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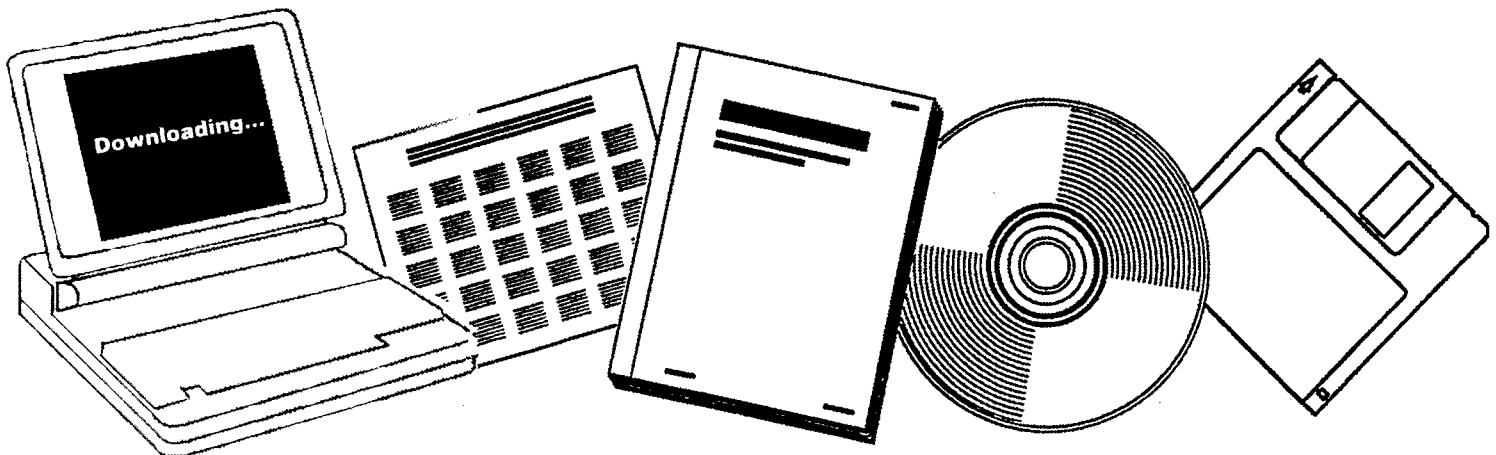
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INVESTIGATION OF SULFUR-TOLERANT CATALYSTS FOR SELECTIVE SYNTHESIS OF HYDROCARBON LIQUIDS FROM COAL-DERIVED GASES

BRIGHAM YOUNG UNIV.
PROVO, UT

30 APR 1982



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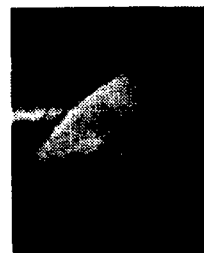
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INVESTIGATION OF SULFUR-TOLERANT CATALYSTS
FOR SELECTIVE SYNTHESIS OF HYDROCARBON
LIQUIDS FROM COAL-DERIVED GASES

Quarterly Technical Progress Report
For Period December 19, 1981 to March 18, 1982

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FOREWORD

This report summarizes technical progress during the tenth quarter (December 19, 1982 to March 18, 1982) 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 Witt provided typing services.

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ABSTRACT

During the tenth quarter samples of Fe, Ni, and Co boride catalysts, both supported and unsupported were prepared for magnetic measurements to be completed at PETC. Moessbauer spectra of two iron/silica catalysts derived from carbonyls revealed that higher metal dispersions can be obtained by this preparation technique. H_2 , CO, and O_2 adsorption on these catalysts provided estimates of dispersion in the range of 10% or greater for these catalysts. Testing of iron/silica and iron boride catalysts at different temperatures in varying H_2S concentrations was performed to determine poisoning kinetics. The Fe/SiO_2 lost activity in proportion to the amount of H_2S adsorbed while the iron boride catalyst showed no effects of deactivation in 6 ppm H_2S over a period of five days. The principal investigator attended one meeting and entertained two 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 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 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. 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 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% H₂S/H₂ over reduced samples at 575 K for a period of 12-16 hours. They will be nitrated 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 (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.

