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

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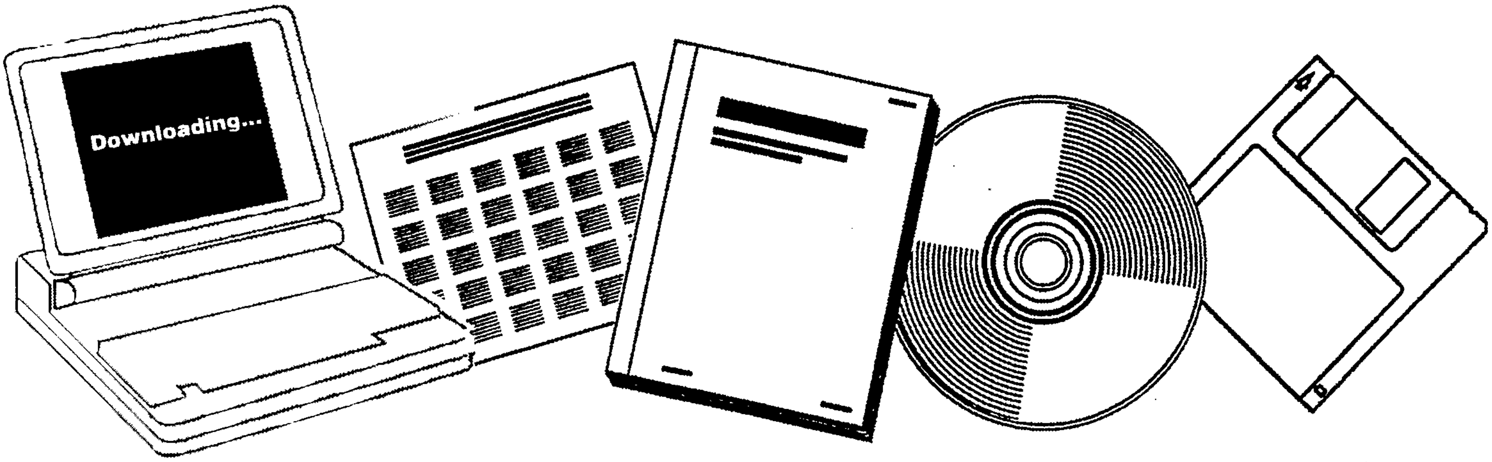

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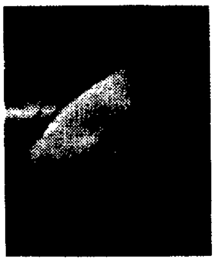

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INVESTIGATION OF SULFUR-TOLERANT CATALYSTS FOR SELECTIVE SYNTHESIS OF HYDROCARBON LIQUIDS FROM COAL-DERIVED GASES

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

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DEPARTMENT OF ENERGY

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DISCLAIMER

FOREWORD

This report summarizes technical progress during the ninth quarter (September 19, 1981 to December 18, 1981) of a three-year study conducted for the Department of Energy (DOE) under Contract No. DE-AC01-79ET14809. The principal investigator for this work was Dr. Calvin H. Bartholomew; Mr. Henry W. Pennline was the technical representative for DOE.

The following students contributed to the technical accomplishments and to this report: Richard M. Bowman, Duane M. Davis, and Jeffery L. Rankin. Mr. Rankin and Dr. Bartholomew were the principal authors. Laurie Witt provided typing services.

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ABSTRACT

During the ninth quarter progress was made in refining the preparation of supported iron and cobalt metal boride catalysts. Moessbauer spectra of freshly dried and reduced iron/silica catalysts were obtained, the results providing estimates of the extents of reduction to iron metal in very good agreement with earlier results obtained by O_2 titration. The analytical calibration of our glass capillary column was completed. Effects of H_2S poisoning on the activity and selectivity properties of Fe/SiO_2 and $Fe/K/SiO_2$ catalysts were examined. A linear loss of activity with increasing sulfur coverage was observed; there were no significantly apparent changes in product distribution with increasing sulfur coverage. The principal investigator visited two companies and attended 2 meetings where he presented papers and/or talks while receiving one visitor.

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 desireable 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 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% H_2S/H_2 over reduced samples at 575 K for a period of 12-16 hours. They will be nitrided by exposing the reduced catalyst to ammonia at 625 K for 12-16 hours followed by treatment in H_2 at 575 K for 12-16 hours to remove all traces of ammonia; thus preventing formation of urea during synthesis. Silica supported iron boride will be prepared according to special techniques recently developed in this laboratory for preparation of supported cobalt and nickel borides (1,2). This approach involves a nonaqueous, low temperature reduction of the impregnated or deposited metal nitrate/support with sodium borohydride followed by washing, drying and high temperature reduction in hydrogen.

The catalysts prepared in this study will be characterized by a number of

Table 1

Catalyst Preparation Plans[a] (Task 1)

Metal-Support Combination	Unpromoted	Promoted	Additive Pretreatments			No. Catalysts
		K_2O	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(3)[b]	x	x	8
Fe/Al_2O_3	x					1
Fe/ZSM-5	x	x	x[d]			3
Fe/Silicalite	x	x				2
					Total	27

[a] 15 wt.% metal unless otherwise noted; 0.5 to 3 wt.% K_2O.

[b] Promoted and unpromoted catalysts will be sulfided.

[c] 3 and 15 wt.% metal loadings.

[d] Promoted catalyst will be sulfided.

