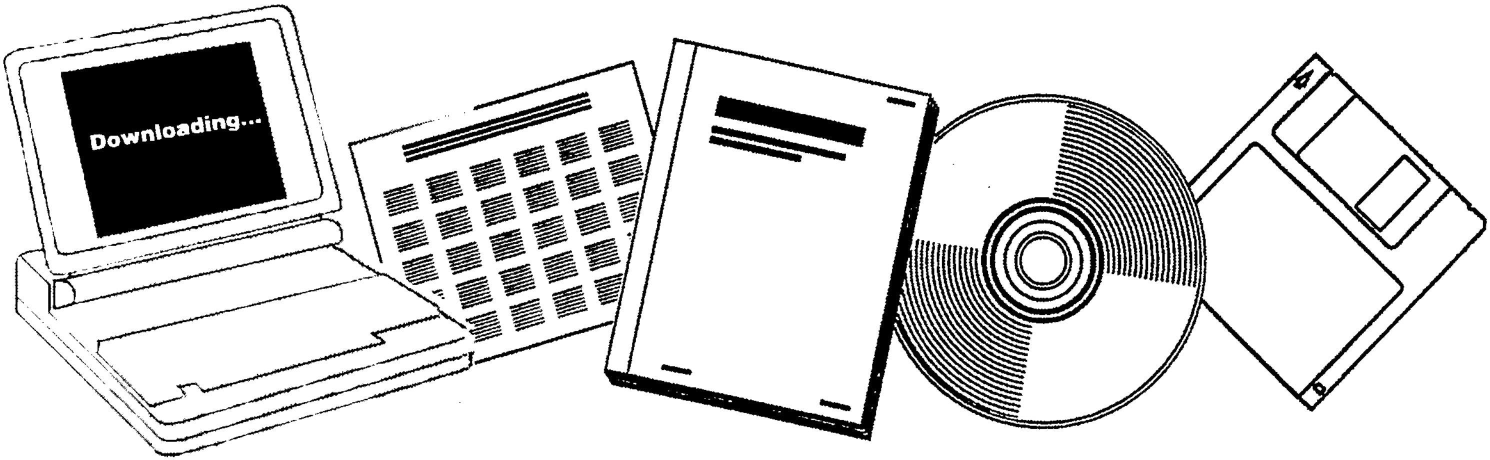
INVESTIGATION OF SULFUR-TOLERANT CATALYSTS FOR SELECTIVE SYNTHESIS OF HYDROCARBON LIQUIDS FROM COAL-DERIVED GASES. QUARTERLY TECHNICAL PROGRESS REPORT, MARCH 19-JUNE 18, 1980

BRIGHAM YOUNG UNIV.
PROVO, UT

10 JUL 1980



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Quarterly Technical Progress Report
For Period March 19, 1980 to June 18, 1980

Calvin H. Bartholomew
Brigham Young University
Provo, Utah 84602

Date Published -- July 10, 1980

PREPARED FOR THE UNITED STATES
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FOREWORD

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

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

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ABSTRACT

During the third quarter a 15% Fe-3% K_2O on SiO_2 catalyst, a 15% Co-3% K_2O on SiO catalyst and a 15% CoB/SiO_2 catalyst were prepared. H_2 and CO chemisorption uptakes were measured for the catalysts prepared to date. It was noted that calcining the iron catalysts in air before reduction in flowing H_2 aided in increasing metal dispersion. Liquid and wax traps for use in the reactor system were completed as were plans for chromatographic product analysis. The principal investigator presented seminars at the University of Delaware and at the University of California at Berkeley. He also attended the DOE-NPI Reviewers' Meeting, visited Catalytica Associates and worked as a visiting consultant for Union Oil. Two papers were published, six accepted, and another five submitted by the Catalysis Group.

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. 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 folowed 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. 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 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 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 carried out intermittently. From previous investigations it is clear that in the case of small samples 6-18 hours reaction in

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/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/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.

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 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 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 that Task 1 accomplishments are on schedule, while Task 2 is behind.

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

Task 1. 15% Fe/SiO_2, 15% $Fe/3\%\ K_2O/SiO_2$, 15% Co/SiO_2, 15% $Co/3\%\ K_2O/SiO_2$, and 15% CoB/SiO_2 catalysts were prepared during the last quarter. All catalysts prepared to date were characterized by H_2 and CO chemisorption.

