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INVESTIGATION OF SULFUR-TOLERANT CATALYSTS FOR SELECTIVE SYNTHESIS OF HYDROCARBON LIQUIDS FROM COAL-DERIVED GASES. QUARTERLY TECHNICAL PROGRESS REPORT, MARCH 19, 1981-JUNE 18, 1981

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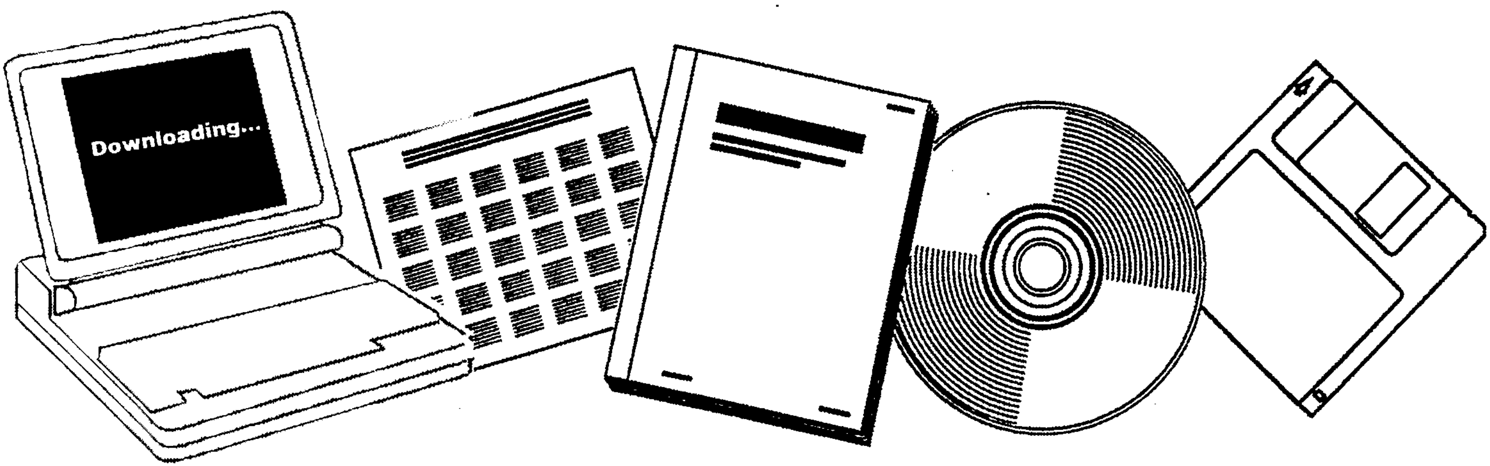

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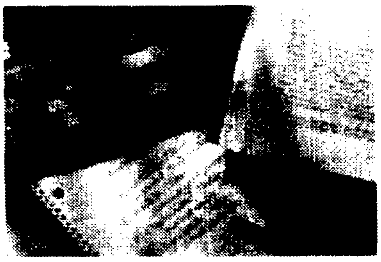

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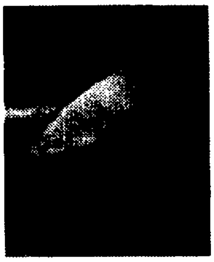

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INVESTIGATION OF SULFUR-TOLERANT CATALYSTS FOR SELECTIVE SYNTHESIS OF HYDROCARBON LIQUIDS FROM COAL-DERIVED GASES

Quarterly Technical Progress Report
For Period March 19, 1981 to June 18, 1981

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Provo, Utah 84602

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PREPARED FOR THE UNITED STATES
DEPARTMENT OF ENERGY

Under Contract No. DE-AC01-70ET14809

FOREWORD

This report summarizes technical progress during the seventh quarter (March 19, 1981 to June 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: Richard M. Bowman, Duane M. Davis and Jeffery L. Rankin. Mr. Rankin and Dr. Bartholomew were the principal authors. Laurie A. Witt provided typing services.

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ABSTRACT

During the seventh quarter, preparation of the proposed boride-promoted catalysts was completed. An aqueous solution technique was found to improve the preparation of the supported metal boride catalysts. Characterization of 3 and 15% cobalt catalysts by O_2 titration and H_2 and CO chemisorptions showed dispersions to be near 7.3%. Reduction was optimum after 36 hours at 623 K.