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 desireable 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,

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/MgO Fe/Al_2O_3, Fe/ZSM-5, Fe/Silicalite, Co, Co/SiO_2
	Effects of metal	Co, Fe
	Effects of metal loading	3 and 15% Fe/Al_2O_3
	Effects of Promoter	K_2O promoted Fe, Fe/SiO_2, Co/SiO_2
	Effects of Sulfiding	Fe, Fe/SiO_2 (unpromoted and K_2O 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 H_2S Deactivation	Effects of support	Fe/SiO_2, Fe/ZSM-5, Fe/Al_2O_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_2O promoted Fe and Fe/SiO_2 (sulfided and unsulfided)
	Effects of Sulfiding	Fe, Fe/SiO_2 (unpromoted and K_2O promoted), Fe/Al_2O_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

---

[a] Fe/ZSM-5 and Fe/Silicalite samples have been obtained from the Pittsburgh Energy Technology Center.

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 H_2S 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), $H_2/CO=2$ and space velocities of 500-2000 hr^{-1} with 10-20 ppm H_2S 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.

Results are best summarized according to task:

Task 1:

Preparation of supported-metal boride catalysts was refined to improve the degree of reduction of the fresh catalysts. Moessbauer spectra of freshly dried and reduced Fe-S-102, Fe-S-103, and FeK-S-100 were obtained.

Task 2:

Analytic calibration of the glass capillary column was accomplished with correlation of retention times with compound characteristics. Analysis of reactor tests of metal boride catalysts was completed.

Task 3:

The effects of H_2S poisoning on the activity/selectivity of 15% Fe/SiO_2 and 15% Fe/3% K_2O/SiO_2 were determined.

Misc.

Dr. Bartholomew visited PETC, the Tri-State Catalysis Club and Ashland Oil Company and presented three different seminars. Mr. Rankin and Dr. Bartholomew attended the 7th North American Meeting of the Catalysis Society where Dr. Bartholomew presented a paper.

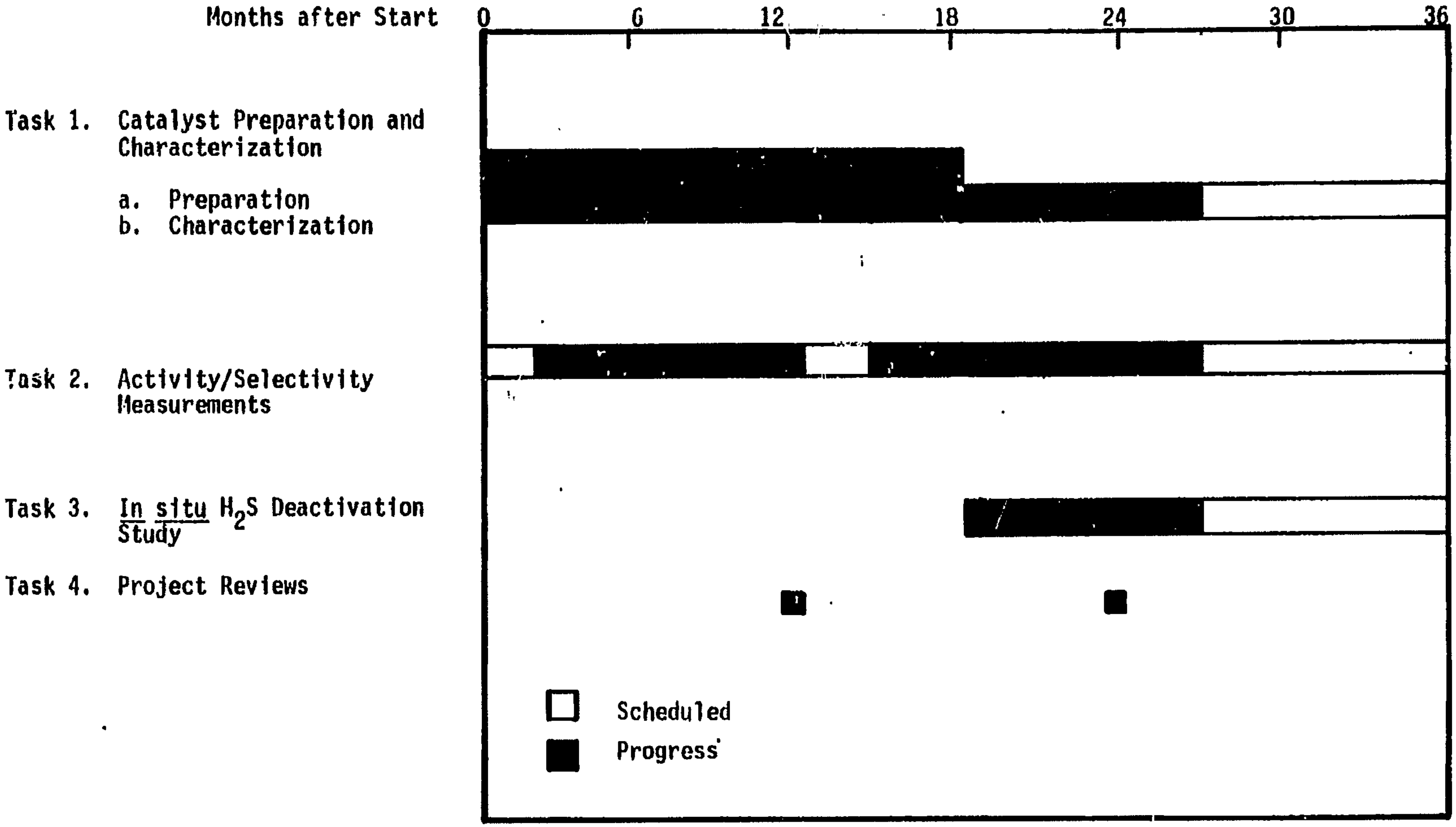

Figure 1. Schedule of Proposed Research Activities and Progress.

III. DETAILED DESCRIPTION OF TECHNICAL PROGRESS

A. Task 1: Catalyst Preparation and Characterization

1. Catalysts Preparation

Work was continued on improving the preparation technique for the supported metal borides. The very low activity and brown oxide color of the fresh chemically reduced catalysts (not H_2 reduced) necessitated development of a better method of preparation. As a result, a combination of filtration and centrifugation has been developed and seems to work quite well.