Task 2. Plans for analysis of products by gas chromatography were finalized. Liquid and wax traps were constructed as designed in the previous quarter, and several components of the reactor system are on order.

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

Misc. Dr. Bartholomew presented seminars at the University of Delaware (Dept. of Chem. Eng.) and University of California (Lawrence Berkeley Laboratory, Materials and Molecular Research Division) and visited Catalytica Associates. He also participated in the DOE-NPI Reviewers' Meeting April 20-22. On May 15 he began work as a visiting consultant at Union Oil for the summer (will finish his work there August 15). He also returned to BYU for visits with research students on June 7-9. He plans two more visits (July 4-7 and 11-15) before his return to the University on August 26. Dr. Erek J. Erekson successfully completed requirements for his Ph.D. on May 12 and left soon thereafter for his new job at Gulf Research. The catalysis group published two papers, had six papers accepted, and submitted another five. Another dozen are in preparation. Several of these, including a review on sulfur poisoning, relate to this contract.

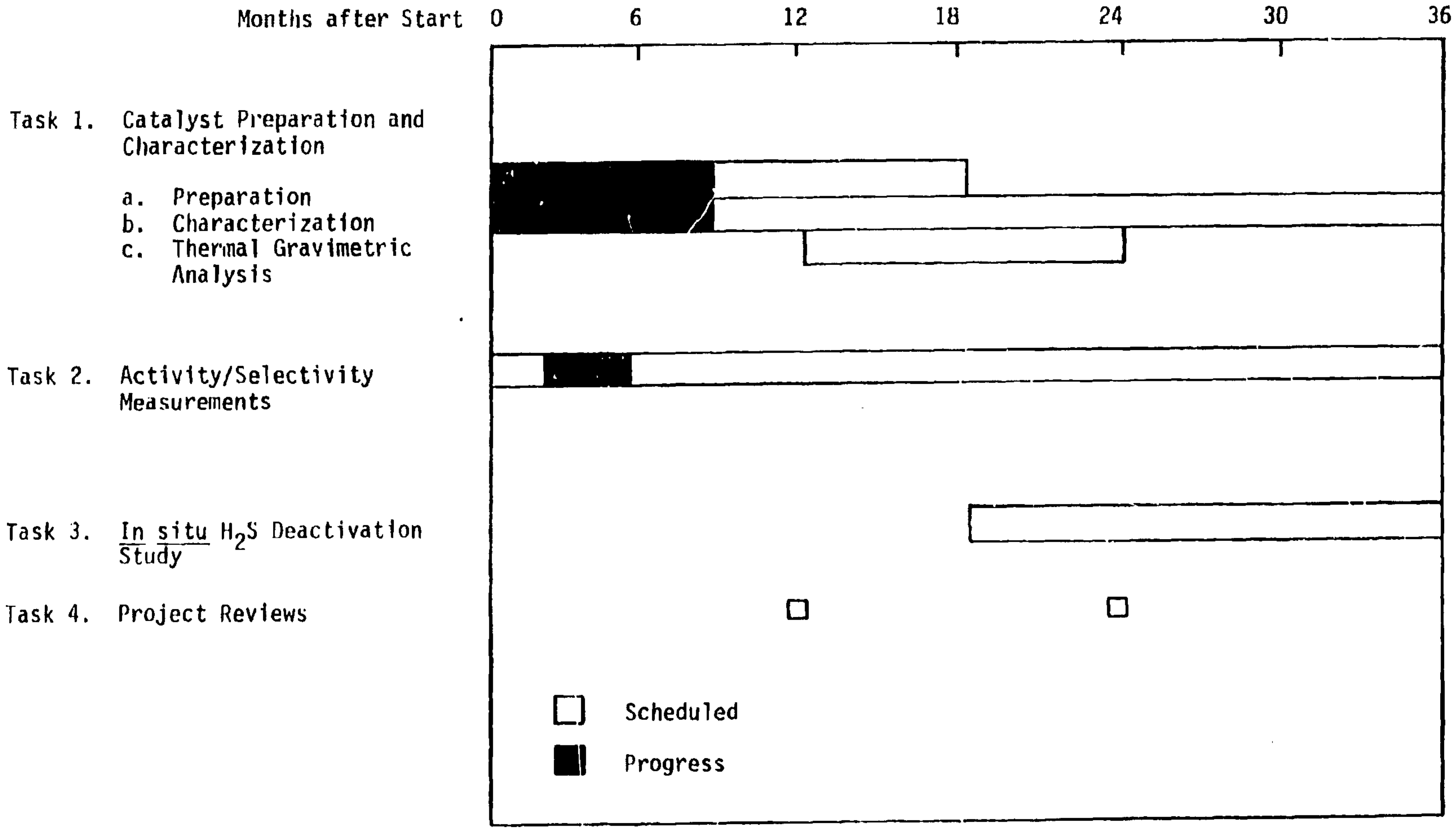

Figure 1. Schedule of Proposed Research Activities and Progress.

