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MASTER

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

Quarterly Technical Progress Report
For Period September 19, 1980 to December 18, 1980

Calvin H. Bartholomew
Brigham Young University
Provo, Utah 84602

Date Published -- January 10, 1981

PREPARED FOR THE UNITED STATES
DEPARTMENT OF ENERGY

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FOREWORD

This report summarizes technical progress during the fifth quarter (September 19, 1980 to December 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: Duane M. Davis, Jeffery L. Rankin, and Glen Witt. Mr. Rankin and Dr. Bartholomew were the principal authors. Laurie A. Witt provided typing services.

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ABSTRACT

During the fifth quarter a 15% iron boride on SiO_2 catalyst was prepared using an alcohol solution reduction with $\text{NaBH}_4 \cdot \text{H}_2\text{O}$. Chemisorption measurements were performed for Fe-S-100 (3% Fe/SiO_2) and are in progress for the iron-boride-silica catalyst. Reduction of Co catalysts at 623 K rather than 723 K is being tested as a method to improve dispersion by decreasing the amount of Co-support interaction. An in depth study of non olefinic and nonparaffinic compound retention times on the 10% SP2100 chromatograph column has shown that the compounds elute in the following order for a specific carbon number: alkene < alkane < aldehyde < ketone < ester < alcohol < acid. Mass flow controllers have been installed in the reactor system and are fully operational.

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 (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)

<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(2) ^c	x				x	4
Fe/SiO ₂	x(2) ^c	x	x	x(3) ^b	x	x	9
Fe/Al ₂ O ₃	x						1
Fe/ZSM-5	x	x		x ^d			3
Fe/Silicalite	x	x					2

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

^bPromoted and unpromoted catalysts will be sulfided.

^c3 and 15 wt.% metal loadings.

^dPromoted catalyst will be sulfided.

Total 28

Catalysts will be sulfided by passing a gaseous mixture of 3% $\text{H}_2\text{S}/\text{H}_2$ 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 Thermo-gravimetric 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), $\text{H}_2/\text{CO} = 2$ 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

<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_2S 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.

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 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 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 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/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 reactor trials are behind due to chromatograph problems.

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

Task 1.

A 15% FeB/SiO₂ catalyst was prepared during the past quarter. The metal surface area of Fe-S-100 (3% Fe/SiO₂) was measured by H₂ adsorption; characterization of Fe-B-S-101² (iron boride/SiO₂) by means of H₂ adsorption is in progress. All catalysts prepared to date have been characterized by H₂ and CO chemisorption.

Task 2.

An in depth study of retention times for oxygenated hydrocarbons was completed. The information from this study will aid chromatogram interpretation and mass balance calculations. An inconclusive reactor test of FeK-S-100 is being repeated to insure accuracy.

Task 3.

Sulfur poisoning studies are scheduled to begin in March 1981.

Misc.

The principal investigator attended 4 meetings, presented three papers (one in connection with this contract at the DOE Contractors Conference on Coal Liquification), and visited three other laboratories, and presented a seminar at the University of Utah.

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

This past quarter, a 15% Fe-B/SiO₂ catalyst, coded Fe-B-S-101, was prepared. Several methods were tried, with the following preparation giving the most satisfactory results. Analytically pure Fe(NO₃)₃ · 9 H₂O was dissolved in methanol and used in the impregnation of commercial Cab-O-Sil/silica support material. After impregnation, the catalyst was dried under vacuum at room temperature for 24 hours. Next, a solution of ethanol and sodium borohydride was prepared by adding NaBH₄ in a four-fold excess (of that required to reduce the Fe) to about 1000 ml ethanol. This solution was placed in an N₂ atmosphere and vigorously stirred while the iron-impregnated silica was slowly added. After the reaction was completed, the flask containing the catalyst was stoppered and the catalyst allowed to settle out of suspension. The catalyst was washed several times with methanol with settling between washes. Final composition of the catalyst will be determined by chemical analysis.

2. Catalyst Characterization

Metal surface area for the iron boride catalyst is currently being measured using H₂ chemisorption at 298 K.