Samples of boride catalysts are also being prepared presently to send to PETC for magnetic measurement studies to determine if a true metal boride compound is present.

2. Catalyst Characterization

Emphasis during the past quarter was placed on the Moessbauer spectroscopy of the iron catalysts studied to date. Figures 2 through 7 display the spectra of Fe-S-102, Fe-S-103, and Fe-K-S-100 in freshly dried and reduced forms. Analysis of used catalyst samples are in progress.

Fe-S-102 is a 15% Fe/SiO_2 catalyst. The large peaks at 0 and 0.6 mm/sec, plus the small peaks at -9.8, -7.3, -3.9, +4.4, +7.1 and +10.1 indicate the presence of large amounts of Fe_2O_3 on the fresh catalyst surface (4). The reduced sample showed nearly complete reduction to metallic Fe, with some traces of remaining oxide. A rough fit of the data yielded approximately 15.0% remaining oxide. This agrees extremely well with the O_2 titration data, showing 78.8% reduction to the metal.

Figures 4 and 5 show similar data for the 3% Fe/SiO_2 catalyst (Fe-S-103). The large peaks (Fig. 4) at -0.3 and +1.5 are evidence of an Fe^{2+} oxide, giving a much larger quadrupole splitting compared to the unreduced 15% Fe/SiO_2. Evidently, the iron is more intimately associated with the support in 3% Fe/SiO_2. Figure 5 is a spectrum of the reduced 3% Fe/SiO_2. The large inner peaks corresponding to unreduced iron are still very evident while the contribution of the outer peaks representing reduced metal is relatively small. A rough fit provides an estimate of 41% oxide remaining or 59% reduction. O_2 titration yielded 23% reduction, a somewhat lower value but one following qualitatively the same trend. The Fe-S-103 catalyst also showed a smaller-fraction of recoil-free atoms resulting in more baseline noise.

Figures 6 and 7 for Fe-K-S-100, a 15% Fe, 3% K_2O catalyst, showed results very similar to the unpromoted 15% Fe catalyst. From the spectrum it was evident that about 85% of the iron had been reduced to the metallic state.

3. Future Plans

Moessbauer studies will be continued on catalysts being prepared presently. These include the silicalite-supported catalysts, and unsupported Fe and Fe-K catalysts. Chemisorption titration of H_2, CO, CO_2 on these samples will also be completed.