Activity/selectivity measurements showed Co/SiO_2 catalysts to be more active by an order of magnitude than corresponding Fe/SiO_2 catalysts in Fischer-Tropsch synthesis. The unsupported cobalt boride was found to be less active, though it produced a higher molecular weight product than similar silica-supported cobalt catalysts.

H_2S deactivation equipment construction and calibration has been completed and preliminary tests performed.

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 (unpromoted 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 presented in Figure 1 and accomplishments during the past quarter are summarized below. Figure 1 shows all Tasks to be on schedule except thermal gravimetric analysis experiments now scheduled for the next quarter.

Results from the past quarter are best summarized according to task:

Task 1:

Preparation of the four proposed boride-promoted catalysts has been completed. H_2, CO and CO_2 chemisorptions have been performed on samples of Co-S-101, Co-S-102, and CoB-102. O_2 titration of cobalt catalysts reduced 36 hours in flowing H_2 at 625 K provided information to calculate extents of reduction and metal dispersions.

Task 2:

Reactor tests of Co-S-101 and CoB-102 were completed. Product distributions and turnover numbers are reported, showing Co/SiO_2 to be more active than Fe/SiO_2 catalysts at atmospheric pressure.

Task 3:

Preliminary experiments have demonstrated that the completed reactor system and product analysis techniques are adequate. Reactant CO and H_2S interact in the feed to produce some COS impurities.

Misc.

The BYU Catalysis Laboratory entertained several visitors including Drs. Anthony Perotta and Richard Pannell of Gulf Research, Prof. Russell Collins of the University of Texas, and Professor Jaques Coenen of the Catholic University, Netherlands. Dr. Calvin Bartholomew presented seminars at the University of Utah and at a GRI sponsored conference. Mr. Jeffery Rankin attended the DOE-sponsored Conference on Indirect Liquifaction of Coal and presented a paper summarizing work in this contract.