H₂ chemisorption was also repeated for a sample of Fe-S-100, a 3% Fe/SiO₂ catalyst. This sample was reduced for 16 hours, and as reported in Table 3, the resulting uptake was comparable to previous measurements showing poor reducibility and relatively low dispersion of this Fe catalyst.

In our work with Co/SiO₂ catalysts we have been able to obtain moderately-well-dispersed catalysts (i.e. % exposed of 5-25%); however we believe it is possible to improve on this. Based upon recent work at Gulf Research with Co/Al₂O₃ (4) we suspect that greater cobalt surface areas can be achieved if the reduction of the catalysts is performed at 623 K rather than 723 K since Co catalysts reduced at 723 K may contain significant amounts of Co combined with support as irreducible oxides (4). Experiments to investigate this possibility are underway.

3. Future Plans

During the coming quarter, electron microscopic examination of Fe catalysts is planned, together with chemical analysis. It is hoped that these experiments will shed light on the effects of H₂ reduction and long-term reactor runs on the active catalyst surface.²

O₂ titration on freshly reduced catalysts using a thermogravimetric analyzer are also planned to determine degree of metal reduction and allow accurate dispersion calculations. In this way, optimum temperatures and times of reduction may be determined quantitatively.

TABLE 3

H₂ and CO Chemisorption Uptakes at 298 K -
Iron and Cobalt Catalysts

<u>Catalyst Code</u>	<u>H₂ Uptake (moles/g)</u>	<u>CO Uptake (moles/g)</u>	<u>CO H</u>
Co-S-101	17.10 ^a 61.44 ^b	- 6.46 ^b	- 0.053
Co-S-102	44.48 ^a 57.61 ^b	- 10.34 ^b	- 0.090
Co-K-S-100	11.73 ^a	-	-
Fe-S-100	2.10 ^f 3.98 ^b 23.17 ^b	2.69 ^a - 0.35 ^b	0.640 - 0.008
Fe-S-101	3.50 ^a 9.92 ^c	4.66 ^a -	0.666 -
Fe-S-102	3.61 ^a 59.22 ^b 57.93 ^d	9.80 ^a - -	1.36 - -
	20.19 ^e	3.52 ^e	0.087
Fe-K-S-100	11.23 ^c	7.23 ^c	0.322
Fe-ZSM-5	22.76 ^b	7.68 ^b	0.169
Fe-Silicalite	20.37 ^b	4.55 ^b	0.117
Co-B-A-101	59 ^a 67 ^d	74 ^a 66 ^d	0.63 0.49
Co-B-S-101	56 ^a	60 ^a	0.54

^aAfter 12 hr reduction in H₂

^bAfter 24 hr reduction in H₂

^cAfter 2 hr calcination in air, 20 hr reduction in H₂

^dAfter 24 hr reactor run

^eAfter 20 hr reduction in H₂

^fAfter 16 hr reduction in H₂

B. Task 2: Activity/Selectivity Measurements

1. Chromatographic Analysis

During the past quarter, efforts were made to determine the identity of chromatogram peaks corresponding to compounds synthesized other than paraffinic and olefinic hydrocarbons. Samples of C_1 to C_4 aldehydes, ketones, acids, acetate esters, and C_1 to C_5 alcohols were used to determine the order of elution of probable oxygenated compounds resulting from the Fischer-Tropsch Synthesis. Repeated trials were made to insure that reproducibility of retention times was possible. Correlation of the carbon number of each type of compound was made to the average temperature of the column from injection of the sample to its elution. The average temperature was achieved by integrating the temperature-time curve as shown in Figure 2. The results obtained are shown in Figure 3. Apparently for any carbon number N, the compounds elute in the following order:

1. Alkene
2. Alkane
3. Aldehyde
4. Ketones
5. Esters
6. Alcohol
7. Acid

It was also observed that iso-compounds elute more rapidly than the straight chain compounds. Alkenes and alkanes and aldehydes and ketones become less distinguishable as carbon number increases.

