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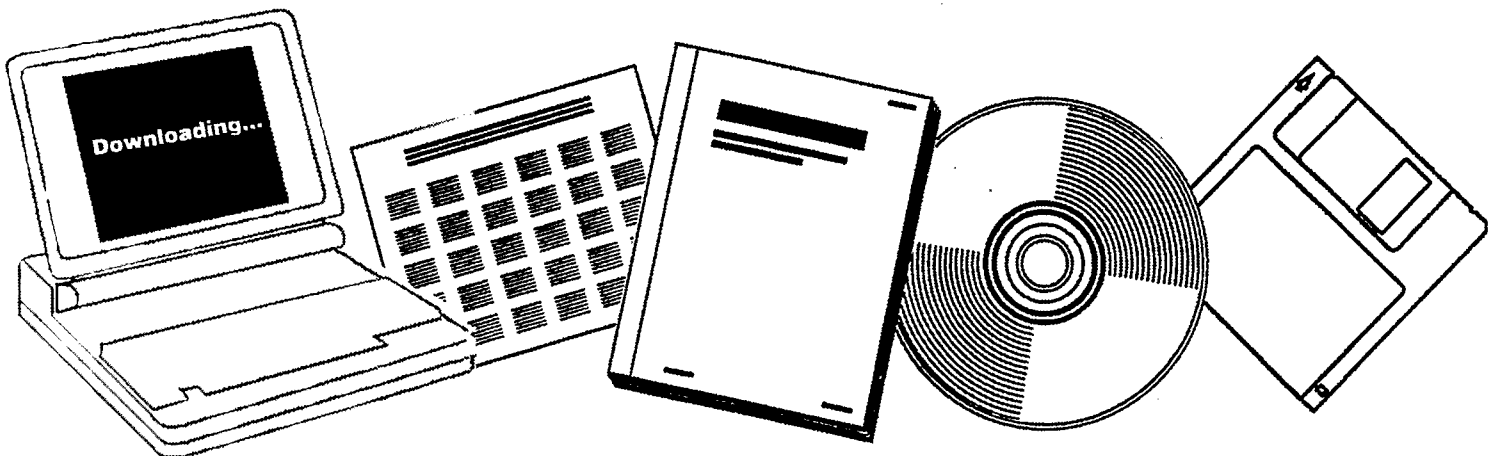
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**INVESTIGATION OF SULFUR-TOLERANT CATALYSTS
FOR SELECTIVE SYNTHESIS OF HYDROCARBON
LIQUIDS FROM COAL-DERIVED GASES. QUARTERLY
TECHNICAL PROGRESS REPORT, SEPTEMBER
18-DECEMBER 18, 1979**

BRIGHAM YOUNG UNIV.
PROVO, UT

10 JAN 1980



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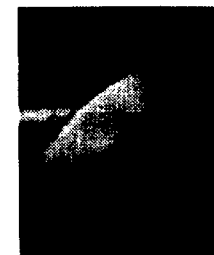
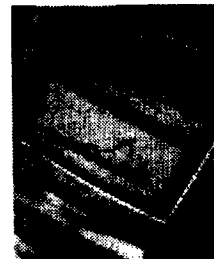
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INVESTIGATION OF SULFUR-TOLERANT CATALYSTS
FOR SELECTIVE SYNTHESIS OF HYDROCARBON
LIQUIDS FROM COAL-DERIVED GASES

Quarterly Technical Progress Report
For Period September 18, 1979 to December 18, 1979

Calvin H. Bartholomew
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Provo, Utah 84602

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PREPARED FOR THE UNITED STATES
DEPARTMENT OF ENERGY

Under Contract No. DE-AC01-79ET14809

FOREWORD

This report summarizes technical progress during the first quarter (September 19, 1979 to December 18, 1979) 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 Arthur H. Uken. Dr. Bartholomew was the principal author. Karen Barrett and Oscar Delgado provided typing and drafting services.

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ABSTRACT

During the first quarter 3% Co/SiO₂, 3% Fe/SiO₂ and 10% Co-B/Al₂O₃ catalysts were prepared and their surface areas were measured by H₂ adsorption. Plans were made for the design and construction of a high pressure laboratory microreactor system. The Principal Investigator attended the University Liquefaction Conference and Oblad Symposium, visited PETC, and prepared and submitted 6 journal publications.