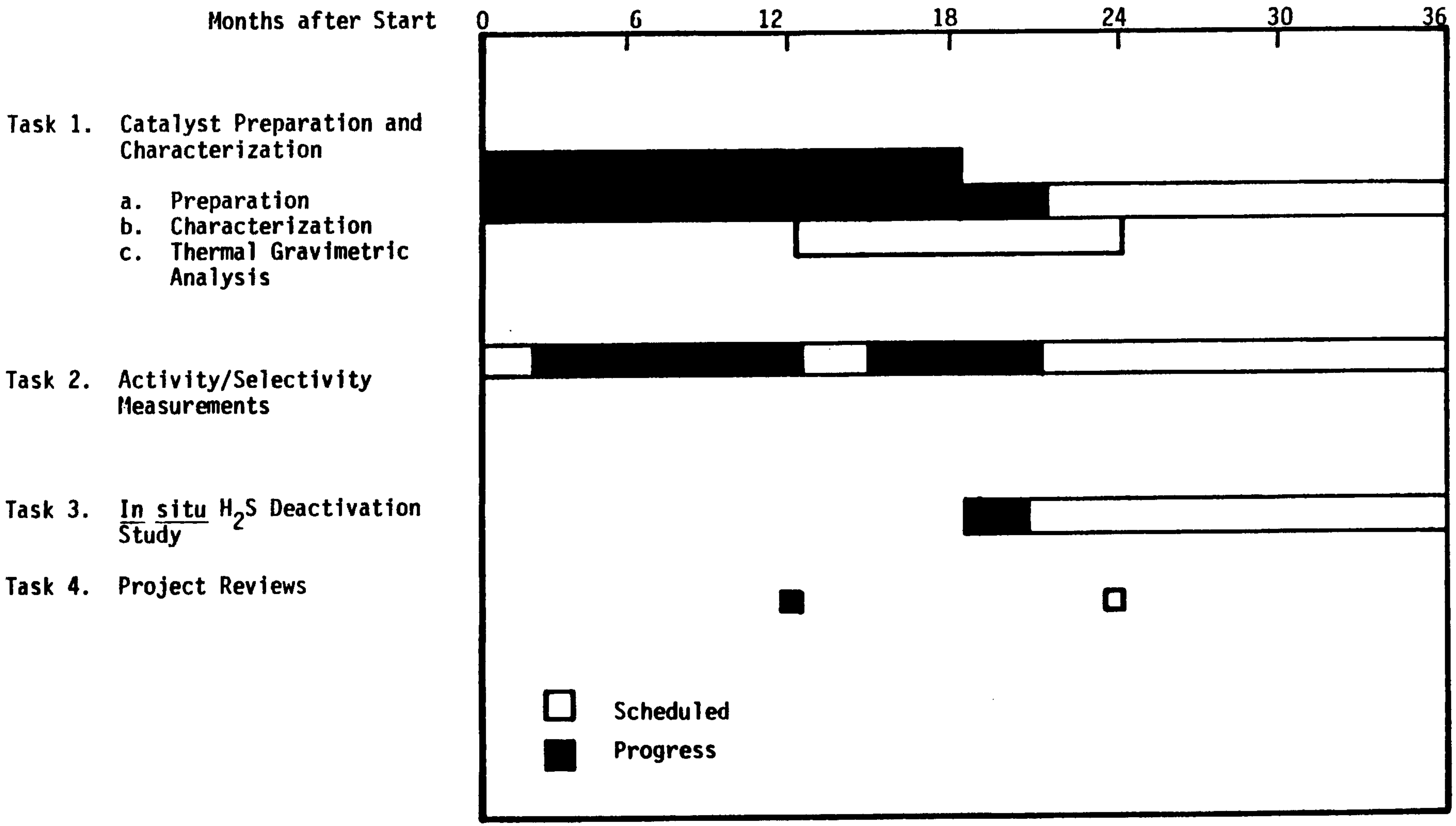

Figure 1. Schedule of Proposed Research Activities and Progress.

III. DETAILED DESCRIPTION OF TECHNICAL PROGRESS

A. Task 1: Catalyst Preparation and Characterization

1. Catalyst Preparation

Preparation of the boron-promoted catalysts has continued with initial samples of all of the proposed catalysts having been completed. Some minor changes in the previously-reported preparation procedures have resulted in a more rapid preparation and pure product. Rather than using a series of decanting, mixing, and settling steps, the catalyst is now filtered using a vacuum filter apparatus. This has cut preparation time from weeks to days. As a result there is less problem with exposure of the catalyst to oxygen.

Problems that were encountered in the reduction procedure with the supported catalysts were also solved this quarter. The rate of reaction between the metal nitrate and the sodium borhydride depends upon the concentration of BH_4^- in solution. In the alcohol solution $NaBH_4$ is less soluble than is the nitrate salt. As a result, in earlier preparations a significant amount of the metal nitrate dissolved before the BH_4^- could reduce it. The resulting product consisted of some metal boride on the support and a separate phase of unsupported metal boride. In order to correct this problem, the supported metal boride was prepared in an aqueous solution of sodium borohydride ($NaBH_4$ is much more soluble in water). The amount of sodium borohydride was increased to six times the stoichiometric requirement to compensate for the reaction between sodium borohydride and water. This preparation yielded somewhat larger particle sizes, but the metal boride appeared to be attached to the surface of the support.

2. Catalyst Characterization

During the past quarter, samples of Co-S-101 and Co-S-102 were reduced 36 hours at 625 K in flowing H_2. Following reduction, H_2, CO, and CO_2 chemisorptions and O_2 uptakes were measured yielding the results listed in Table 3. Also included in Table 3 are data for iron catalysts of similar loading. Suprisingly, the lower loading 3% cobalt catalyst CO-S-101 appeared to be more easily reduced than the 15% Co-S-102. The result will be rechecked. The 3% Co catalyst also adsorbed an unexpectedly larger amount of CO (CO/H = 1) than the 15% Co or iron catalysts. Also, CO_2 adsorbed more readily on the 15% cobalt catalyst than on the iron catalyst of similar loading. Since the 3% Co catalyst was apparently reduced to a greater extent than 15% Co, dispersions of these two catalyst were both the same, i.e. 7.3%, taking into account the unreduced metal fraction. However, the CO/H ratios for 3 and 15% Co were significantly different (0.4 and 1.0) suggesting, a support effect, i.e. an effect of metal loading and state of reduction on CO adsorption.

