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INVESTIGATION OF SULFUR-TOLERANT CATALYSTS FOR SELECTIVE SYNTHESIS OF HYDROCARBON LIQUIDS FROM COAL-DERIVED GASES. ANNUAL TECHNICAL PROGRESS REPORT, SEPTEMBER 19, 1981-SEPTEMBER 18, 1982

BRIGHAM YOUNG UNIV.
PROVO, UT

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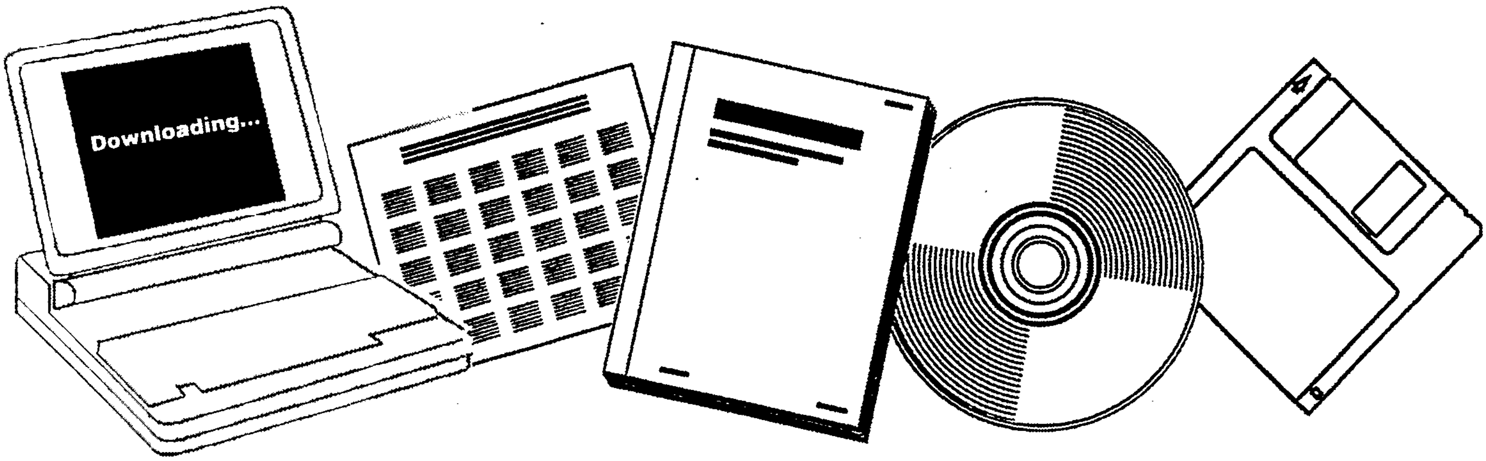

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INVESTIGATION OF SULFUR-TOLERANT CATALYSTS FOR SELECTIVE SYNTHESIS OF HYDROCARBON LIQUIDS FROM COAL-DERIVED GASES

Annual Technical Progress Report
For Period September 19, 1981 to September 18, 1982

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Brigham Young University
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PREPARED FOR THE UNITED STATES
DEPARTMENT OF ENERGY

Under Contract No. DE-AC22-79ET14809

FORWARD

This report summarizes technical progress during the third year (September 19, 1981 to September 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. Bowman and Dr. Bartholomew were the principal authors. Carla Anderson provided typing services.

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ABSTRACT

During the third year the preparation of boride-promoted catalysts was improved, resulting in more active catalysts. Unsupported and 15% iron on silicalite catalysts were also prepared. Moessbauer spectra were obtained for several iron catalysts which showed that catalysts prepared from carbonyls yield higher metal dispersions. Activity/selectivity tests on iron and cobalt catalysts show that boride-promoted cobalt catalysts exhibit a high selectivity to C_5 - C_{15} hydrocarbons. Zeolite-supported iron catalysts show promise as producers of chemical feedstocks. *In situ* poisoning tests produced a linear loss of activity with increasing sulfur coverage. The addition of potassium or boron extends the life of Fe/SiO_2 catalysts; indeed an iron boride catalyst showed only 5% deactivation after five days.

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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 caried 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 phenomen 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 rreaction 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 follwed 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-Suppport Combination	Unpromoted	Promoted	Additive Pretreatment			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(2)[b]	x	x	7
Fe/Al_2O_3	x					1
Fe/ZSM-5	x					1
Fe/Silicalite	x	x	x[d]			3
Fe/C	x					1
					Total	26

[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 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 <u>in situ</u> 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/Al_2O_3
	Effects of metal	Fe, 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
Effects of Sulfiding	Fe, Fe/SiO_2 (unpromoted and K_2O promoted)
Effects of Nitriding, Boriding	Nitrided and Borided Fe, Fe/SiO_2
Effects of Pressure (Runs at 25 atm)	5 "best" catalysts based on runs at 1 atm
Kinetics of Deactivation	Fe/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 rreactor 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

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 500 K, 1 atm (again the 4-5 most promising catalysts also at 25 atm), $H_2/CO = 2$ and space velocities of 200 to 1000 hr^{-1} with 5 ppm H_2S in the reactant mixture. The analysis of hydrocarbons will be made intermittantly using chromatography over a period of 24 hours. During the majority of tests, each catalyst will be housed in a Pyrex differential tubular reactor cell.

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. Since Tasks 1, 2 and 3 are behind schedule, a no-cost-increase extension has been obtained to June 1, 1983 at which time the final report will be written.

Task 1:

Preparation of supported and unsupported Fe, Co and Ni boride catalysts was completed. Fe/Silicalite, Fe/Al_2O_3, Fe/ZSM-5, Fe/C and unsupported Fe and Co catalysts were prepared. Improved techniques for preparation of supported boron-promoted catalysts resulted in samples with much higher surface areas. Two carbonyl-derived silica-supported catalysts were received from Corning Glass Works for testing.

Moessbauer spectra were obtained for many of the samples under study. Results agreed well with O_2 titration measurements. Carbonyl-derived catalysts appear to be more highly dispersed than conventionally prepared samples. Spectra of boron-promoted catalysts also reveal two unidentified peaks which may be caused by the presence of borides on the catalyst surface.