I. OBJECTIVES AND SCOPE

A. Background

Cobalt and iron catalysts find wide application in the oil, gas and chemical industries, particularly in ammonia synthesis, hydro-treating 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. 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 C₂-C₅ hydrocarbons or C₆-C₁₂ 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 H₂S.

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/Al₂O₃, 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-Al₂O₃, (Conoco) with aqueous solutions of cobalt and iron nitrates. Co/SiO₂ and Fe/SiO₂ will be prepared by a modification of a new developed controlled-pH precipitation technique which results in very high nickel dispersions in Ni/SiO₂ catalysts. Fe/MgO catalysts will be prepared by a new coprecipitation technique developed at Haldor Topsoe which enables very high iron dispersions to be obtained. The Al₂O₃ and SiO₂ 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 KNO₃ or Zn(NO₃)₂ in such proportions as to obtain 0.5% K₂O and 15% ZnO in the final product.

Table 1
Catalyst Preparation Plans^a (Task 1)

<u>Metal-Support Combination</u>	<u>Unpromoted</u>	<u>Promoted</u>		<u>Additive Pretreatments</u>			<u>No. Catalysts</u>
		<u>K₂O</u>	<u>ZnO</u>	<u>S</u>	<u>N</u>	<u>B</u>	
Fe (unsupported)	x	x		x(2) ^b	x	x	6
Co (unsupported)	x			x		x	3
Co/SiO ₂	x	x				x	3
Fe/SiO ₂	x	x	x	x(3) ^b	x	x	8
Fe/MgO	x						1
Fe/Al ₂ O ₃	x(2) ^c						<u>2</u>
						Total	23

^a15 wt.% metal unless otherwise noted; 0.5 wt.% K₂O, 15% ZnO

^bPromoted and unpromoted catalysts will be sulfided.

^c3 and 15 wt.% metal loadings.

Catalysts will be sulfided by passing a gaseous mixture of 3% H₂S/H₂ 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 H₂ 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. 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 H₂ 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 carried out 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 H₂ have also been included. These experiments are affected by surface additives. Gravimetric Analysis will also be used to determine the kinetics of carburizing 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), H₂/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 in the absence of diffusional influences may be obtained. 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 taken intermittently. From previous investigations it is clear that in the case of small samples 6-18 hours reaction in the synthesis

Table 2
Experimental Plan

<u>Task</u>	<u>Purpose of Study</u>	<u>Catalysts</u>
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 ₂ O ₃ , Fe/MgO, Co and Co/SiO ₂
b. H ₂ and CO Adsorption Measurements on K ₂ O 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 ₂ O 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 ₂ O ₃ , Fe/ZSM-5, Fe/Silicalite, Co, Co/SiO ₂
	Effects of metal	Co, Fe
	Effects of metal loading	3 and 15% Fe/Al ₂ O ₃
	Effects of Promoter	K ₂ O promoted Fe, Fe/SiO ₂ , Co/SiO ₂ ; ZnO promoted Fe/SiO ₂
	Effects of Sulfiding	Fe, Fe/SiO ₂ (unpromoted and K ₂ O 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 ₂ S Deactivation	Effects of support	Fe/SiO ₂ , Fe/MgO, Fe/Al ₂ O ₃
	Effects of metal	Co, Fe, Co/SiO ₂ and Fe/SiO ₂
	Effects of metal loading	3 and 15% Fe/Al ₂ O ₃
	Effects of Promoter	K ₂ O promoted Fe and Fe/SiO ₂ ; ZnO promoted Fe/SiO ₂ (sulfided and unsulfided)
	Effects of Sulfiding	Fe, Fe/SiO ₂ (unpromoted and K ₂ O 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

^aFe/ZSM-5 and Fe/Silicalite samples have been obtained from the Pittsburgh Energy Technology Center.

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 higher pressure. It is also possible that some of the catalysts 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 H₂S 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), H₂/CO = 2 and space velocities of 5,000 to 30,000 hr⁻¹ with 10 ppm H₂S in the reactant mixture. The analysis of gaseous hydrocarbons will be made intermittently 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/SiO₂ and Co/SiO₂ 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 that Task 1 accomplishments are on schedule while Task 2 is behind schedule since much of our effort was devoted to redesign of our high pressure reactor system.