H_2 and CO uptakes for the cobalt boride catalyst were comparable with those of Co/SiO_2 and much larger than those for the supported Fe boride previously examined. In other words the unsupported cobalt boride is quite well dispersed.

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] (μmoles/g)	CO Uptake[b] (μmoles/g)	CO_2 Uptake[c] (μmoles/g)	O_2 Uptake[d] (μmoles/g)	%[e] Reduction
Fe-S-102[f]	15	20.19	3.52	--	--	--
Fe-S-102	15	17.10	24.80	1.16	1622	80.5
Fe-S-103	3	3.10	4.82	--	50.16	12.5
FeK-S-100[g]	15	9.11	4.94	6.56	856	42.5
FeB-S-101[h]	10	6.37	--	--	--	--
Co-S-101	3	13.24	24.80	--	242	71.2
Co-S-102	15	35.95	31.93	3.79	656	38.6
CoB-102[h]	10	47.5	32.6	--	--	--

---

[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

3. Future Plans

The next quarter plans include continuation of H_2, CO, and CO_2 chemisorption studies on the iron and cobalt catalysts including the newly prepared borides. Also planned are thermal gravimetric analysis (TGA) experiments on the supported iron catalysts. These should provide valuable information on carbide formation and adsorption stoichiometries

The preparation and characterization of unsupported iron catalysts is also planned.

B. Task 2: Activity/Selectivity Measurements

1. Chromatographic Analysis

At the time of writing, a new capillary column apparatus for upgrading the Hewlett-Packard gas chromatograph was received. Installation and operational shake-down are progressing well. This new column is expected to provide more accurate analysis of hydrocarbons, oxygenates, olefins and paraffins during reaction tests.

2. Experimental Measurements

Activity/selectivity tests of Co-S-101, a 3% cobalt/silica catalyst, and CoB-103 an unsupported cobalt boride catalyst were performed. The resultant turnover numbers for CO conversion and product analyses are summarized in Tables 4 and 5 together with previously obtained data on iron catalysts. 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 2 and Table 5. Our results to date show that without exception cobalt catalysts produce higher molecular weight products than iron catalyst of similar loading (Table 5). Our work also shows 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).

3. Future Plans

Activity/selectivity measurements will be continued in the next quarter on the recently prepared boride-promoted catalysts, and several iron and cobalt catalysts prepared but yet to be reactor tested at atmospheric pressure. Calibration and development of an operational technique for the new capillary analysis will be completed as rapidly as possible to avoid delay in reactor testing of catalyst samples.

C. Task 3: In Situ H_2S Deactivation Study

Several trial runs were made to facilitate set up and modifications of an existing reactor system for *in situ* H_2S studies (The data obtained were not considered quantitative enough to report but helped us to establish qualitative behavior and good procedures for obtaining data in the future.) The resulting reactor flow system is shown in Figure 3. It is essentially the same as the one in use for activity/selectivity