Task 2:

A capillary column and new gas sampling valves for hydrocarbon analysis were installed and are in operation. Tests were performed on the two carbonyl-derived catalysts and a boron-promoted silica-supported cobalt catalyst. The carbonyl catalysts deactivated rapidly, but steady state activities were comparable with conventional catalysts due to their higher initial activity. The activity of the boron-promoted catalyst increased rather than decreased with time. Silica supported cobalt boride also displayed a 70% selectivity to C_{5+} hydrocarbons.

Task 3:

In situ deactivation tests of unsupported Fe, Fe/SiO_2 and Co/SiO_2 catalysts show that deactivation is dependent on the concentration of H_2S. Lower concentrations appear to deactivate the catalyst more severely per given sulfur exposure. A boron-promoted Fe catalyst showed almost no deactivation when exposed to 5 ppm H_2S. The addition of potassium also slows the rate of deactivation of Fe due to sulfur poisoning.

Misc. Accomplishments

During the past year the PI and students attended 9 meetings, presented 7 papers (3 directly concerned with this contract) and 4 seminars (3 directly concerned with this contract), received 9 visitors and submitted 2 papers in connection with this contract.

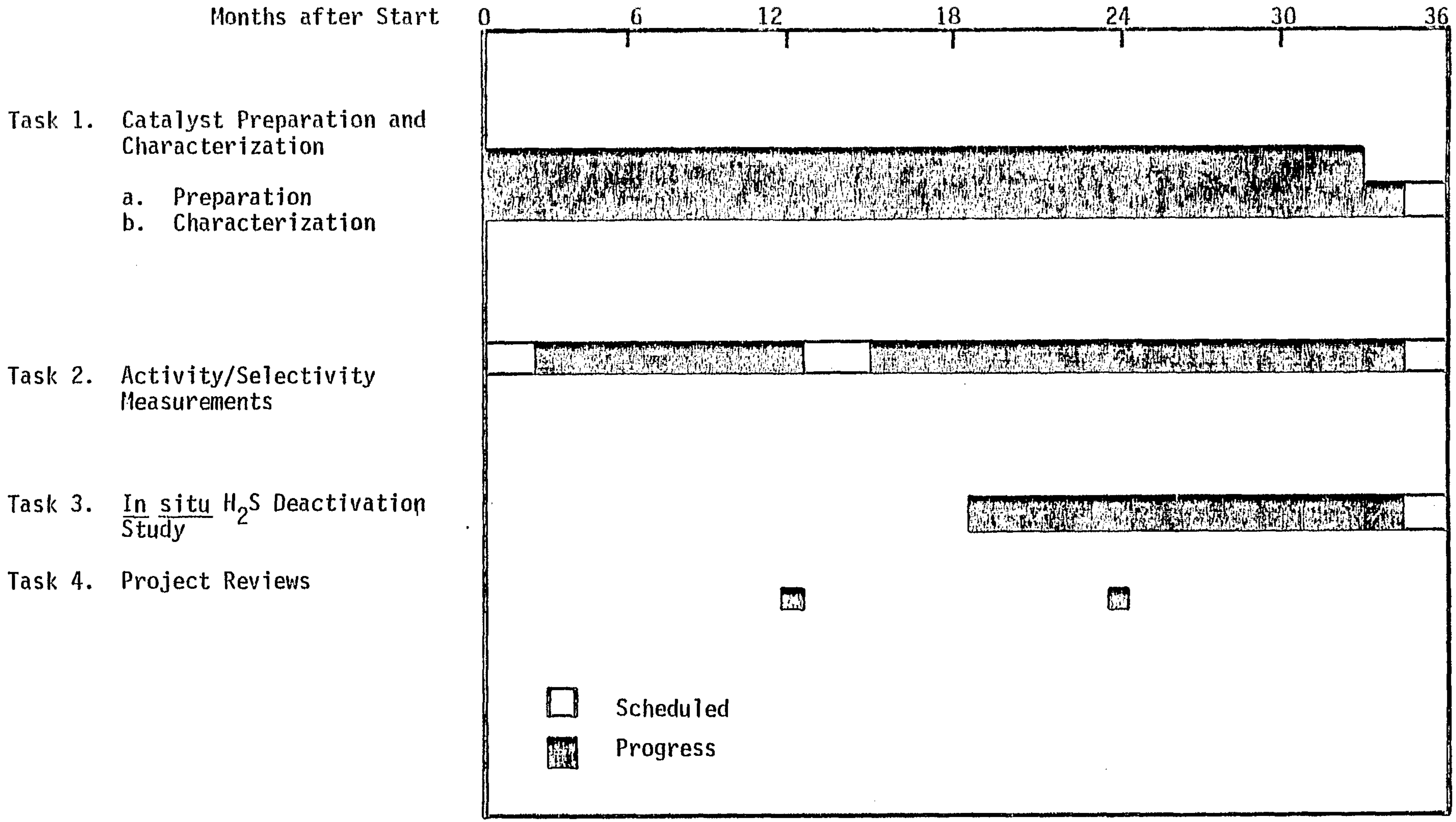

Figure 1. Schedule of Proposed Research Activities and Progress.

III. DETAILED DESCRIPTION OF TECHNICAL PROGRESS

A. Task 1: Catalyst Preparation and Characterization

1. Catalyst Preparation

Three more iron catalysts were prepared and readied for testing. These were an unsupported iron (designated Fe-100), 15% iron/alumina (designated Fe-A-100) and a 15% iron/silicalite (designated Fe-L-101). The silicalite-supported catalyst was prepared by impregnation to incipient wetness of a silicalite support sample ELZ-115 received from Union Carbide. After drying in air at 100°C, the catalyst was crushed to a fine powder and stored.