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

Task 1. Three catalysts, 3% Co/SiO₂, 3% Fe/SiO₂ and 10% Co-B/Al₂O₃ were prepared and characterized by H₂ adsorption.

Task 2. Plans were made for design and construction of a high pressure laboratory microreactor system. Several reactor designs were considered and a 0.65 cm tubular reactor was constructed. The design and construction of wax and liquid traps is in progress.

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

Misc. Two graduate students were assigned to the project. A survey was made of Fischer-Tropsch literature and previous experimental work. The Principal Investigator and students attended the University Coal Liquefaction Conference and presented a talk at the Oblad Symposium; the PI also visited PETC and presented a seminar. He also prepared and submitted 6 different publications.

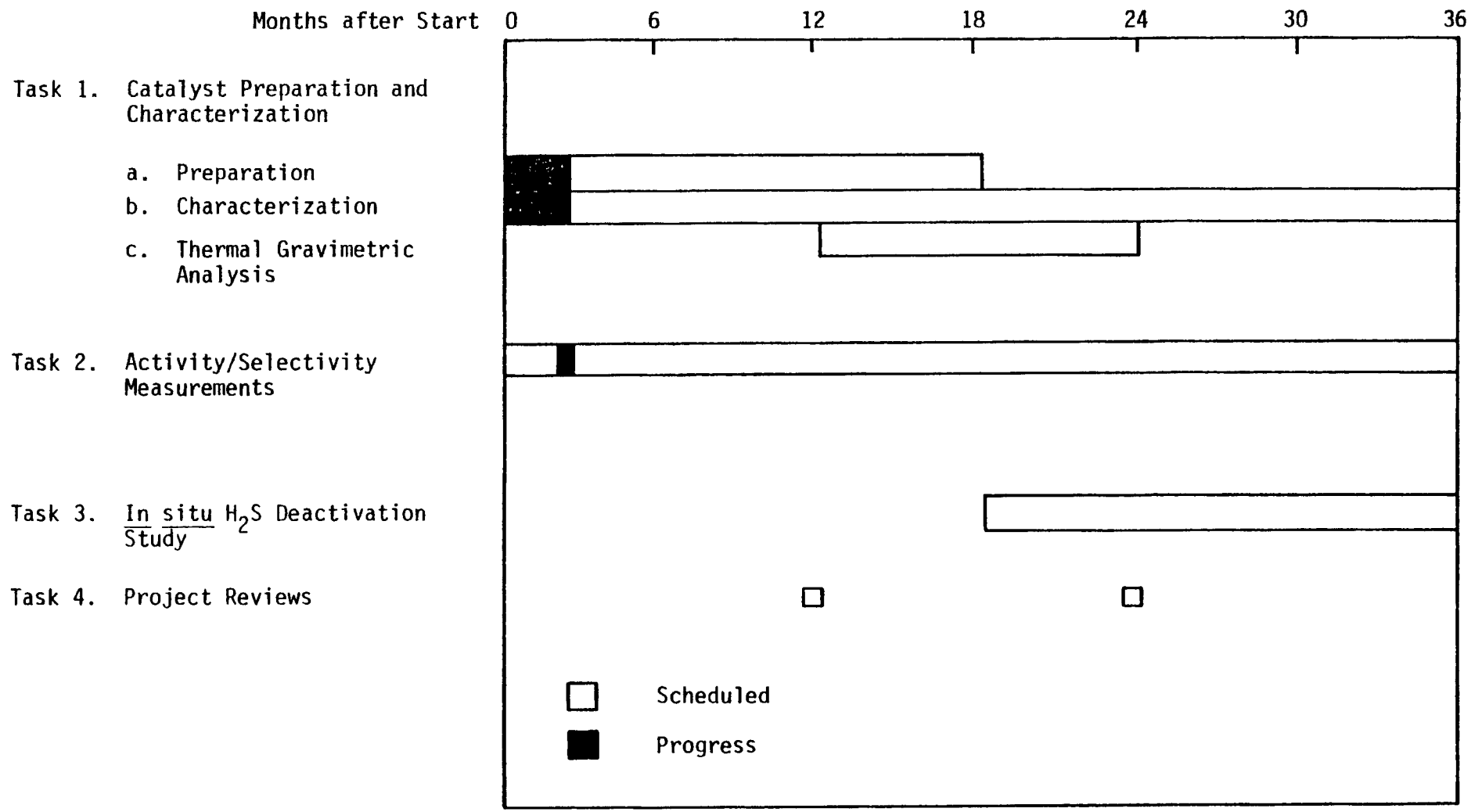


Figure 1. Schedule of Proposed Research Activities and Progress.

