONS

1. O_2 titration data show that 36 hour reduction of iron/silica and cobalt/silica catalysts in flowing H_2 at 725 K and 625 K is adequate to reach a near maximum state of reduction. Percent reductions range from 12-80% in 3 and 15% iron/silica catalysts. Percent reductions range from 40 to 70% in the 3% and 15% cobalt/silica catalysts. Dispersions of iron/silica and cobalt/silica catalysts are 2-9% and 7.2 to 7.3% respectively after being reduced for 36 hours in flowing hydrogen.

2. The elution of oxygenated hydrocarbon compounds on an SP2100 chromatograph column is as follows:

   Alkenes < Alkanes < Aldehydes, Ketones < Esters < Alcohols < Acids

   Addition of 0.1% carbowax 1500 to a packed column containing SP2100 liquid phase allows greater reproducibility for alcohol separation in gas analysis. The use of an SP2100 coating on a capillary column improves separation and resolution while shortening analysis time and preventing baseline drift.

3. Cobalt/silica catalysts are more active on a per-site basis than the corresponding iron/silica catalysts in Fischer-Tropsch synthesis by approximately an order of magnitude. Cobalt catalysts produce relatively small amounts of CO_2 and higher molecular weight products compared to iron catalysts in Fischer-Tropsch synthesis. Iron catalysts produce relatively larger amounts of C_2 hydrocarbon.

4. As metal loading is increased from 3% to 15% for iron supported on silica, less methane production is observed and an increase in molecular weight of the hydrocarbon product occurs.

5. Potassium promotion of the 15% iron/silica catalyst shifts carbon numbers at the expense of methane and ethane production. K_2O is concentrated on the surface of the promoted iron catalyst to as much as 30 times its bulk concentration in agreement with previous work.

6. Iron boride supported on silica as prepared in our laboratory is relatively less active, less selective for higher molecular weight hydrocarbons, but more selective for lower molecular weight hydrocarbons compared to Fe/SiO_2. This behavior may be due to our method of preparation. Cobalt boride (unsupported) is less active than Co/SiO_2 in Fischer-Tropsch synthesis and about as active as Fe/SiO_2. However, its hydrocarbon product is of higher molecular weight than either Co/SiO_2 or Fe/SiO_2 and it produces significantly more alcohols and less CH_4. Its interesting properties merit further investigation.

7. During _in situ_ H_2S poisoning of iron and cobalt catalysts in CO/H_2 synthesis some interaction occurs between reactant CO and H_2S which produces COS. COS does not appear to affect catalyst activity/selectivity characteristics to the same extent as H_2S. H_2S poisoning causes a shift in product distribution to higher molecular weight products. This effect passes through a maximum with partial

poisoning and declines with complete poisoning. CO_2 production declines significantly and continuously with the addition of H_2S.

V. REFERENCES

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3. Bartholomew, C.H., Pannell, R.B. and Butler, J.L., "Support and Crystallite Size Effects in CO Hydrogenation on Nickel," J. Catal., 65, 335 (1980).

4. Emmett, P.H., and Brunauer, S., "Accumulation of Alkali Promoters on Surfaces of Iron Synthetic Ammonia Catalysts," J. Amer. Chem. Soc. 59, 210 (1937).

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