Table 1
Catalyst Preparation Plans^a (Task 1)

Metal-Support Combination	Unpromoted	Promoted	Additive Pretreatments			No. Catalysts
			<u>K₂O</u>	<u>S</u>	<u>N</u>	
Fe (unsupported)	x	x	x ^(?) ^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 ₂ O ₃	x					1
Fe/ZSM-5	x	x	x ^d			3
<u>Fe/Silicalite</u>	<u>x</u>	<u>x</u>				<u>2</u>
					Total	27

^a15 wt.% metal unless otherwise noted;
0.5 to 3 wt.% K₂O.

^bPromoted and unpromoted catalysts will be sulfided.

^c3 and 15 wt.% metal loadings.

^dPromoted catalyst will be sulfided.

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, 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 desirable selectivity properties at lower pressures and this approach will reveal such a phenomenon.

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 , 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
	Effects of Sulfiding	Fe, Fe/SiO ₂ (unpromoted and K ₂ O 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 H₂S
Deactivation

Effects of support	Fe/SiO ₂ , Fe/ZSM-5, Fe/Al ₂ O 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 ₂ O promoted Fe and Fe/SiO ₂ (sulfided and unsulfided)
Effects of Sulfiding	Fe, Fe/SiO ₂ (unpromoted and K ₂ O promoted), Fe/Al ₂ O 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

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

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 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 H₂S 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), H₂/CO=2 and space velocities of 500-2000 hr⁻¹ with 10-20 ppm H₂S 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 quarter are summarized below. Figure 1 shows all tasks to be progressing on schedule, with the exception of Task 2.

Results are best summarized according to task:

Task 1:

Preparation of samples of supported and unsupported Fe, Co, and Ni boride catalysts was completed. A slower heating ramp during reduction resulted in a higher surface area for Co-B/SiO₂. Two carbonyl-derived silica-supported iron catalysts were received and characterized by H₂, CO, O₂ adsorption and Moessbauer spectroscopy. The results indicated that significantly higher dispersions of iron can be obtained by the decomposition of metal carbonyls.

Task 2:

Minor changes in the gas sampling valve compartment insured more accurate analysis even at low conversions. Three catalysts, including the two carbonyl-derived catalysts were prepared for reactor testing.

Task 3:

The effects of H₂S poisoning at different temperatures and concentrations on 15% Fe/SiO₂ were tested. This catalyst loses activity proportional to the quantity of sulfur adsorbed. The unsupported Fe boride catalyst was tested for in situ activity in the presence of H₂S, showing no significant deactivation over a period of 5 days!

Misc.

The laboratory received two visitors and guest speakers during the quarter. The Principal Investigator and students attended one symposium.