Preparation of iron/alumina by impregnation was unsuccessful, yielding very large, hard lumps of material with extremely small pore volume. The preparation therefore followed the technique reported by Vannice, Carter and Savini (4,5). The appropriate amounts of support and reagent grade $Fe(NO_3)_3 \cdot 9H_2O$ were weighed out and finely crushed in a mortar and pestle. After physically mixing the materials, they were placed in a muffle furnace and slowly heated to 100°C. This melted the nitrate into the alumina; after 2 hours the temperature was raised to 200°C to drive off any remaining water. After drying, the catalyst was crushed and stored. Unsupported iron was prepared using the same heat treatment as that in the preparation of iron/alumina.

Work was continued on improving the preparation techniques for supported metal borides. A combination of filtration and centrifugation was developed and the new catalysts appeared to be of much higher quality than earlier samples. Limiting H_2 reduction heating rates to less than 2°C/min greatly increased active surface areas as evidenced by higher H_2 uptakes.

Two catalysts samples were received from Corning Glass Works which were prepared in their laboratory. They consisted 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 was felt that these samples could provide important data on metal-support and crystallite size effects in Fischer-Tropsch synthesis.

2. Catalyst Characterization

Table 3 lists chemisorption data obtained to date for iron and cobalt catalysts. As can be seen, cobalt is generally more dispersed, absorbs CO more readily and also chemisorbs CO_2 to a much greater extent than iron. Of particular interest are the low extents of reduction determined from the O_2 titrations and the unexpectedly high percent dispersion of 41% for the 3% Co/SiO_2 (Co-S-103). To our knowledge there are no previous reports of such highly dispersed cobalt!

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. Samples have also been sent for ESCA and chemical

TABLE 3

H_2, CO, CO_2 and O_2 Uptakes on Iron and Cobalt Catalysts After 36-Hour Reductions in Hydrogen

Catalyst Code	% Metal Loading	H_2 Uptake[a] (μmoles/g)	CO Uptake[b] (μmoles/g)	CO_2 Uptake[c] (μmoles/g)	O_2 Uptake[d] (μmoles/g)	%[e] Reduction	% D[j]
Fe-S-102[f]	15	20.19	3.52	--	--	--	--
Fe-S-102	15	16.02	12.16	1.09	1588	79	1.5
Fe-S-103	3	2.36	1.21	--	91.6	23	3.9
FeK-S-100[g]	15	9.11	4.94	6.56	856	42.5	1.7
FeB-S-101[h]	10	6.37	--	--	--	--	--
CoS-101	3	13.24	24.80	--	242	71.2	7.2
Co-S-102	15	52.39	89.94	17.87	590	35	11.85
Co-S-103	3	18.76	55.50	--	60.5	18	41.36
CoB-102[b]	--	47.5	32.6	--	--	--	--
CoB-S-100[i]	15	6.20	4.11	--	--	--	--
FeB-101	--	4.13	1.85	--	--	--	--
CoB-S-101	15	21.19	24.37	--	--	--	--
FeB-S-105	15	10.72	3.58	--	--	--	--
C6[k,l]	7.0 (Fe)	20.61	2.13	--	--	100	1.6
C7[k,m]	3.9 (Fe)	17.25	12.96	--	319	88	9.4

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[a] At 298 K
[b] At 298 K
[c] At 373 K
[d] At 673 K
[e] Based on Fe_2O_3 or Co_3O_4 stoichiometry
[f] After 20 hour reduction in H_2
[g] Containing 3% K_2O promoter
[h] Containing Boride promoter
[i] After 12 hour reduction in H_2
[j] Percent dispersion or percent exposed
[k] Carbonyl derived catalysts from Corning Glass Works.
[l] Calcined at 773 K
[m] Calcined at 473 K

analysis. TEM data indicate that boron-promoted catalysts are made up of small, uniformly sized particles.

Moessbauer spectra were obtained for many of the iron catalysts being studied. Figure 2 shows the spectrum of fresh 15% Fe on Silica (Fe-S-102). 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. 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, having 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 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. A smaller fraction of recoil-free atoms was evident for the Fe-S-103 catalyst, a factor 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.

Two carbonyl-derived iron catalysts from Corning Glass Works were also tested. The six-peak spectrum in Figure 8 for the catalyst calcined at 500°C is evidence of large particles of Fe_2O_3, to be expected from such high temperature treatment. Moreover, the characteristic six line spectrum for metallic iron in Figure 9 shows that these particles were nearly 100% reduced to that metal after 36 hour reduction in H_2 at 450°C. Figures 10 and 11 for the fresh and reduced 200°C calcined catalyst are poorly resolved, even after over a week's time in the Moessbauer beam. Considering that the iron loading on the catalyst is about 4% one would expect much sharper lines to appear in the spectrum, behavior which again suggests that the recoil free fraction is considerably lower. Nonetheless, chemisorption measurements provided evidence of high reducibility and dispersion for this catalyst as evidenced by the H_2 chemisorption and O_2 titration data in Table 3 for catalyst C7. The calculated dispersion of 9.4% is a factor of 3 higher than for the corresponding impregnated catalyst. Moreover its extent of reduction is much greater. This shows the significant possibilities for preparing well-dispersed, highly-reduced catalysts by carbonyl preparations. Repeated CO uptake on catalyst C6, together with O_2 titration is being performed presently in our laboratory. This will provide a check on the abnormally low CO/H ratio of catalyst C6.

Spectra for boron-promoted catalysts are shown in Figures 12-15. Both supported and unsupported samples reduced 36 hours in H_2 at 400°C (Figs. 12-13) show the typical six line spectrum of metallic iron with two unidentified peaks superimposed over the middle two peaks. This doublet could possibly be