III. DETAILED DESCRIPTION OF TECHNICAL PROGRESS

A. Task 1: Catalyst Preparation and Characterization

1. Catalyst Preparation

Three catalysts were prepared: 3% Co/SiO₂, 3% Fe/SiO₂, and a 10% cobalt boride on alumina designated respectively as Co-S-101, Fe-S-100, and CoB-A-101. These catalysts were prepared in the following manner:

Analytically pure Co(NO₃)₂ · 6H₂O and Fe(NO₃)₃ · 9H₂O salts and commercial Cab-O-Sil silica were used to prepare the 3% silica-supported cobalt and iron catalysts. Samples were prepared by simple impregnation 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 dried samples were then bulk reduced in flowing hydrogen at a space velocity of 2000 h⁻¹. The temperature was raised during reduction at a rate of 1.5-2.0 K/min until 725 K was attained, then held for 12 hours. The reduced catalysts were next passivated with 1% air in nitrogen and crushed to a fine powder for use.

The cobalt boride on alumina catalyst (CoB-A-101) was prepared under an N₂ blanket in a sealed reaction vessel to avoid the formation of boron oxide, which cannot be reduced in flowing H₂ even at 675 K. Enough alumina was used so that if all the cobalt adhered to the support 18 wt.% 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 at 873 K and cobalt nitrate in vacuo at about 350 K to remove most of the water of hydration, the cobalt nitrate was added to a slurry of alumina and dried acetone. Then the solution was completely dried, and added to a reaction vessel with dried isopropanol as the reaction medium. NaBH₄ was added in a ratio of 4 moles NaBH₄ to 1 mole of cobalt nitrate and the mixture was allowed to react at 298 K 4 days. The resulting fine particles were washed several times with methanol over a period of 20 days. The catalyst was 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 boride catalyst into the Pyrex reactor in inert atmosphere. Approximately 0.5 g of CoB-A-101 was dried to paste in a glove box that was thoroughly purged with N₂ and then loaded into the reactor in the glove box after which the reactor was sealed until the H₂ 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 hydrogen for 16 hours at 725 K at a space velocity of 2000 h⁻¹.

2. Aquisition of Zeolite Supported Iron Catalysts

During his visit to the Pittsburgh Energy Technology Center, the principal investigator, Dr. Bartholomew, obtained two samples of novel zeolite catalysts for testing in our laboratory. These include an 8.3% Fe on silicalite coded Fe-SIL-LS-8-6-14, and a 14.7% Fe on ZSM-5 zeolite coded Fe-ZSM-5-LS-16-17-NH₄⁺-7-6-10-17-79. Surface area measurements and reactor testing of these zeolites are planned during the coming quarter.

3. Catalyst Characterization

Metal surface areas were measured for all three of the freshly prepared catalysts 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 adsorption uptakes were measured as a function of pressure and the isotherm was extrapolated to obtain the adsorption at zero pressure. The results are listed in Table 3. The uptakes for cobalt and iron are in the range one might expect for 3 wt.% catalysts. The value for the cobalt boride is unexpectedly large for an alumina-supported cobalt catalyst, suggesting that the boron promoter enhances the dispersion of cobalt.

CO chemisorption measurements were in progress for these samples during the time of writing of this report.

4. Future Plans

Plans for future work in this area include the preparation and characterization by H₂ and CO adsorption and chemical analysis of unsupported Fe, alumina supported Fe, and K₂O and ZnO promoted silica supported Fe catalysts for use in comparative reactor testing. These will provide a wide range of iron catalyst compositions to give insight into promoter and support effects on product yields.

The preparation and characterization of unsupported and silica-supported cobalt catalysts and the characterization of zeolite-supported iron catalysts is also planned for the next quarter.