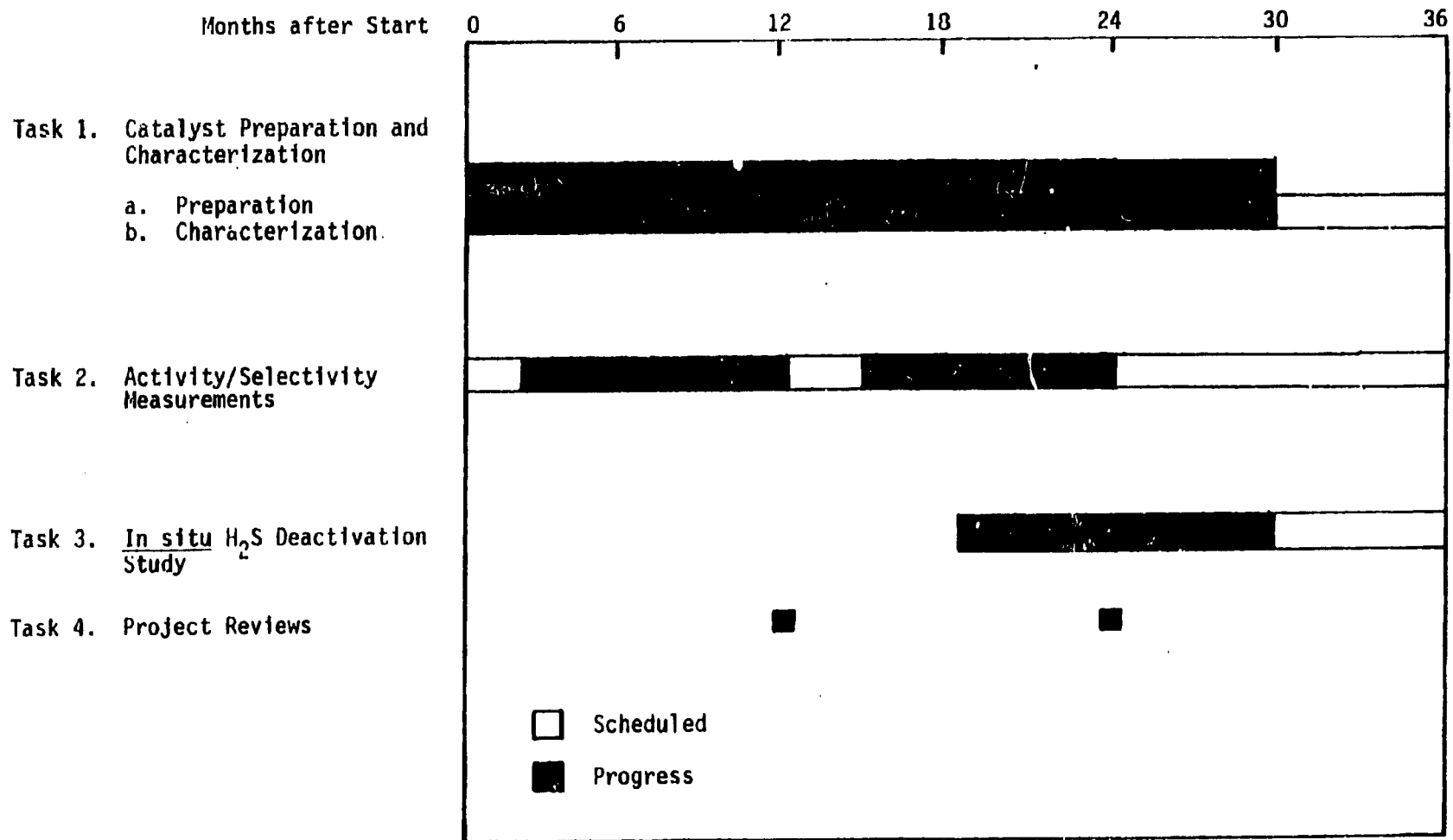


Figure 1. Schedule of Proposed Research Activities and Progress.

III. DETAILED DESCRIPTION OF TECHNICAL PROGRESS

A. Task 1: Catalyst Preparation and Characterization

1. Catalysts Preparation

A large portion of our efforts during the past quarter were spent in preparing samples of unsupported and silica-supported boron-promoted Co, Fe and Ni catalysts. These new supported catalysts seem to be of much higher quality than those previously prepared as indicated by their black color and the lack of significant water evolution during high temperature reduction in H₂. More careful control of H₂ reduction heating rates to less than 2°C/minute allowed for significantly increased active surface areas as evidenced by higher H₂ uptakes as reported below.

During the quarter, two catalysts samples were received from Corning Glass Works which were prepared in their laboratory. They consist of iron supported on Cab-O-Sil silica powder derived by decomposition of iron carbonyl. One sample had been calcined at 500°C previous to their shipment to us. The other was calcined at 200°C for 90 minutes in our own laboratory when received. It is felt that these samples could provide important data on metal-support and crystallite size effects in Fischer-Tropsch synthesis.

2. Catalyst Characterization

Arrangements were made with Dr. Udaya Rao of the Pittsburgh Energy Technology Center to perform magnetic measurements on our supported and unsupported Fe, Co and Ni boride catalysts. These tests will provide important data to show whether the boride compounds are indeed present in these catalysts.