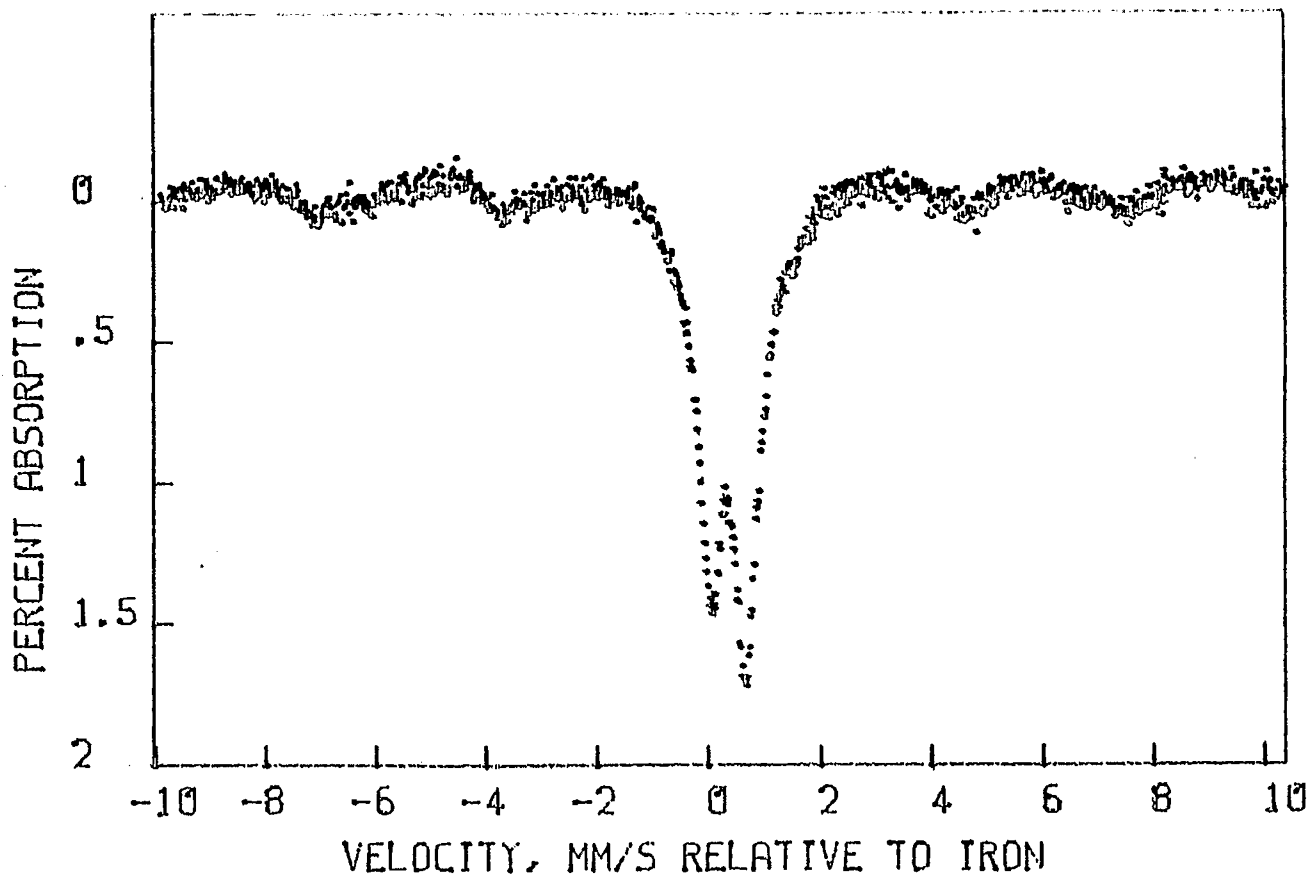

Figure 2. Moessbauer Spectrum of Fresh Fe-S-102

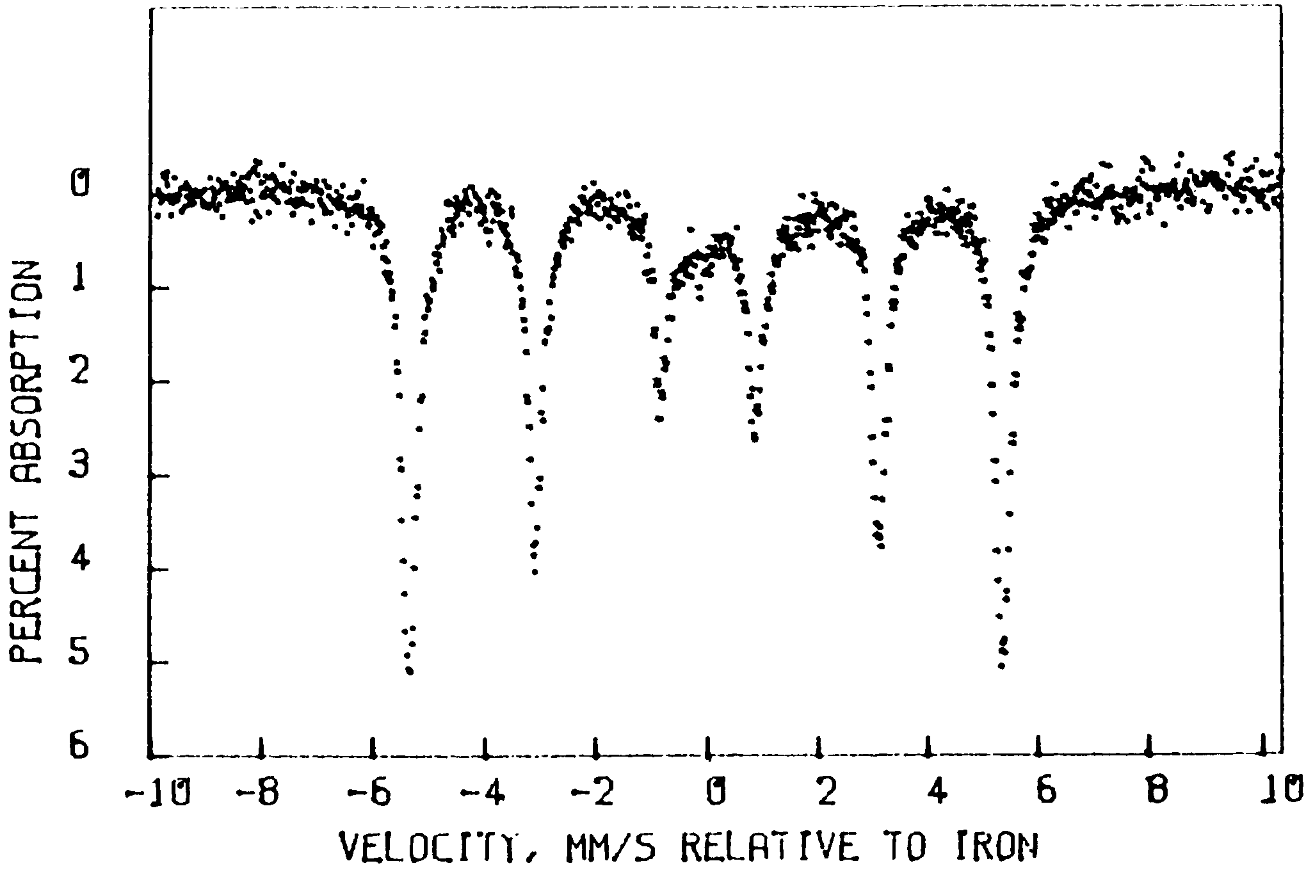

Figure 3. Moessbauer Spectrum of Reduced Fe-S-102