III. DETAILED DESCRIPTION OF TECHNICAL PROGRESS

A. Task 1: Catalyst Preparation and Characterization

1. Catalyst Preparation

In the past quarter, a 15% Co-B/SiO_2 catalyst coded CoB-S-101 was prepared. The method of preparation was developed earlier in this laboratory. Analytically pure $Co(NO_3)_2 \cdot 6H_2O$ was used in a 95% acetone-5% water solution to impregnate a commercial Cab-O-Sil silica support material. After impregnation, the catalyst was dried overnight in a vacuum oven at 450 K. After being crushed to a fine powder, the catalyst was placed in deaerated isopropanol under a blanket of nitrogen. $NaBH_4$ was added to the solution with 4 moles of $NaBH_4$ for every mole of impregnated cobalt. The solution was allowed to react four days with constant stirring, then the solution was washed six times with deaerated methanol over a period of 3 weeks. The washing consisted of adding the methanol, stirring, and then decanting the methanol. This method developed in our laboratory has produced well-dispersed metal boride catalysts with low amounts of residual sodium on the surface. The catalyst was then dried under a N_2 blanket and stored in an air-free container under nitrogen.

A large batch of 15% Fe/SiO_2 catalyst was prepared this quarter also. It was coded Fe-S-102. Approximately 10 g of Fe-S-102 was impregnated to incipient wetness with an aqueous solution of KNO_3 to reach a K atom to Fe atom ratio of 0.2. This composition is based on findings of Alexis T. Bell recently reported in which he found 20 K/100 Fe atomic ratio to maximize the effects of the K_2O promoter. Following impregnation, the catalysts were dried in an oven at 355-375 K for several hours. After being crushed to a fine powder the catalyst was ready for reduction in flowing H_2 at 725 K and a space velocity of 2000 hr^{-1} for 12 hours.

In a similar manner, a 15% Co/SiO_2 (Co-S-102) catalyst was prepared by impregnation on Cab-O-Sil support using an aqueous solution of $CO\ (NO_3)_2 \cdot 6H_2O$. Approximately 10 g of this batch was reimpregnated with KNO_3 in aqueous solution. As with the Fe catalysts, the nitrates were decomposed and the catalysts dried in an oven at 355-375 K for several hours. At present, reduction and characterization of those cobalt catalysts are underway.

2. Catalyst Characterization

Further chemisorption measurements were made this quarter using both H_2 and CO gases as adsorbates. These chemisorptions were performed at 298 K in a conventional high vacuum apparatus. Following reduction at 725 K, samples were evacuated to 10^{-6} torr at 675 K. Gas adsorption uptakes were measured as a function of pressure and the isotherm was extrapolated to obtain the adsorption at zero pressure.

In the case of CO chemisorption, a second titration of the gas followed to make correction for physisorption of CO on the catalyst. The difference between the two extrapolated uptakes was taken as the chemisorption uptake. Similar experiments on samples of pure silica support showed that both chemisorption and physisorption on the support are negligible.

Results of the chemisorption measurements are listed in Table 3. The results for Fe-S-102 and Fe-K-S-103 were taken after calcination of the catalyst in air at 675 K for 12 hrs and then reduction in flowing H_2 for 24 hrs at 725 K. It was felt that this might aid in increasing the Fe dispersion and active surface area of the catalyst. As can be seen, the effect of calcination was positive, though not as helpful as was hoped.

3. Future Plans

Samples of pure silicalite support are being obtained from Union Carbide Corporation so K_2O promoted Fe on silicalite may be prepared. The preparation of K_2O promoted ZSM-5 is planned, and possibly unpromoted Fe and Co in the next quarter. Also, cobalt boride and iron boride unsupported catalysts will be made with a procedure similar to that used to prepare Co-B-S-101. A sample of Co-B-S-101 will be sent to another laboratory for complete chemical analysis.