Mossbauer spectroscopy was performed on the fresh and reduced Fe carbonyl-derived silica-supported catalysts. The results are displayed graphically in Figures 2 through 5. The six-peak spectrum in Figure 2 for the catalyst calcined at 500°C is evidence of large particles of Fe₂O₃, to be expected from such high temperature treatment. However, the characteristic six line spectrum for metallic iron in Figure 3 shows that these particles were nearly 100% reduced to that metal after 36 hour reduction in H₂ at 450°C. Figures 4 and 5 for the fresh and reduced 200°C calcined catalyst are poorly resolved, even after over a week's time in the Mossbauer beam. Apparently the loading on the catalyst is very small. It is possible iron was lost in shipping since the catalyst had not been calcined. Nonetheless, chemisorption measurements evidenced high reducibility and/or dispersion for this catalyst as evidenced by the chemisorption data in Table 3 for catalyst C7. If the iron was completely reduced (probably not true), the catalyst's dispersion would be about 10%, a factor of 10 times more dispersed than the corresponding impregnated catalyst. This shows the significant possibilities for preparing well dispersed catalysts by carbonyl preparations. Repeated CO uptake on catalyst C6, together with O₂ titration is being performed presently in our laboratory. This will provide a check on the abnormally low CO/H ratio of catalyst C6 reported in Table 3.