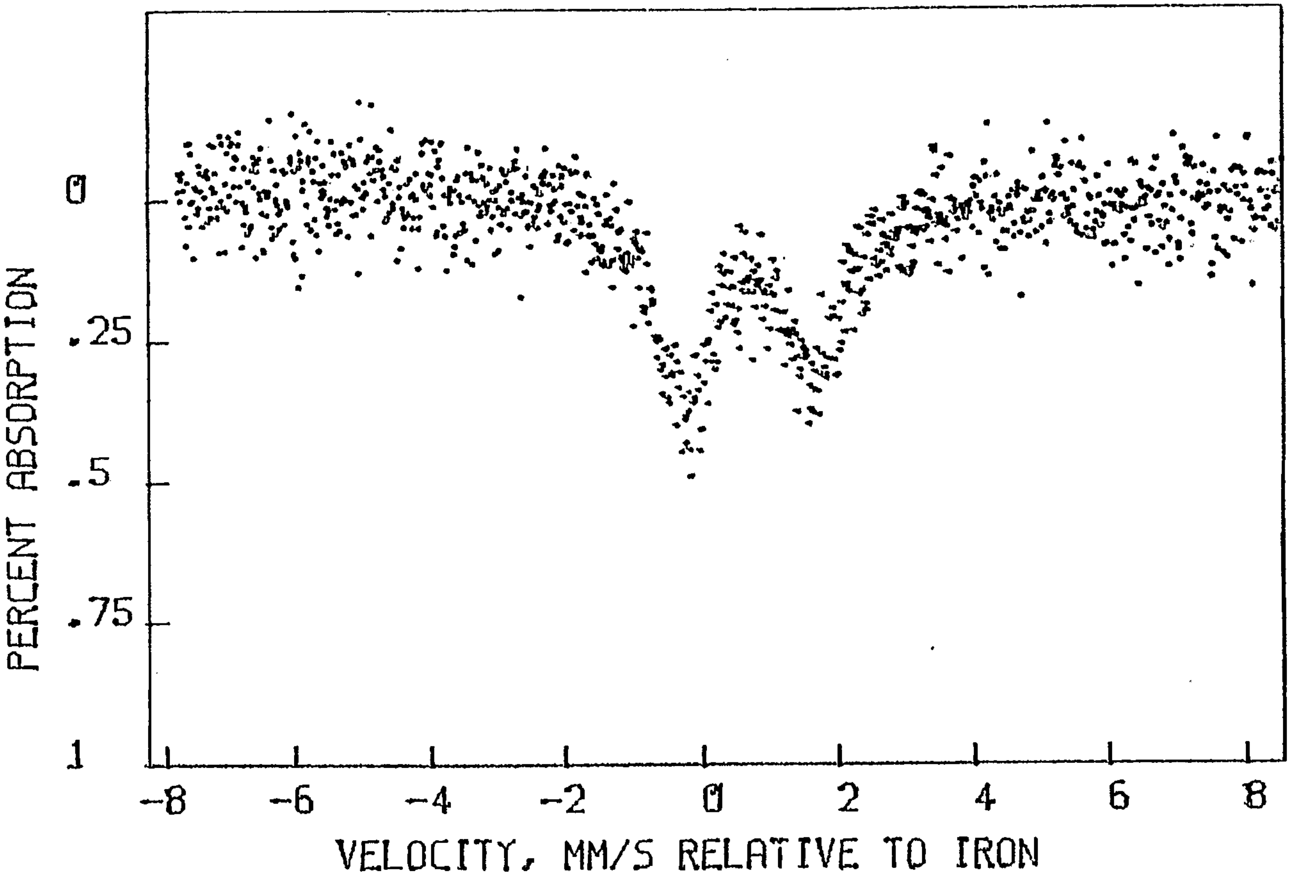

Figure 4. Moessbauer Spectrum of Fresh Fe-S-103

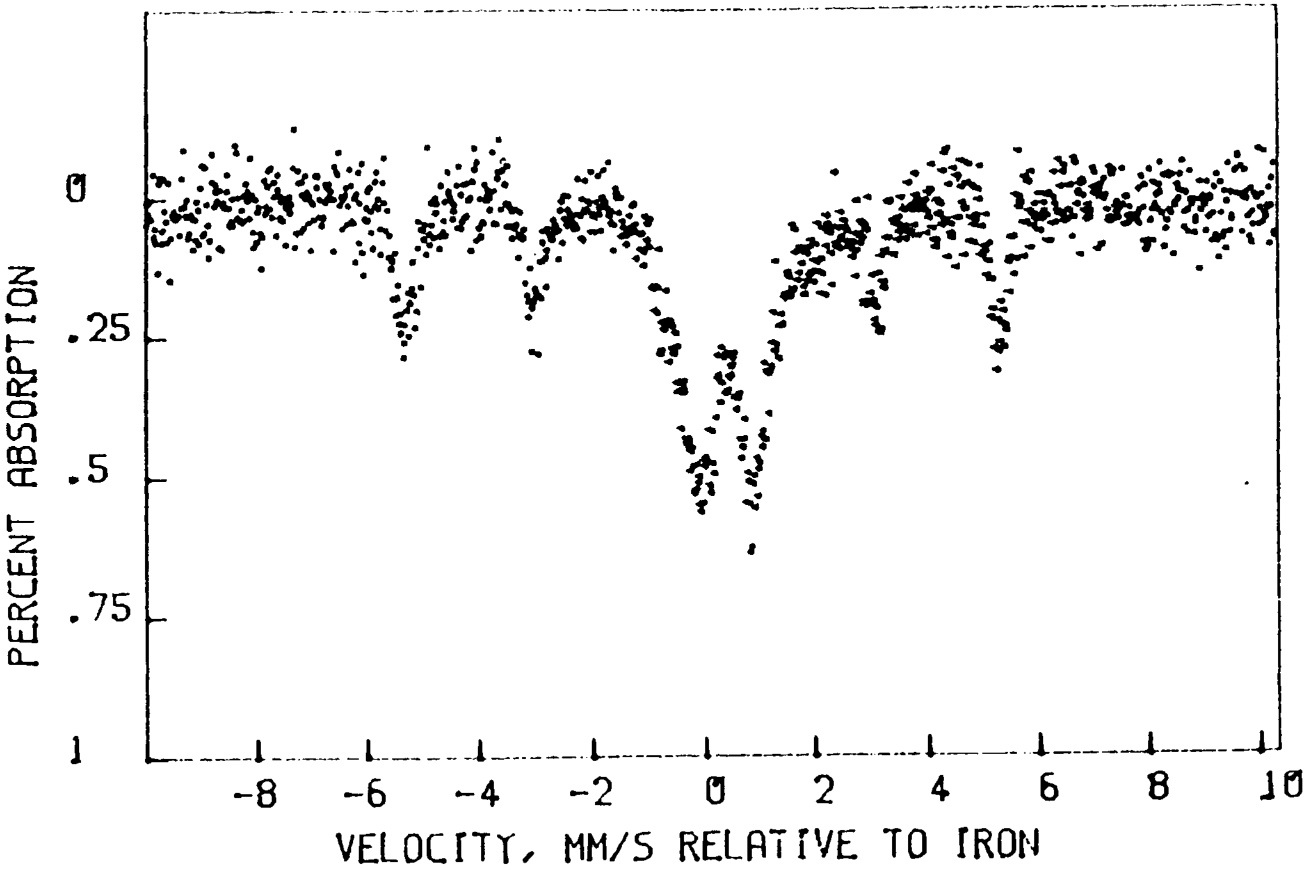