B. Task 2: Activity Selectivity Measurements

1. Equipment Construction

During the past quarter several reactor system designs were examined and considered. It was decided to construct a 0.25 inch (0.64 cm) diameter stainless steel tubular reactor designed to withstand pressures up to 25 atm. The design incorporated a metal ring to facilitate heat transfer from the tube furnace presently in operation in the laboratory. A diagram of the reactor is shown in Figure 2. Two such reactors were constructed in the University's machine shop.

Table 3

Hydrogen Chemisorption Measurements (298 K)
for Supported Cobalt and Iron Catalysts

<u>Catalyst</u>	<u>H₂ Uptake (μmoles/g)</u>
Co-S-101	17.1
Fe-S-100	5.0
Co-B-A-101	160 ^a

^aThis value is approximate since the catalyst weight was only estimated. It will be determined precisely after a series of tests has been completed.

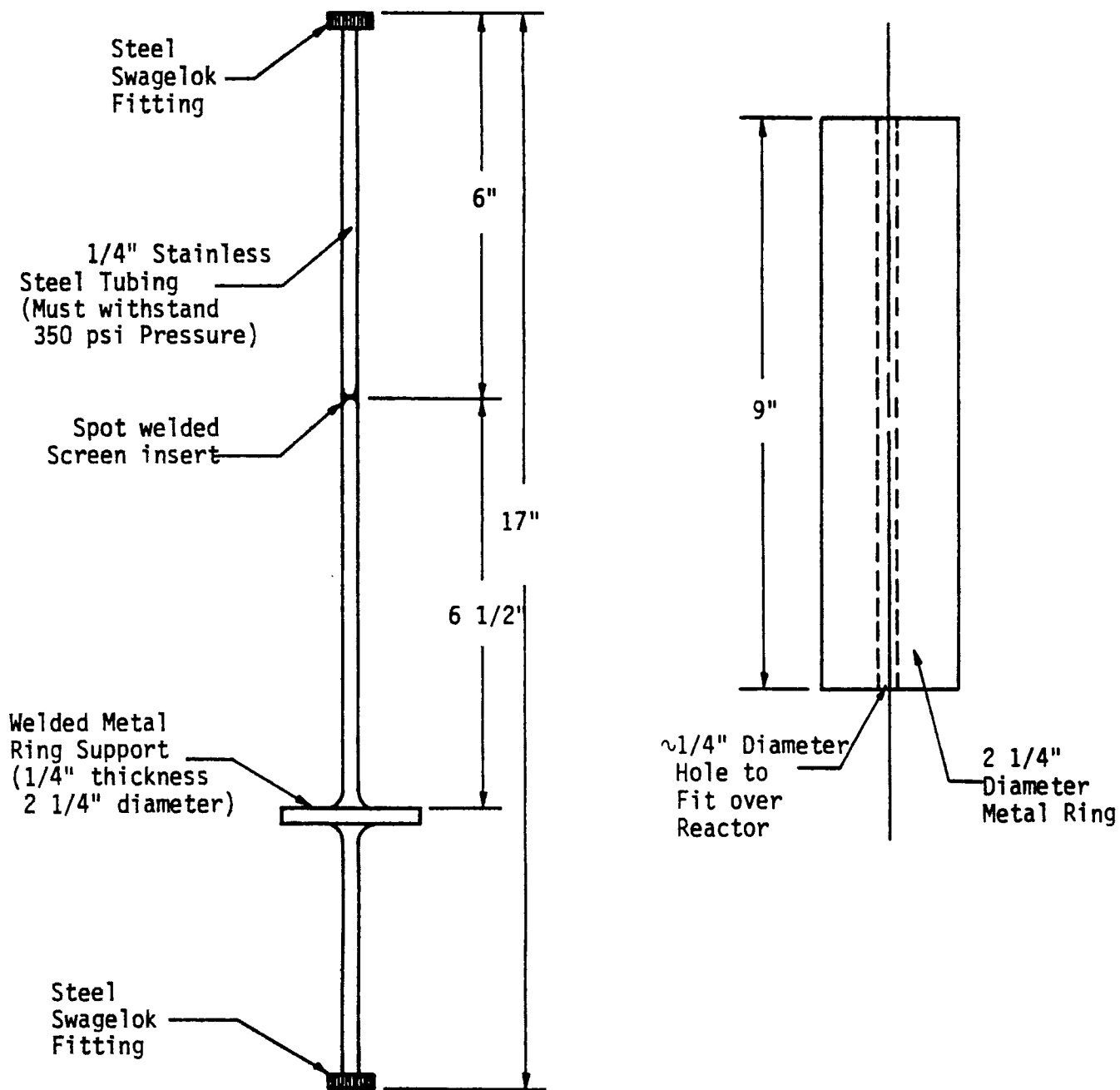


Figure 2. High Pressure "FT" Reactor.