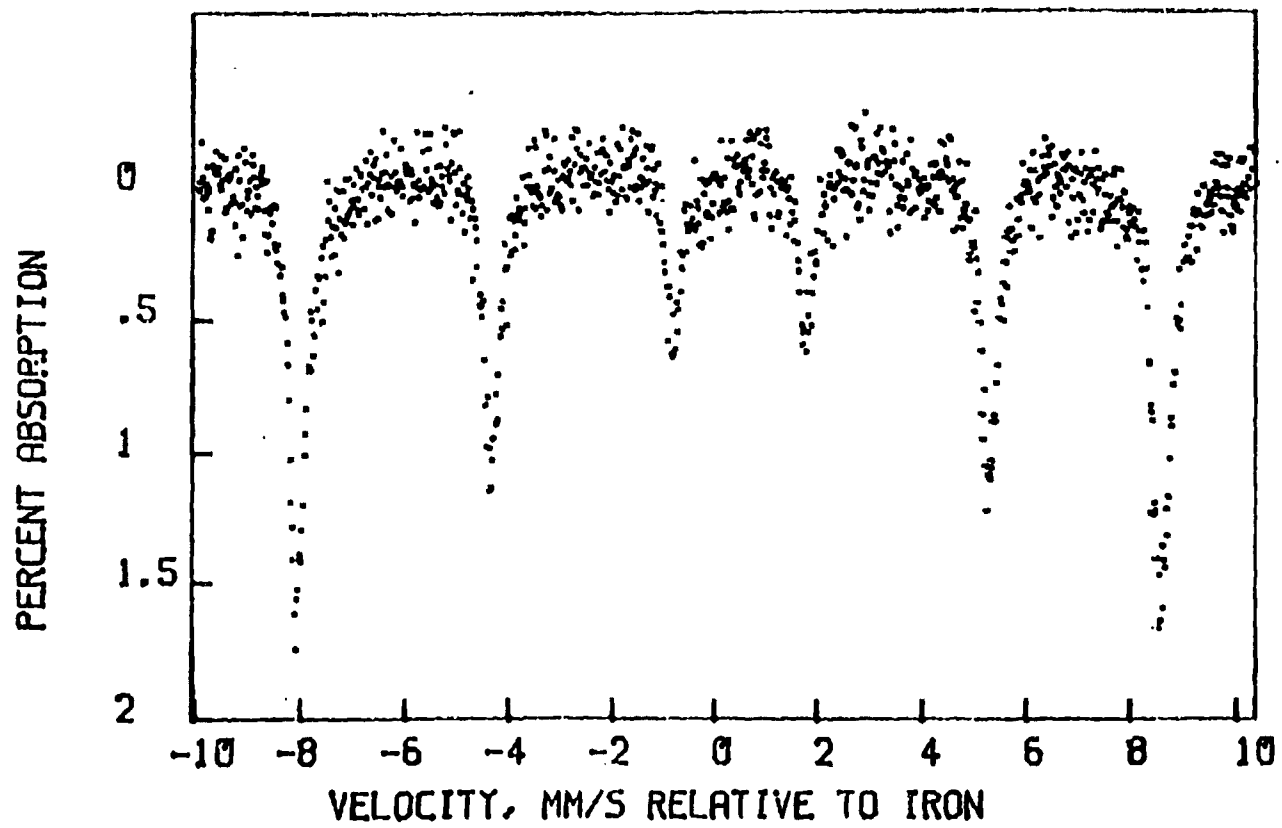


Figure 2. Moessbauer Spectrum of Fresh 500 C Calcined Catalyst

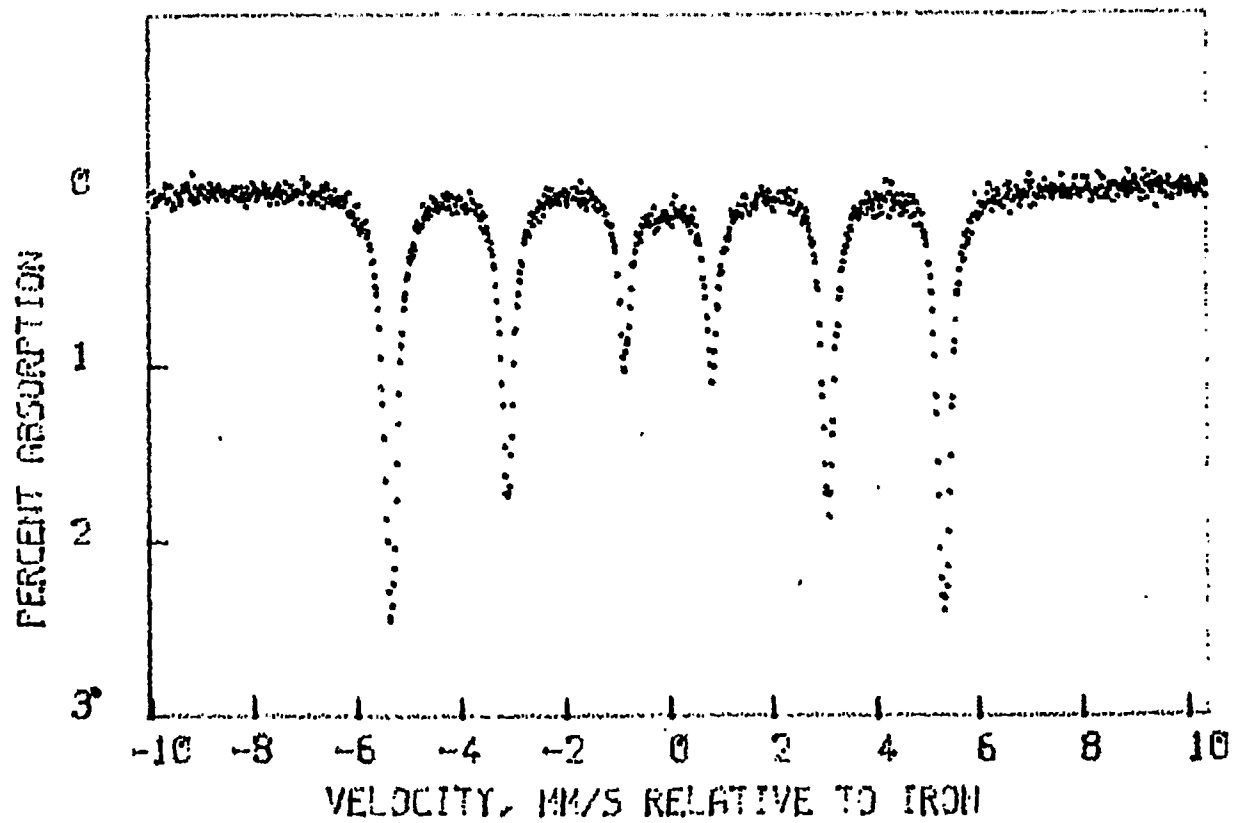


Figure 3. Moessbauer Spectrum of Reduced 500 C Calcined Catalyst

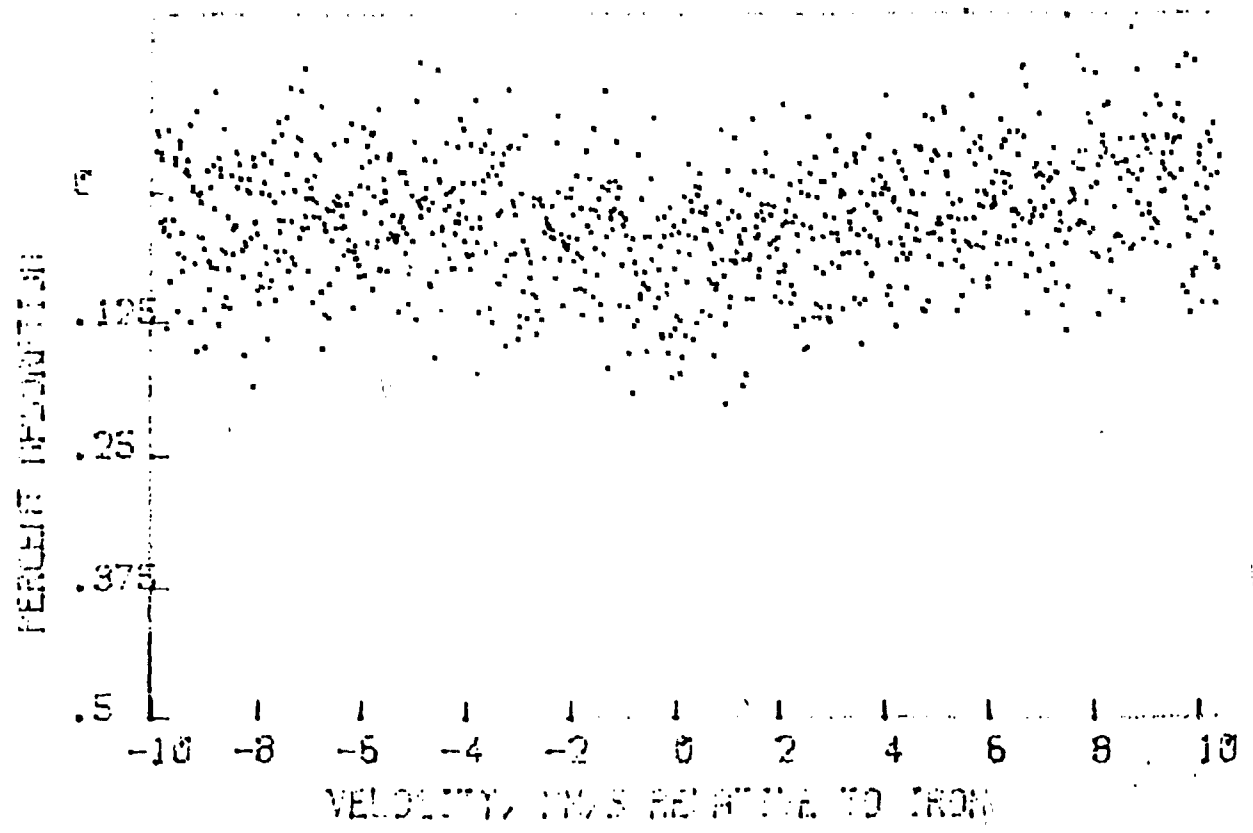


Figure 4. Moessbauer Spectrum of Fresh 200 C Calcined Catalyst

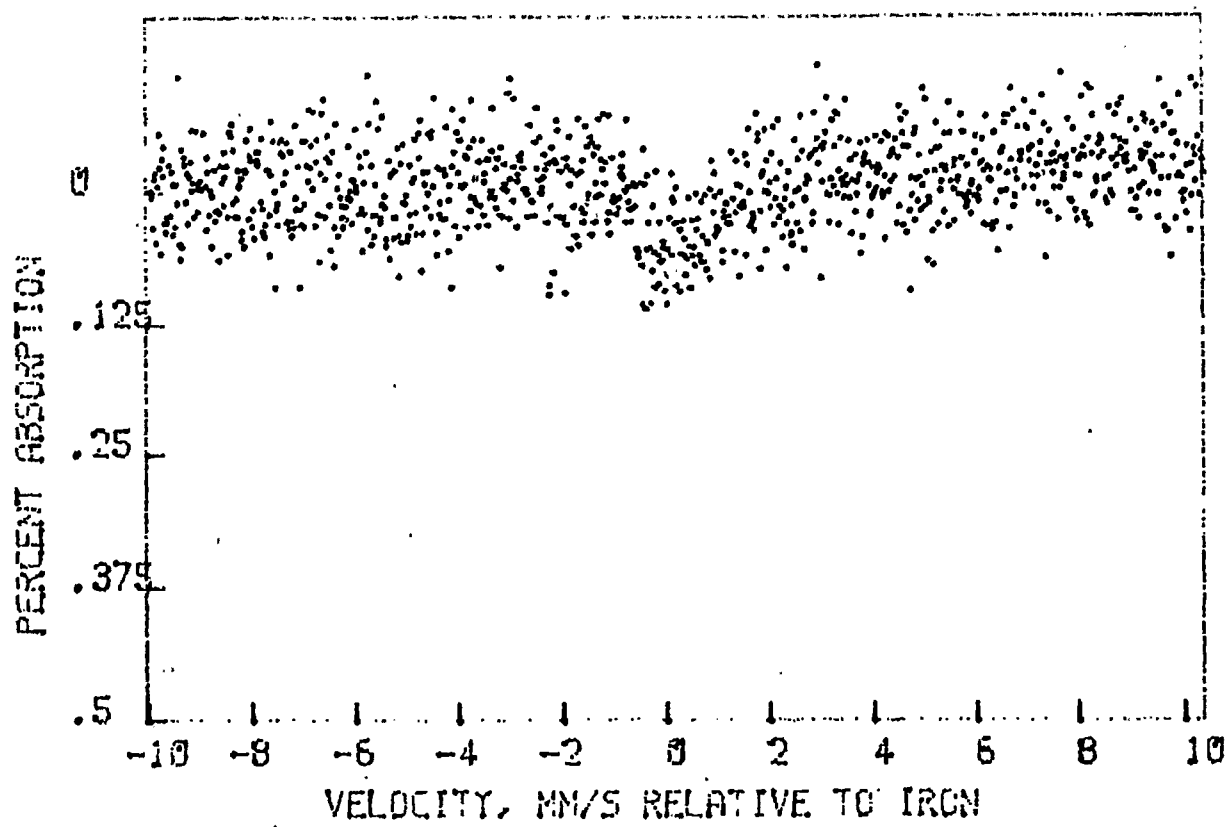


Figure 5. Moessbauer Spectrum of Reduced 200 C Calcined Catalyst

Table 3

Chemisorption Data - Fe-Carbonyl-Derived Catalysts

Catalysts	Calcination Temp (°C)	H ₂ Uptake (25°C, μmole/g)	CO Uptake (25°C, μmole/g)	O ₂ Uptake (400°C, μmole/g)	CO/H
C6	500	20.61	2.13	--	0.076
C7	200	17.25	12.96	319.24	0.376

Also completed during the past quarter were chemisorptions on the newly prepared CoB/SiO₂ catalyst, CoB-S-101. H₂ uptake was 21.2 μmoles/g and CO uptake 24.4 μmoles/g, giving a CO/H ratio of 0.58.

3. Future Plans

In the next weeks the boride catalyst samples will be sent to PETC for magnetic measurements as well as to Rocky Mountain Geochemical Co. for chemical analyses. O₂ titrations and BET adsorption measurements will be performed on the boride catalysts, including fresh and reduced samples. Moessbauer spectroscopy is continuing, as are the preparation of other Fe catalysts outlined in Table 1.