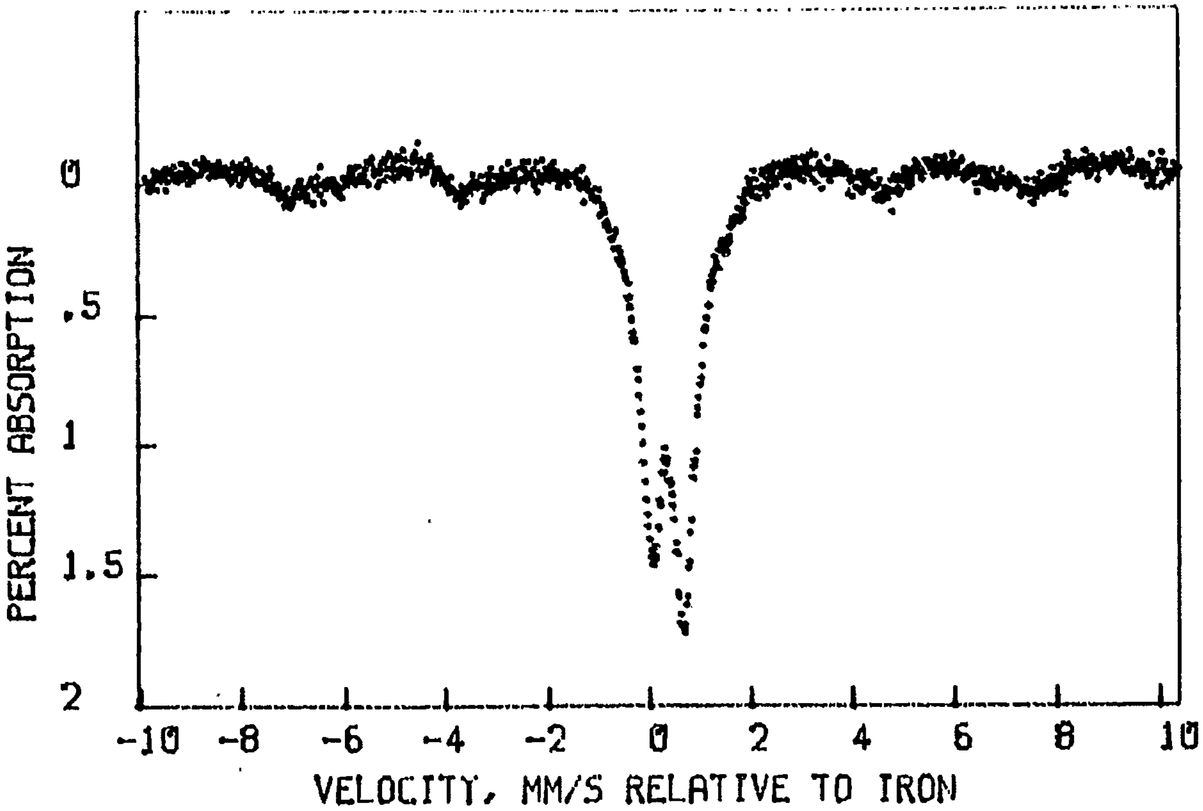

Figure 2. Moessbauer Spectrum of Fresh Fe-S-102

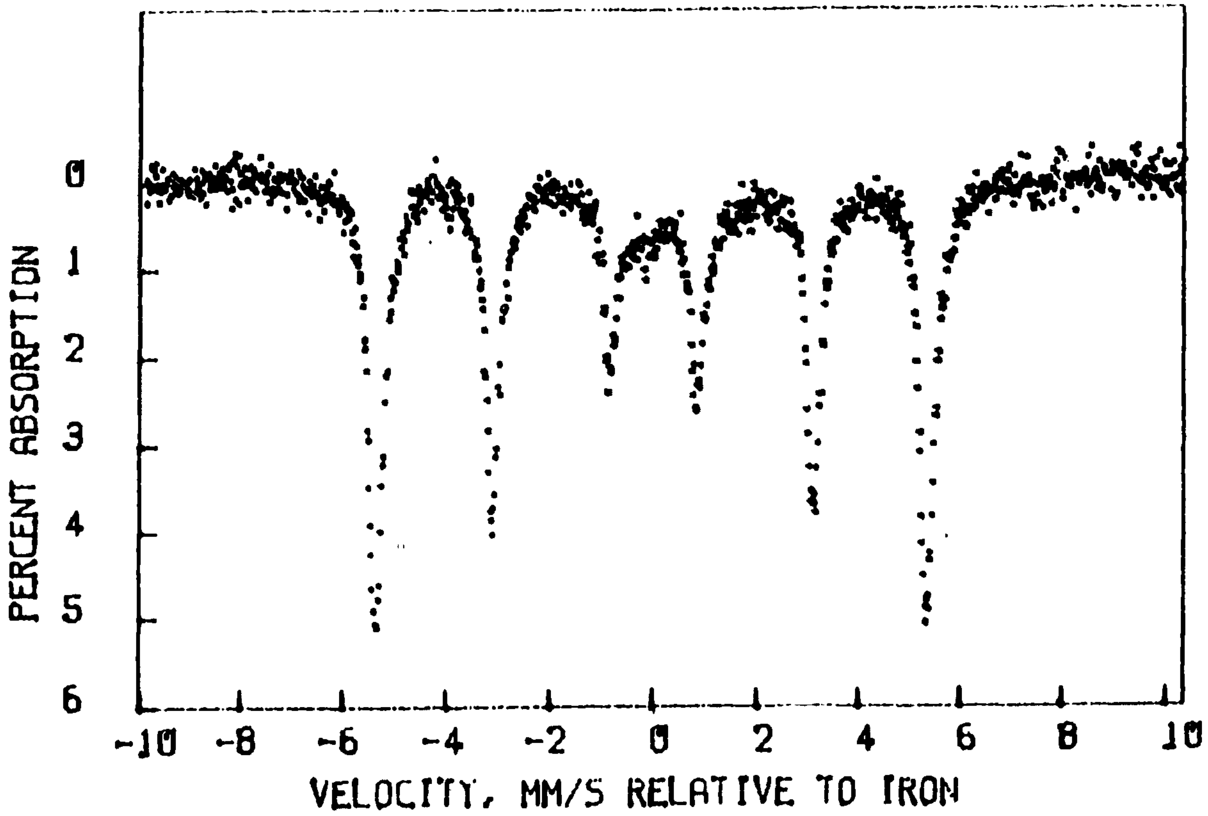

Figure 3. Moessbauer Spectrum of Reduced Fe-S-102

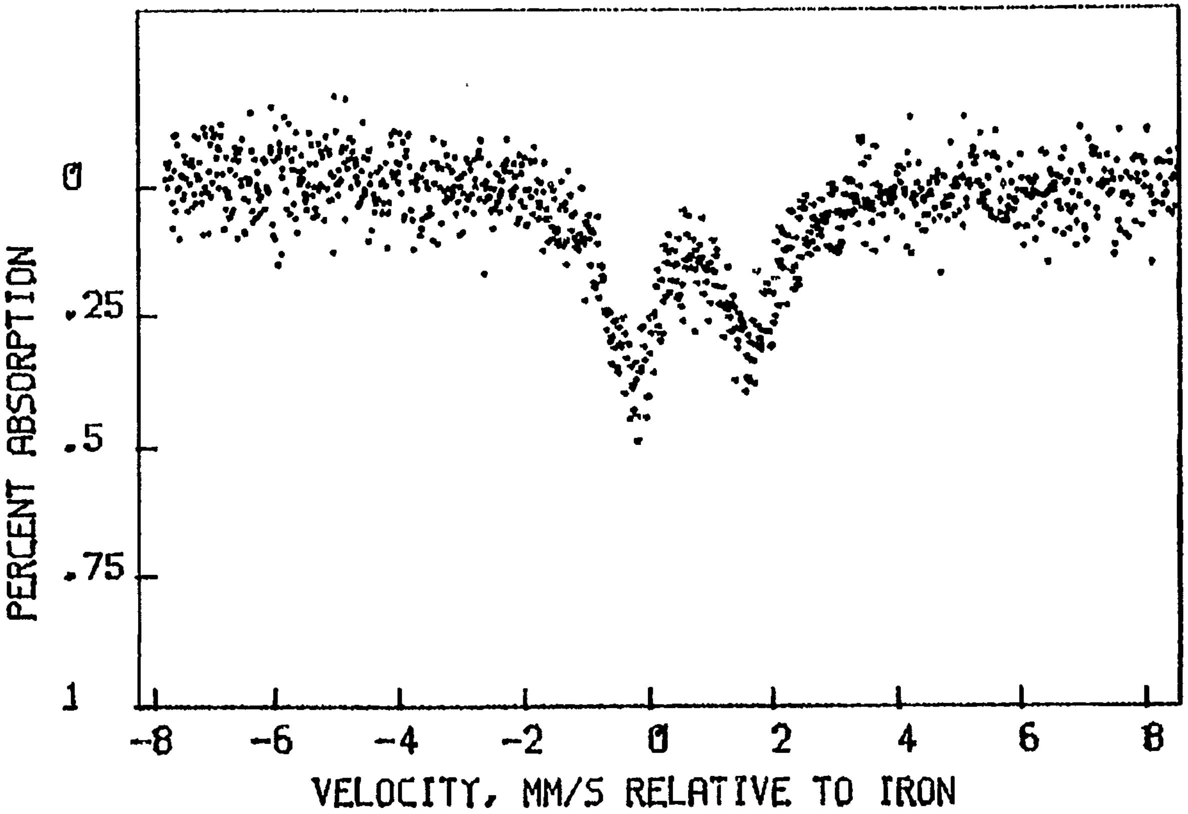

Figure 4. Moessbauer Spectrum of Fresh Fe-S-103

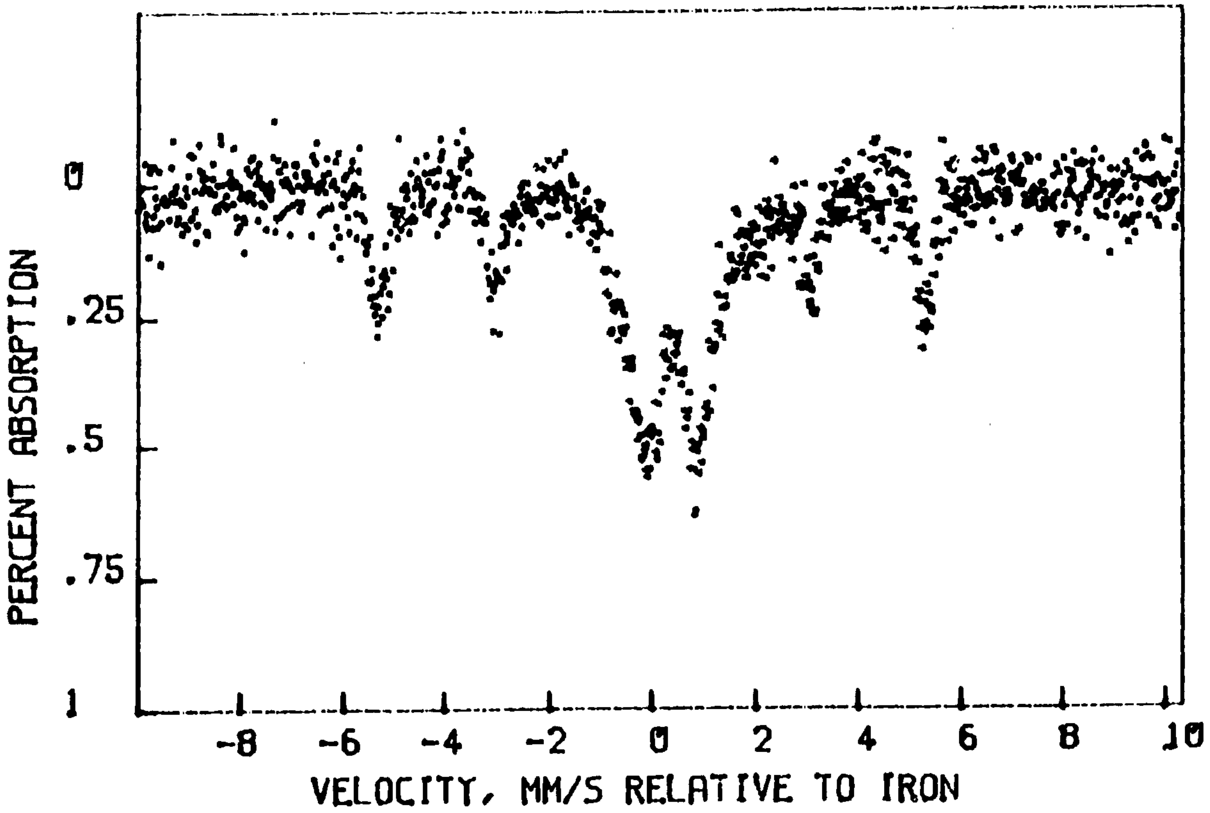

Figure 5. Moessbauer Spectrum of Reduced Fe-S-103

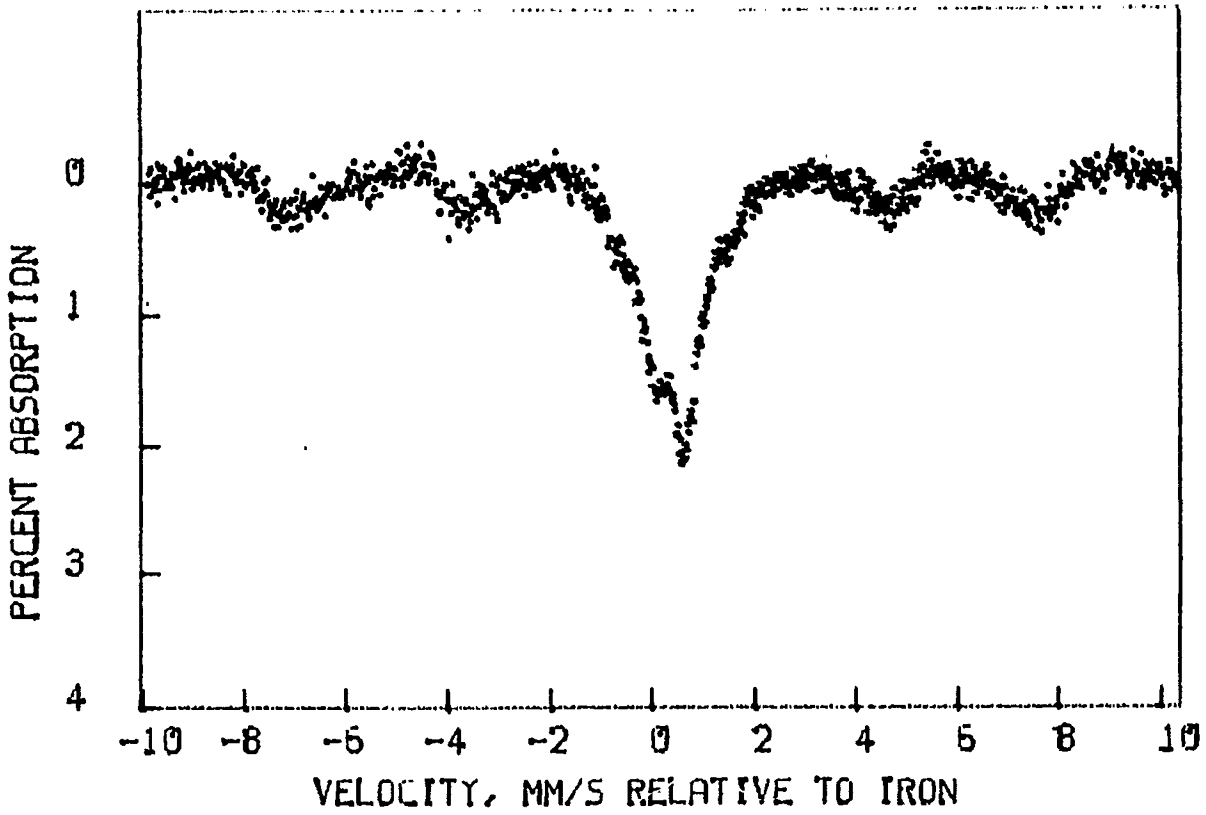

Figure 6. Moessbauer Spectrum of Fresh Fe-K-S-100

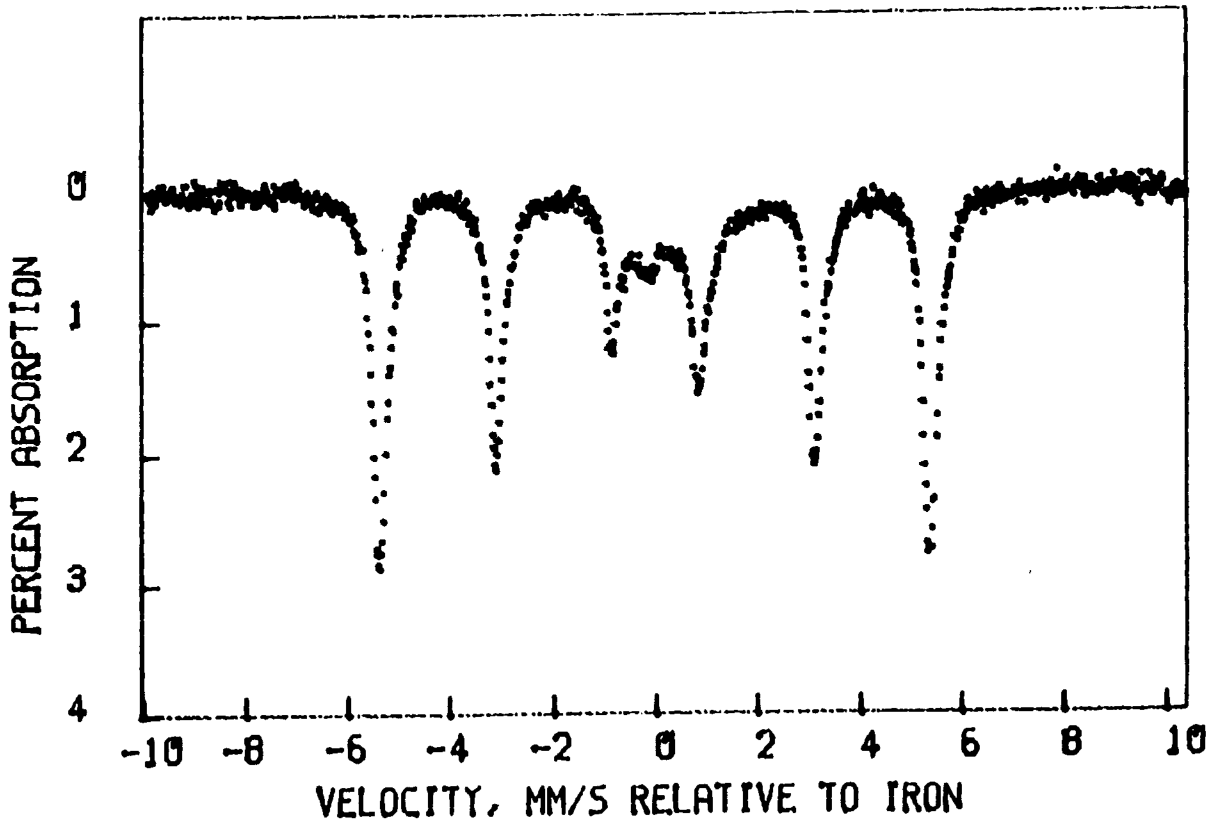

Figure 7. Moessbauer Spectrum of Reduced Fe-K-S-100

B. Task 2: Activity/Selectivity Measurements

1. Chromatographic Analysis

A complete correlation of retention times of hydrocarbons in the capillary column system recently installed was worked out. Figure 8 displays this data graphically, showing that hydrocarbons of a specific carbon number are eluted in the following time sequence:

isoalkane < alkene, alkane < alkyl benzene < aldehyde, ketones

< acetate ester < isoalcohol < alcohol < acid

2. Experimental Measurements

It was observed during the past quarter that the boride catalysts characteristically produce a relatively high molecular weight group having carbon numbers 17 to 20. This is especially pronounced in the fresh catalysts. In some tests this group appeared even before the low-molecular weight hydrocarbons became abundant. The same group has not been noticed in tests of other iron and cobalt catalysts performed on the same equipment which suggests that this is a unique characteristic, of the metal boride catalysts.