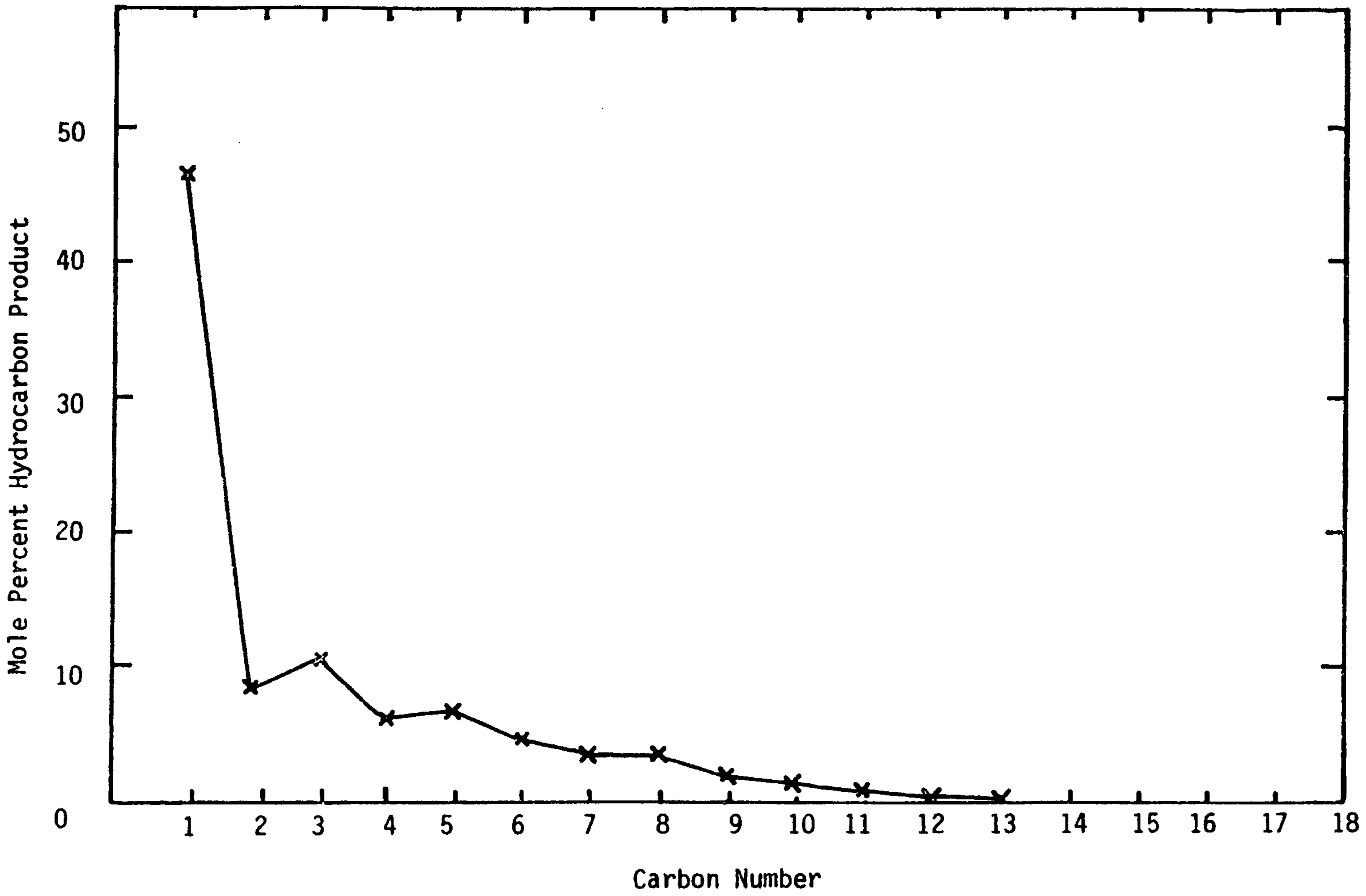

Figure 2. Product Distribution for CoB-102 At 473 K, $H_2/CO=2$.