Plans are presently being finalized for the construction of the necessary reactor system and accessories, including traps designed to capture solid and liquid products for sampling and analysis.

2. Experimental Measurements

None were carried out during the first quarter, although measurements were in progress for CoB-A-101 at the time of writing.

3. Future Plans

During the coming quarter low pressure activity tests of unsupported and supported iron, cobalt and cobalt boride catalysts are planned. These tests will be run at $H_2/CO = 2$, 525 K, 1 atm and 1,000-5,000 h^{-1} in a Pyrex reactor cell. Analysis of products will be quantitative for CO , CH_4 and CO_2 . Hydrocarbons will be determined by difference; in other words, a detailed breakdown of the different hydrocarbons will not be made yet but will be made in later tests as we complete the construction of a reactor system dedicated for analysis of FT products.

C. Task 3: In Situ H_2S Deactivation Study

Experimental work on this task is not scheduled to begin for another 15 months (i.e. March 1981).

D. Miscellaneous Accomplishments and Technical Communication

During the first quarter the principal investigator formalized hiring arrangements and assignment of Mr. Jeffery L. Rankin and Glenn W. Davis to this project.

Mr. Rankin, a Ph.D. candidate, has been assigned the preparation, characterization and activity testing of iron (and a few cobalt) catalysts with the exception of the metal borides. Mr. Davis has been assigned to prepare, characterize and activity test cobalt and iron boride catalysts.

A substantial portion of the effort during this first quarter was devoted to reviewing the proposal, literature dealing with Fischer-Tropsch Synthesis, and formulating plans to begin the experimental work.

The principal investigator also attended several important conferences and meetings where he was able to obtain valuable insights and specifics through discussions with others doing Fischer-Tropsch research. For example, on September 6-7 he attended the DOE sponsored conference on University Coal Liquefaction held in Pittsburgh where he had the opportunity to meet Mr. Pennline and discuss the contract and proposed research. The PI and four graduate students, Erik Erikson, Edward Sughrue, Jeffery Rankin and Gordon Weatherbee, attended Advances in Catalysis I, a symposium held in honor of Professor Alex Oblad,

October 3-5 at Snowbird, Utah. Dr. Bartholomew presented a paper on "Surface Intermediates in Methanation of CO." The meeting was well organized and well attended by the most noted and productive researchers in catalysis. It was thought by most participants to be one of the finest dealing with catalysis in years.

On October 31, Dr. Bartholomew enjoyed a stimulating and productive visit with research personnel in the Process Sciences and Engineering Divisions at the Pittsburgh Energy Technology Center. He toured research facilities concerned mainly with testing of Fischer-Tropsch catalysts and presented a seminar on "Metal Boride Catalysts in CO Hydrogenation." He was also able to obtain ideas for microreactor design and zeolite supported iron catalysts for testing in our DOE sponsored study of FT catalysts.

On the following day, Dr. Bartholomew participated on an NSF proposal review panel in Washington, D.C.

During the past quarter, Dr. Bartholomew was engaged in several writing projects including the completion and submission of 6 different journal publications.

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 (3 wt.%) evidence relatively poor metal dispersion relative to 3% Ni/SiO₂ catalysts (3).

V. REFERENCES

1. A.H. Uken, "Methanation Catalysts: Activity and Sulfur Tolerance Studies of Borohydride-Reduced Catalysts," M.S. Thesis, Brigham Young University, December 1979.
2. A.H. Uken and C.H. Bartholomew, "Metal Boride Catalysts, I. Initial Activity and Conversion-Temperature Behavior of Unsupported Catalysts," Submitted to J. Catal., Dec. 14, 1979.
3. C.H. Bartholomew, Richard B. Pannell, and Jay L. Butler, "Support and Crystallite Size Effects in CO Hydrogenation on Nickel," Submitted to J. Catal., Dec. 13, 1979.

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