3. Future Plans

Emphasis during the next quarter will be placed on reactor testing of the unsupported iron, nitrided iron, and zeolite-supported iron catalysts. Tests at H_2/CO ratios of 2 and 1 are planned.

C. Task 3: In Situ H_2S Poisoning Measurements

Tests were run on 15% Fe/SiO_2 at 505 K, 1 atm and a space velocity of 1500 hr^{-1}. 5 ppm H_2S was added to the feed stream ($H_2/CO = 2/1$). The CO conversion dropped from 14 percent to less than two percent as the catalyst was poisoned. Breakthrough occured after six days.

Tests were also run on a potasium promoted 15% Fe/SiO_2 catalysts at a space velocity of 350 hr^{-1} and 505 K. 5 ppm H_2S was added to the feed mixture to deactivate the catalyst. Twice during the run the temperature was increased to 725 K and 66 ppm H_2S in H_2 was introduced into the reactor to speed catalyst deactivation. After 2-4 hrs the reactor was cooled to operating temperature and the reaction mixture was reintroduced to the reactor. CO conversion dropped from 7% to 2% as the catalyst deactivated.

Neither catalyst showed appreciable changes in product selectivity as poisoning occured (Figure 9). Both catalysts did exhibit a linear loss of activity with respect to sulfur coverage. That is, the unpromoted catalyst lost 90% of its initial activity after being exposed to enough sulfur to cover 90% of its active metal surface (assuming a 1:1 surface stoichiometry). Similarly after exposure to sufficient H_2S to cover 70% of its surface the promoted catalyst lost 70% of its initial activity.

During the next quarter *in situ* deactivation tests will continue on unsupported Fe catalysts. The effects of presulfiding will also be studied on