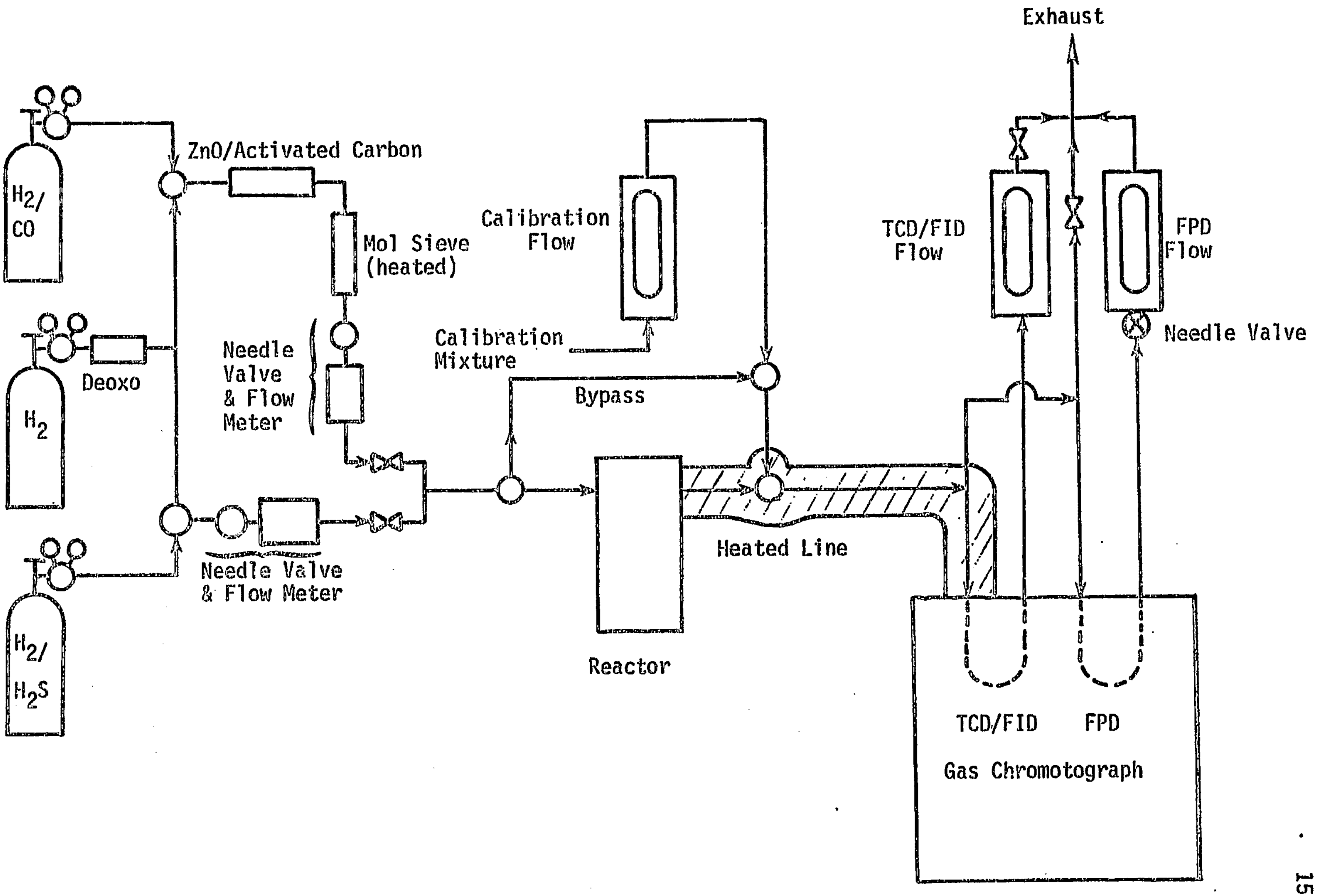

Figure 3. Fischer Tropsch Sulfur Deactivation System

TABLE 4

CO Turnover Numbers for Supported Iron and Cobalt Catalysts

Catalyst Code	H_2/CO Ratio	Temperature (K)	Turnover Number ($N_{CO} \times 10^3$)	Activation Energy (kJ/gmole)
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	
	2	473	1.7	151.6

TABLE 5

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

Catalyst Code	Selectivity (mole fraction)					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	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

---

[a] $H_2/CO = 2$

[b] $H_2/CO = 1$

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 4. 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 added 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 5 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.

Quantitative deactivation tests are planned 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 2-5 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.

D. Miscellaneous Accomplishments and Technical Communication

During the past quarter we enjoyed visits from Dr. Anthony Perotta, Gulf Research, who discussed his interesting work on coking of hydrotreating catalysts; Dr. Richard Pannell, Gulf Research, who discussed his recent work on supported cobalt catalysts in Fischer-Tropsch synthesis; Professor Russell Collins, University of Texas (Austin), who delivered our new Moessbauer spectrometer, a totally computerized system; and Professor Jaques Coenen of the Catholic University (Netherlands) who spoke to us regarding the preparation and characterization of nickel catalysts. Professor Coenen has been working in areas of nickel catalysis closely related to ours and recently completed a study of the kinetics of methanation of CO over nickel at high temperature similar to ours performed in the previous DOE contract.