Figure 5. Moessbauer Spectrum of Reduced Fe-S-103

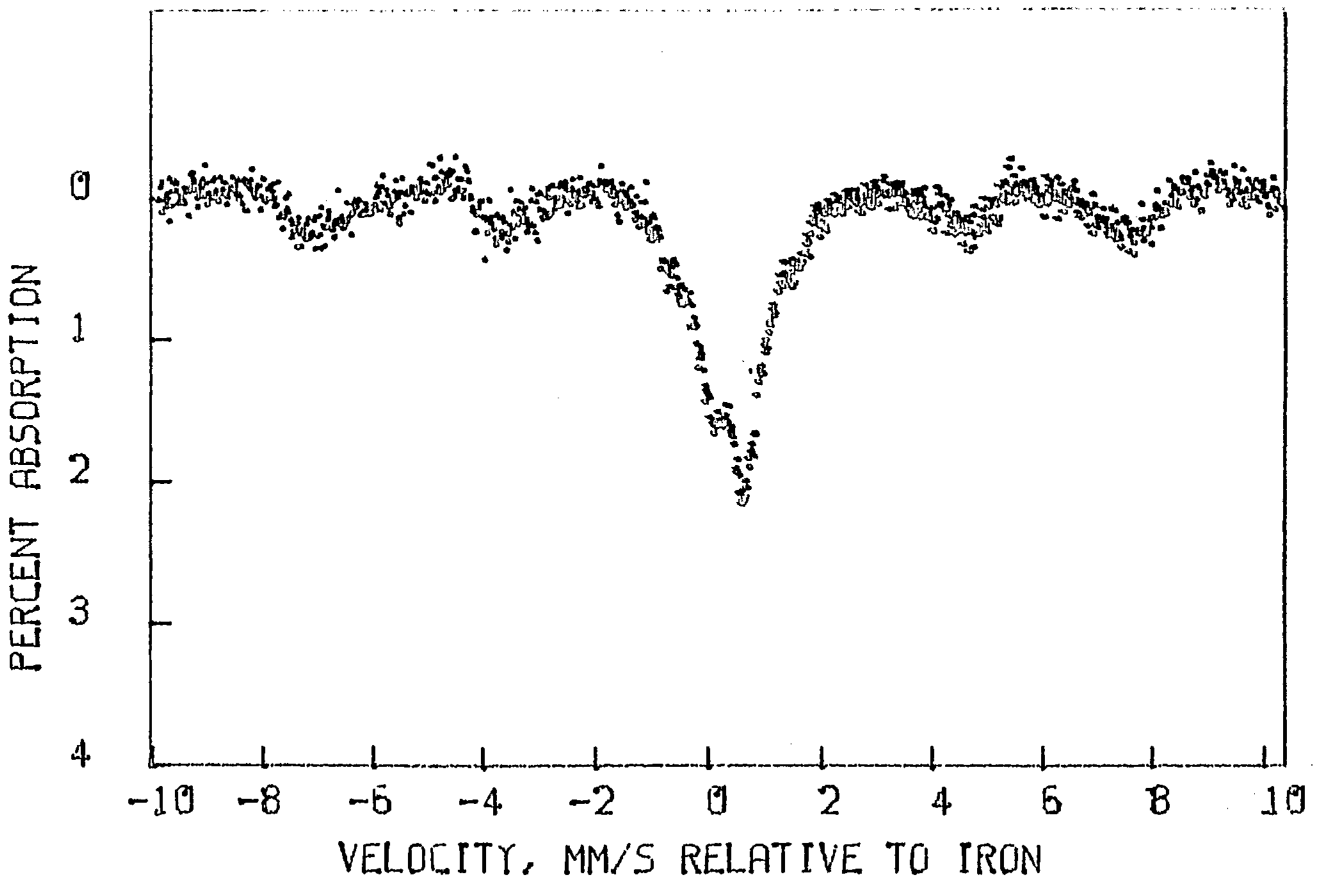

Figure 6. Moessbauer Spectrum of Fresh Fe-K-S-100

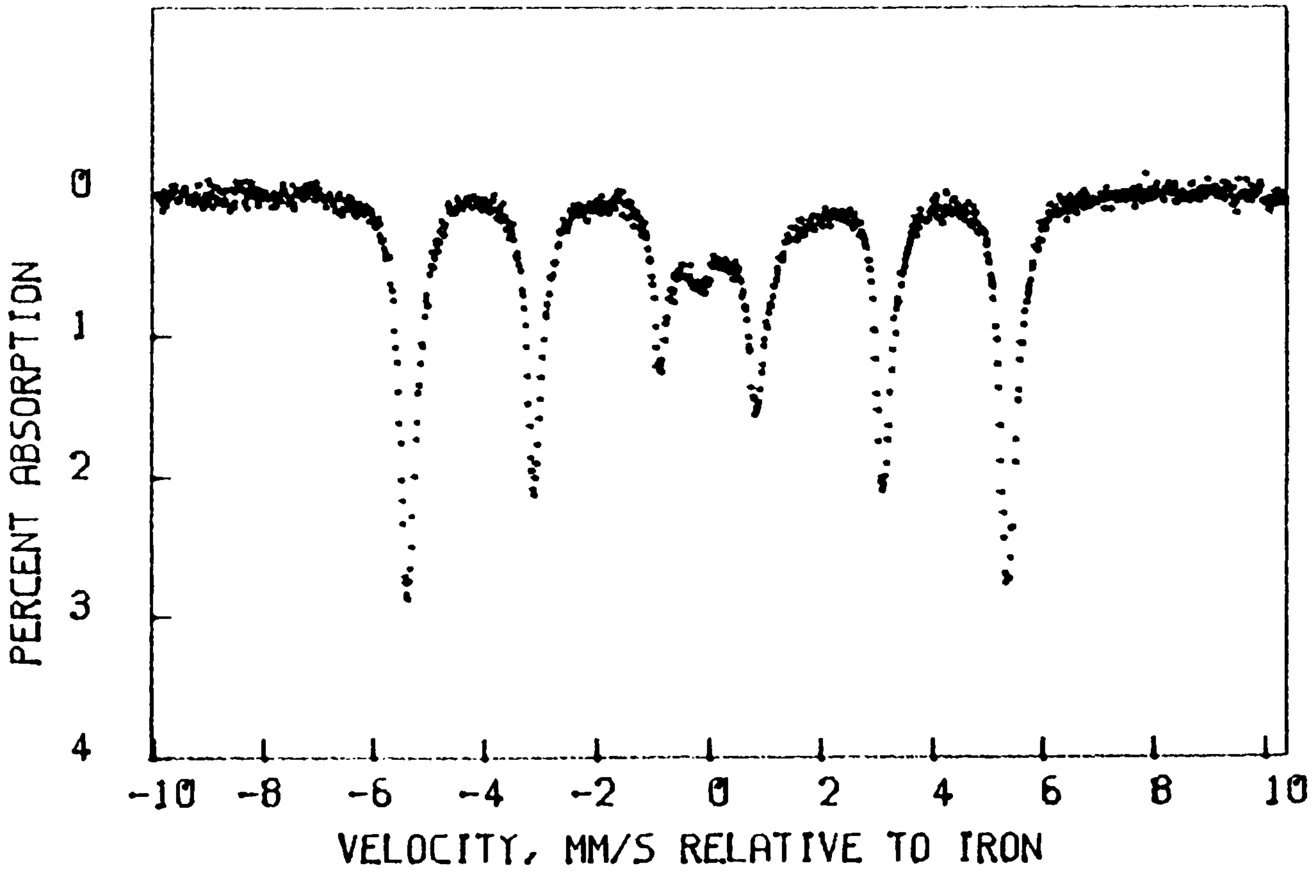