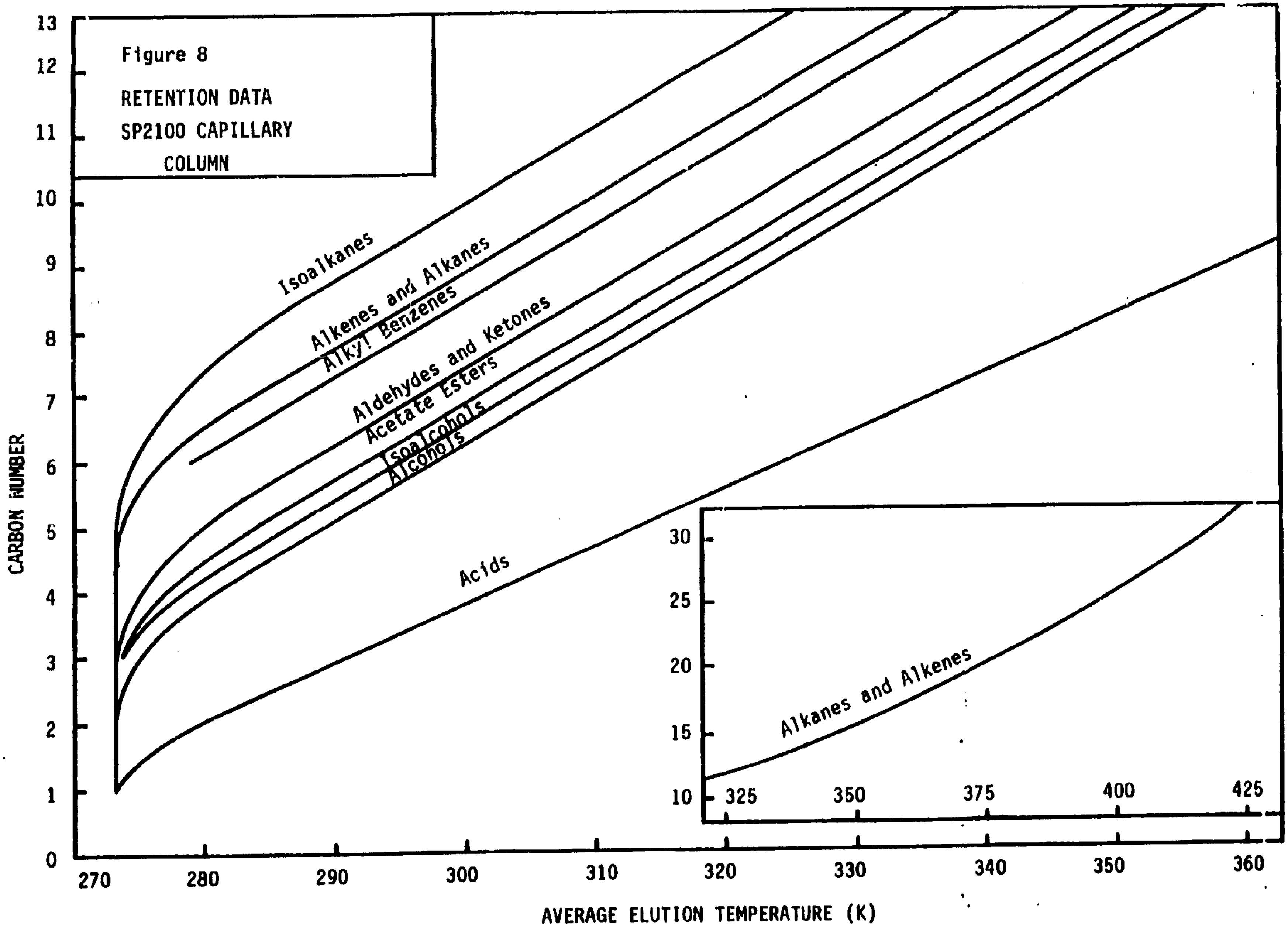

Figure 8

RETENTION DATA

SP2100 CAPILLARY

COLUMN

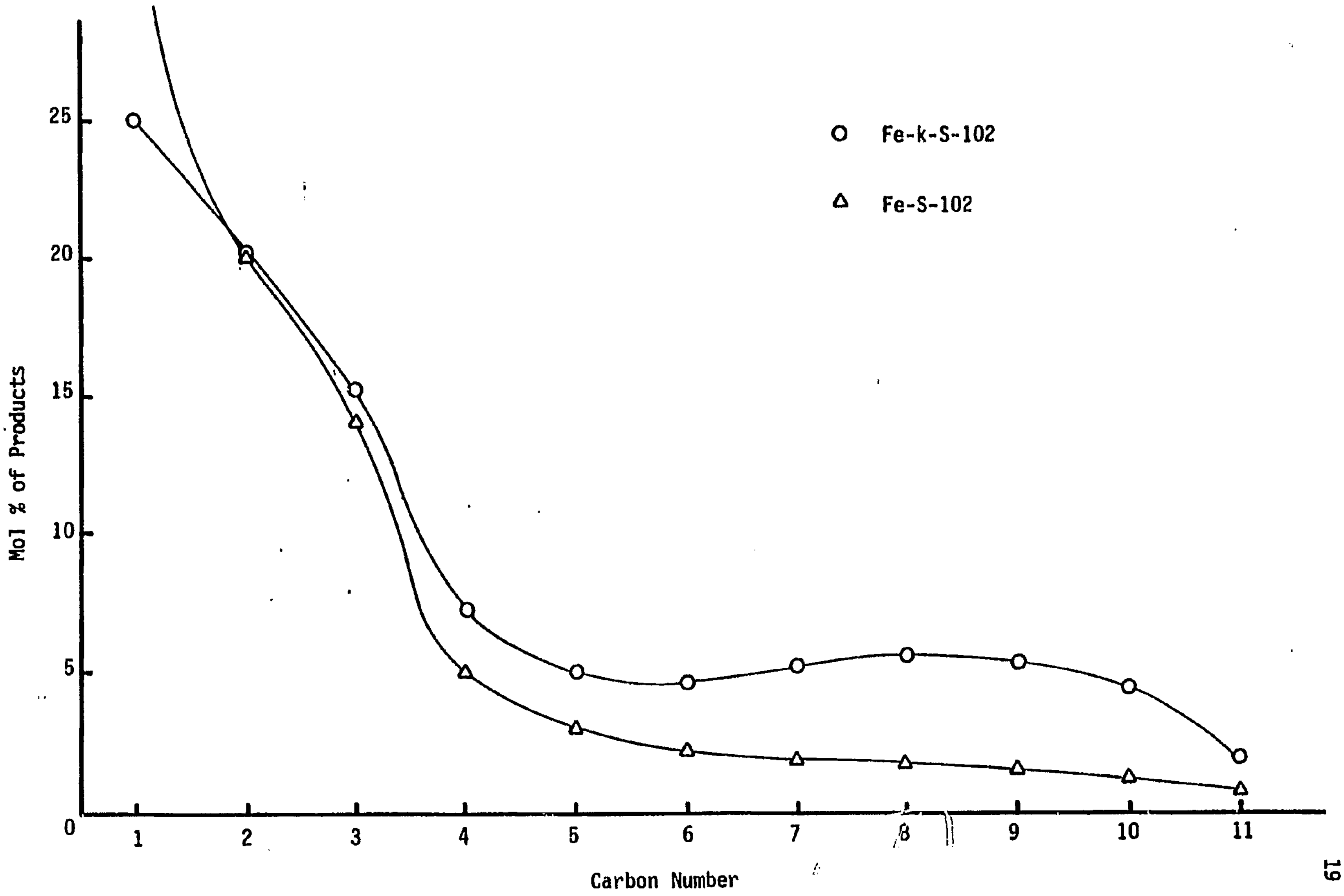

Figure 9. Product Distribution of Poisoned Fe/SiO$_2$ Catalysts.

these same catalysts.

D. Miscellaneous Accomplishments and Technical Communication

During the ninth quarter Dr. Bartholomew visited the Process Science and Engineering Division of PETC (Oct. 9) and presented a seminar on "H_2 and CO Adsorption on Co-ZSM-5 Catalysts." Gordon Weatherbee, Jeffery Rankin and Dr. Bartholomew attended the Seventh North American Meeting of the Catalysis Society held in Boston, Oct. 11-15, 1981. Dr. Bartholomew presented a paper on the "Specific Acitivty and Kinetics of CO_2 Hydrogenation on Nickel." On November 18 and 19th Dr. Bartholomew presented seminars at the Tri State Catalysis Club and at Ashland Oil Company in Ashland, Kentucky on "Methanation Kinetics" and on "Sulfur Poisoning and Carbon Deposition." Dr. Eric Moorehead of Union Oil Research visited the Department of Chemical Engineering and the Catalysis Laboratory on November 5 and presented a seminar on "The Catalytic Synthesis of Maleic Anhydride".

IV. CONCLUSIONS

1. A combination of filtration and centrifugation of freshly supported metal-boride catalysts improves their state of reduction.

2. Moessbauer studies reveal that degree of reduction to metal in unpromoted and promoted 15% Fe/SiO_2 catalysts are nearly the same. Further, these results agree well with those from O_2 titration. The Moessbauer data provide evidence that 3% Fe/SiO_2 reduces much less readily than 15% Fe/SiO_2 due to a more intimate association of iron with the support in the farmer catalyst.

3. Metal boride catalysts produce abnomally large amounts of hydrocarbons in the C_{17} to C_{20} range.

4. The activity of Fe/SiO_2 catalysts declines linearly with respect to sulfur coverage. Addition of H_2S to the reactant mixture at 5 ppm concentration does not cause appreciable changes in product selectivity over Fe/SiO_2 catalysts.

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