On May 19th Dr. Bartholomew visited the Department of Chemistry at the University of Utah and presented a seminar on the topic of "CO Hydrogenation on Metal Boride Catalysts;" he also presented a paper on

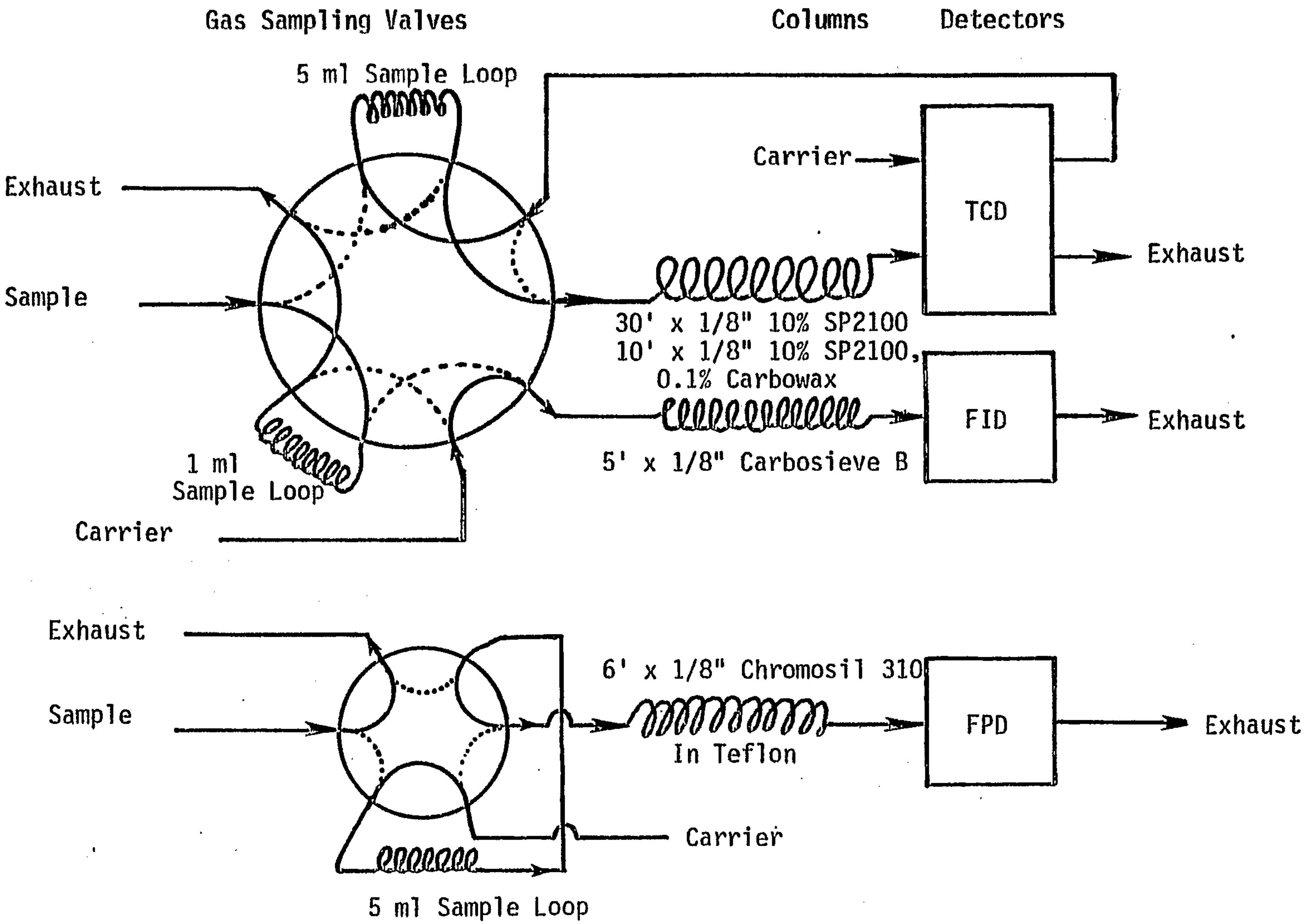

Figure 4. Gas Chromatograph Schematic for H_2S Deactivation Studies

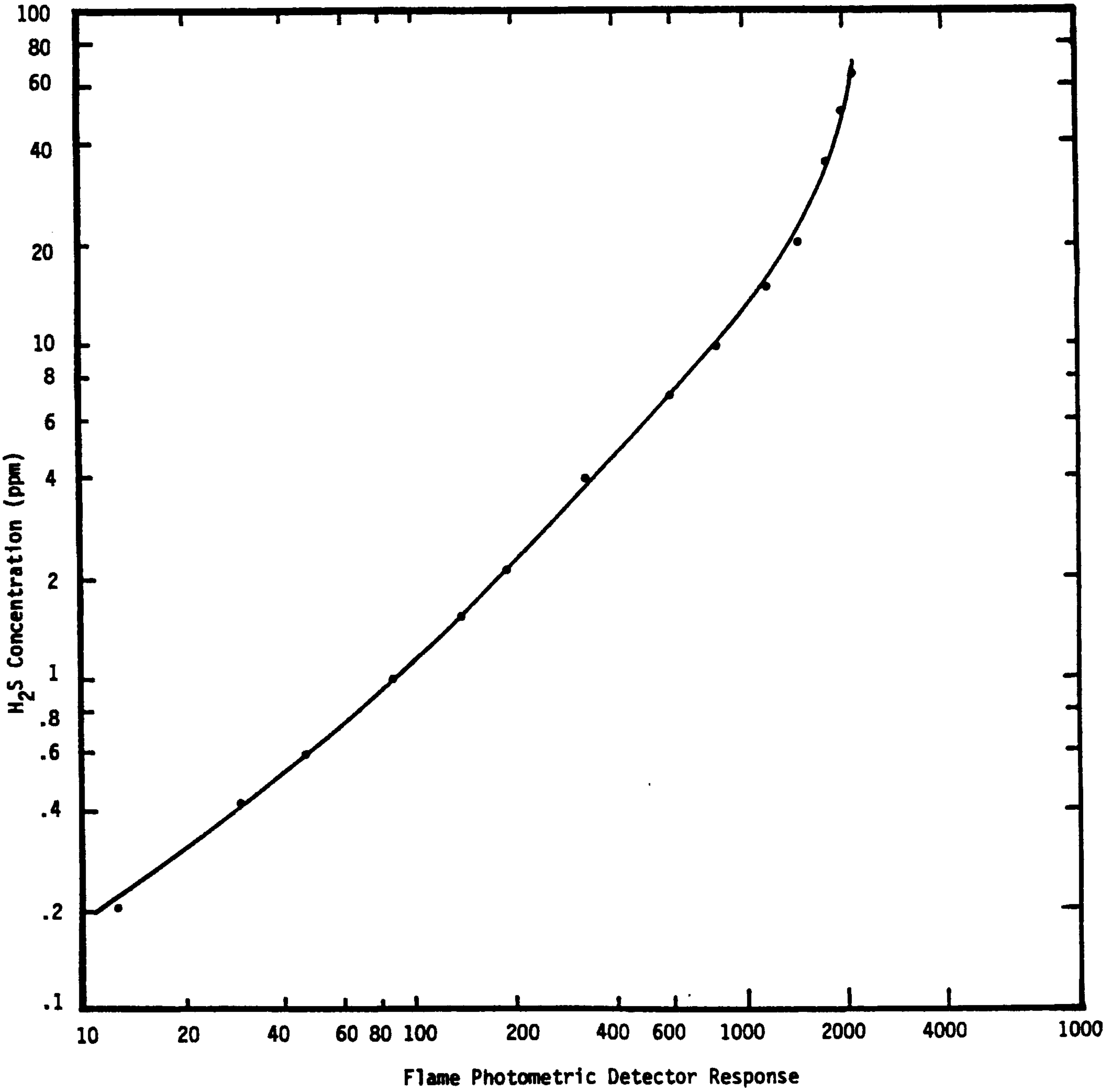

Figure 5. Flame Photometric Detector Calibration Curve

"Sulfur Poisoning of Nickel" at the Annual GRI Contractors Meeting on Heterogeneous Catalysis held in Chicago June 15-16. Mr. Jeffery Rankin attended the DOE sponsored Conference on Indirect Liquification of Coal held May 20-21 in Pittsburgh and presented a paper summarizing work performed in this contract.

IV. CONCLUSIONS

1. A 36 hour reduction in hydrogen at 625 K for cobalt/silica catalysts is adequate to reach a near maximum state of reduction. Percent reductions range from 40 to 70% in the 3% and 15% loading catalysts. Dispersions of cobalt/silica catalysts are 7.3% after being reduced for 36 hours in flowing hydrogen.

2. 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 less CH_4. Its interesting properties merit further investigation.

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.

4. Preparation of supported boride catalysts in aqueous solution has been shown more effective in bonding the metal to the support than alcohol preparations.

5. 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.

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