Figure 7. Moessbauer Spectrum of Reduced Fe-K-S-100

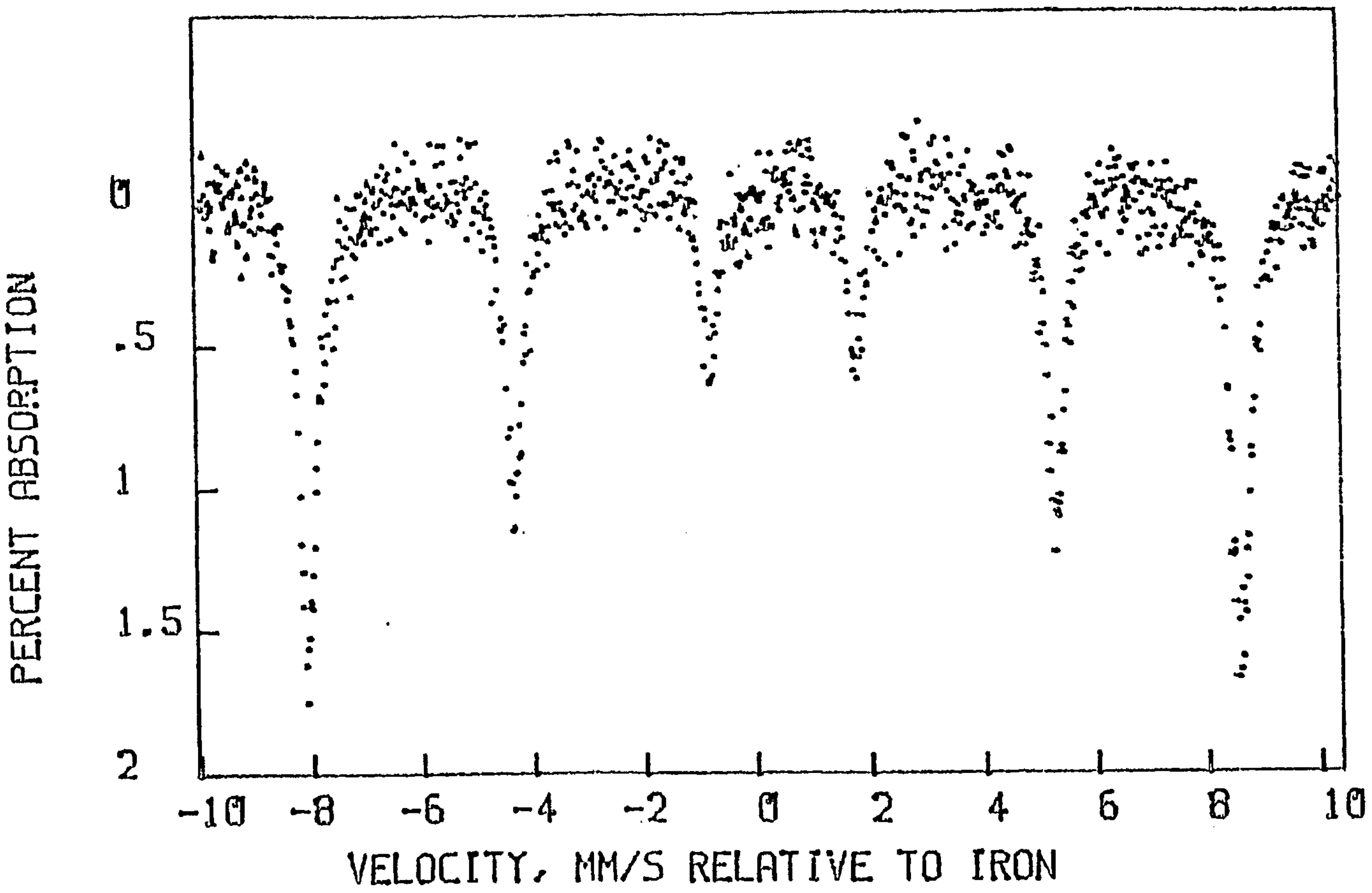

Figure 8. Moessbauer Spectrum of Fresh 500^{o}C Calcined