B. Task 2: Activity/Selectivity Measurements

1. Chromatographic Analysis

Several minor adjustments were made in the sampling valve temperature control this quarter so that sample size could be held more constant. The temperature is now controlled at 300°C ± 2°C. This will insure accurate and reproducible results even at low conversions. New valves were ordered and are being delivered at the time of writing to replace those presently in use. This will avoid previously experienced mechanical failures and down time.

2. Future Plans

The installation of the new valves will be completed within two days of their delivery. Several catalysts are now ready for reactor testing, including the two carbonyl-derived catalysts. Testing of nitrided iron, unsupported iron, and zeolite-supported iron will be completed.

C. Task 3: In Situ H₂S Poisoning Measurements

In-situ deactivation tests were performed on several catalysts this quarter. 15% iron on silica catalysts were tested at 200°C and 250°C with 5-6 ppm sulfur in the feed stream. The same catalyst was also tested at 200°C with 2 ppm H₂S in the feed. All these catalysts exhibited a loss of activity proportional to the amount of sulfur added. While the evaluation of the data is still incomplete, no changes in selectivity were noted during these tests.

An unsupported iron catalyst, promoted with boron was also tested at 225°C with 6 ppm H₂S present in the feed. This catalyst did not exhibit any loss of activity due to the addition of sulfur to the feed stream over a period of 5 days! Further analysis of this data is needed but the addition of boron apparently prevents sulfur from adversely affecting catalyst activity.

During the next quarter, unsupported iron catalysts, with and without the addition of alkali promoters will be tested. Supported iron catalysts will be tested at different temperatures and H₂S concentrations to determine the kinetics of sulfur deactivation.

D. Miscellaneous Accomplishments and Technical Communication

During this past quarter the Principal Investigator and several students attended the Seventh Annual Symposium of the Rocky Mountain Fuel Society. Dr. Bartholomew chaired a session on fundamental research, while Mr. Travis Bordrero presented a paper on O₂ adsorption on Mo and NiMo sulfides.

Our laboratory also hosted two guests. Professor Robert J. Madix of Stanford visited on February 3 and presented a seminar on the effects of additives such as sulfur on adsorption and reaction. Professor Lawrence Dahl of the Chemistry Dept. at Madison, Wisconsin visited our campus as a guest of the local ACS section of which Dr. Bartholomew is chairman. Professor Dahl talked on the preparation and characterization of metal cluster compounds.

The PI also submitted a proposal to continue our work on metal borides for Fischer-Tropsch synthesis to the advanced Coal Research Program.

IV. CONCLUSIONS

1. Controlling H_2 reduction heating rates to less than $2^\circ C/min$ significantly increases active surface areas of cobalt boride/silica catalysts.
2. Calcining Fe-carbonyl derived catalysts at $500^\circ C$ greatly increases crystallite size relative to calcination at $200^\circ C$.
3. Fe-carbonyl-derived silica-supported catalysts may be prepared with much higher dispersions than conventional Fe catalysts.
4. 15% Fe/SiO₂ exhibits a loss of activity proportional to the amount of H_2S added. Unsupported iron boride does not exhibit significant deactivation in 6 ppm H_2S at $225^\circ C$ over a period of 5 days.

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16. Abstracts During the tenth quarter samples of Fe, Ni, and Co boride catalysts, both supported and unsupported were prepared for magnetic measurements to be completed at PETC. Moessbauer spectra of two iron/silica catalysts derived from carbonyls revealed that higher metal dispersions can be obtained by this preparation technique. H ₂ , CO, and O ₂ adsorption on these catalysts provided estimates of dispersion in the range of 10% or greater for these catalysts. Testing of iron/silica and iron boride catalysts at different temperatures in varying H ₂ S concentrations was performed to determine poisoning kinetics. The iron boride catalyst showed no effects of deactivation in 6 ppm H ₂ S over a period of five days. The principal investigator attended one meeting and entertained two visitors.					
17. Key Words and Document Analysis. 17a. Descriptors Coal liquefaction Fischer-Tropsch Synthesis Catalysts Sulfur poisoning					
17b. Identifiers/Open-Ended Terms					
17c. COSATI Field/Group					
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