B. Task 2: Activity Selectivity Measurements

1. Equipment Construction

Liquid traps as designed and reported in the previous report were constructed in the last quarter. Components in the reactor system including flow controllers and chromatograph supplies are presently on order. Much detailed discussion and planning was conducted concerning the chromatographic analysis of products, with many fruitful ideas surfacing. It was found that the use of capillary columns would be convenient for analysis but difficult and expensive to install in our existing system. Thus, packed columns will be used for hydrocarbon and gas product analysis. These supplies are presently on order.

2. Experimental Measurements

The preliminary tests reported previously showed several problems which had to be solved before final tests were conducted. These problems are now being solved and reactor testing should resume in the next month. No experimental data was obtained the past quarter.

3. Future Plans

During the coming quarter, the reactor system should be made completely operational, including the analysis of all products. It is hoped that reactor tests at H_2/CO ratios of 2 and 1 may be conducted on all catalysts prepared to this point, and those to be prepared in the next quarter.

Table 3

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

Catalyst Code	H_2 Uptake (μmoles/g)	CO Uptake (μmoles/g)	CO/H[c]
Fe-S-100	2.1	2.7	0.64
Fe-S-101	3.5	4.7	0.67
Fe-S-102[d]	3.6	9.8	1.36
Fe-K-S-103[d]	11.2	6.2	0.28
Co-S-101	17.1	---	----
Co-B-A-101[a]	58.6	73.7	0.63
Co-B-A-101[b]	66.9	66.2	0.50

---

[a] Before long term reactor test.

[b] After long term reactor test.

[c] Ratio of CO moles to H atoms adsorbed.

[d] After calcination in air.

C. Task 3: In Situ H_2S Deactivation Study

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

D. Miscellaneous Accomplishments and Technical Communication

On April 10th the principal investigator, Dr. Bartholomew, visited the Department of Chemical Engineering at the University of Delaware and presented a seminar on "Metal Boride Methanation Catalysts." Besides touring facilities and visiting with other faculty members (including Bruce Gates and Glenn Schrader) he spent three days with Professors James Katzer and Pradeep Agrawal (Georgia Tech.) working on a literature review dealing with sulfur poisoning. Dr. Bartholomew was also invited by the Materials and Molecular Research Division of the Lawrence Berkeley Laboratory to present a seminar on April 16th dealing with "Metal-Support Interaactions in CO Hydrogenation on Nickel." During his visit he toured research facilities in the catalysis and surface science areas and met with several faculty members including Alex Bell, Earl Muetterties, Eugene Peterson, and Heinz Heinemann. Some of the work at Delaware and Berkeley dealing with CO/H_2 synthesis, metal-support interactions and poisoning is quite pertinent and complementary to the ongoing and planned work supported by this contract.

On April 15th Dr. Bartholomew visited Catalytica Associates, met with officers of the company including Ricardo Levy, Robert Garten, and Ralph Dalla Belta, and toured their facilities. That evening he appeared as a guest expert on the Art Finley Talk Show on KGO San Francisco (the leading radio station in the Bay Area) discussing and debating coal gasification and other energy topics.

The PI also participated in the DOE-NPI Reviewers' Meeting held April 20-22 in Pittsburgh where he assisted in the review of over 20 proposals dealing with coal and catalysis research.

On May 13th Dr. Erek J. Erekson completed requirements for his Ph.D. and left for his new job at Gulf Research. Dr. Erekson's dissertation deals with sulfur poisoning.

On May 15th Professor Bartholomew began work at the Union Oil Research Center in Brea, California as a visiting consultant. This summer job in catalysis research which extends through August 15th is part of his sabattical year plans. In his spare time he has kept in touch with his research students by phone, mail and occasional visit. For example, Dr. Bartholomew visited with members of the catalysis group and discussed their progress June 7-9 and plans two more visits on July 4-7 and 11-14. He will return to BYU on August 26 (following a weeks's vacation in California).

During the past quarter the catalysis group submitted five new papers for publication; another six were acccepted and two were published. The PI and students are also currently preparing another dozen papers and reviews for publication. At least half of these are very pertinent to the work planned in this contract.

IV. CONCLUSIONS

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

2. The CO/H adsorption ratios varied from 0.28 to 1.36 in the K promoted and unpromoted Fe catalysts. The very low value (0.28) is probably an effect of the K promoter.

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