With these determinations, more accurate peak identification, and thus mass balances can be achieved during reactor testing.

2. Equipment Construction

Brooks mass flow meter-controller units were received during the past quarter and made fully operational. These allow control of CO and H_2 flows to set values and minimize the fluctuation of H_2/CO ratio and space velocity of reactor feed gas. The controllers were calibrated to volumetric flows after installation.

3. Experimental Measurements

Catalyst FeK-S-100, a 15% Fe catalyst promoted with K_2O , was tested in a Pyrex cell reactor at 1 atm pressure and 500 K. However, due to the elution of several unidentifiable peaks and irreproducible retention times, the results were not usable. At time of this report the chromatograph column had been conditioned and tested for retention time reproducibility and the reactor run repeated. The results will be analyzed and presented in our next report.

Figure 2. Temperature Program for Chromatographic Analysis.

Figure 3. Carbon Number versus Time-Averaged Elution Temperature - SP2100 Column Analysis

4. Future Plans

Activity/selectivity tests of the following catalyst are planned for the next quarter:

1. Fe-S-100
2. Fe-S-102
3. FeK-S-100
4. Co-S-101
5. Co-S-102
6. CoK-S-100

These runs will include a variation of H_2/CO ratio from 2 to 1 and a variation of temperature to allow calculation of activation energies for each reaction.

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

During the past quarter, the principal investigator established and maintained communications with several other laboratories involved in similar research.

Dr. Bartholomew attended the International Conference on Catalyst Deactivation held Oct. 13-15 in Antwerp Belgium at which he presented a review paper on "Sulfur Poisoning of Nickel in CO Hydrogenation." Following this meeting on Oct. 16 he visited with Professor G. F. Froment and Dr. Prasod Menon at the University of Gent and toured facilities in the Petrochemical Institute of Technology. On Oct. 17, he visited Professor Helmut Knözinger of the Institute of Physical Chemistry at the University of Munich.

Following his trip to Europe, the PI attended the DOE sponsored Conference of University Contractors on Coal Liquifaction at which he presented a paper describing results obtained during the first year of this contract.

The PI also attended the Annual Meeting of the Materials Research Society Nov. 17-18 in Boston at which he presented a paper, "Crystallite Size and Support Effects in CO Hydrogenation." He also attended the 73rd Annual Meeting of The American Institute of Chemical Engineers at which Edward L. Sughrue (BYU graduate) presented a paper on "Kinetics of CO Hydrogenation on Monolithic Nickel" based on work performed as part of our previous DOE contract.

On December 22, Dr. Bartholomew presented a seminar at the University of Utah Department of Fuels Engineering on "Metal-Support

Interactions in CO Hydrogenation," and visited with Faculty in the Fuels Department.

Mr. Duane Davis joined our research group in December and will take over the metal boride catalyst work formerly carried out by Mr. Glenn Davis, as the latter Mr. Davis has taken a job locally in industry.

IV. CONCLUSIONS

1. Reduction of Co catalysts at 723 K may cause formation of a cobalt silicate compound, and thus decrease dispersion. Reduction at 623 K may avoid this effect.
2. The elution of oxygenated hydrocarbon compounds on a 10% SP2100 chromatograph column is as follows:

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

V. REFERENCES

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16. Abstracts During the fifth quarter a 15% iron-boride on SiO ₂ catalyst was prepared using an alcohol solution reduction with NaBH ₄ . H ₂ chemisorption measurements were performed for Fe-S-100 (3% Fe/SiO ₂) and are in progress ² for the iron-boride-silica catalyst. Reduction of Co catalysts at 623 K rather than 723 K is being tested as a method to improve dispersion by decreasing the amount of Co-support interaction. An in depth study of non olefinic and nonparaffinic compound retention times on the 10% SP2100 chromatograph column has shown that the compounds elute in the following order for a specific carbon number: alkene < alkane < aldehyde < ketone < ester < alcohol < acid. Mass flow controllers have been installed in the reactor system and are fully operational.					
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