Fe/SiO$_2$ (carbonyl derived - C6) Catalyst.

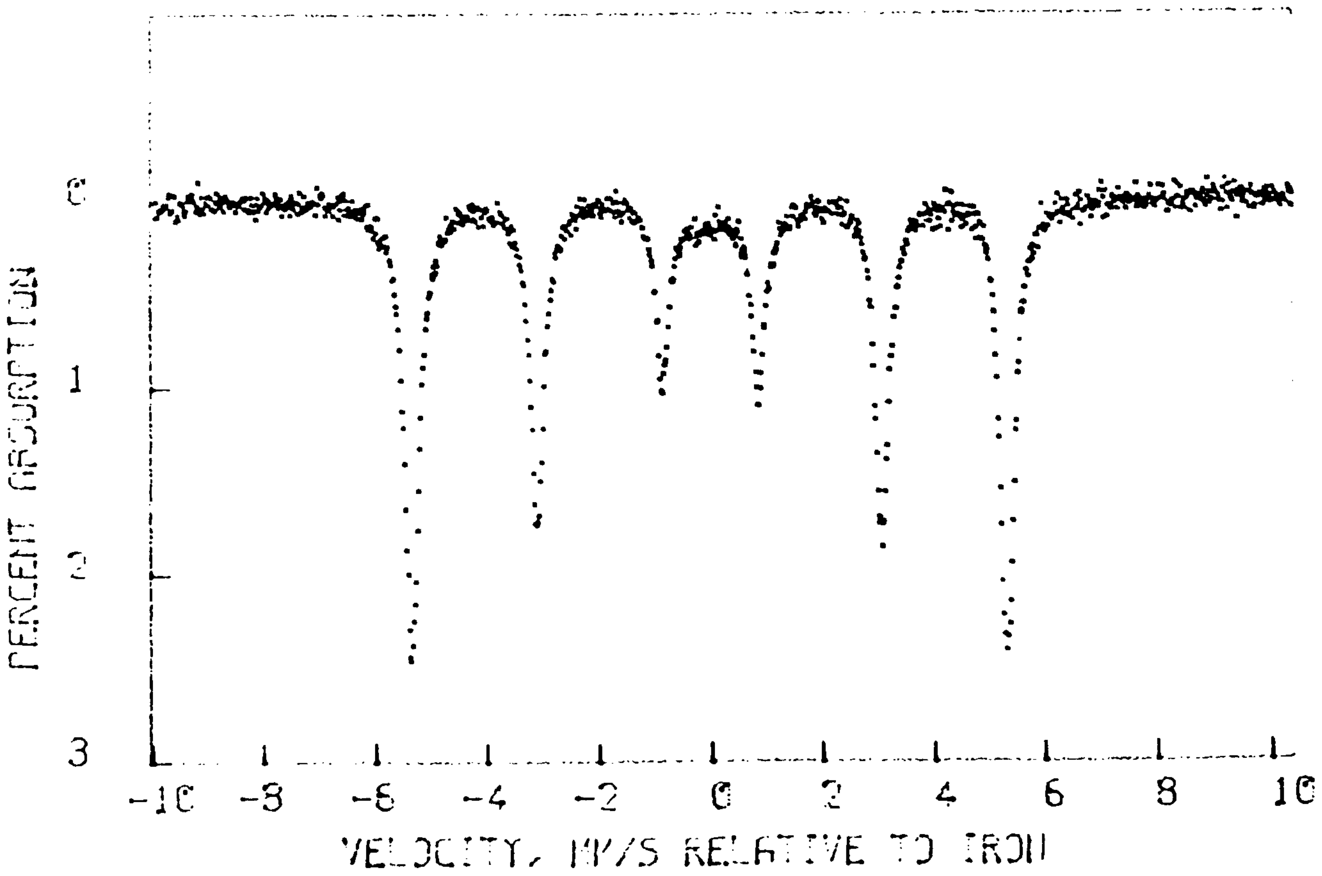

Figure 9. Moessbauer Spectrum of Reduced 500°C Calcined Fe/SiO_2 (C6) Catalyst.

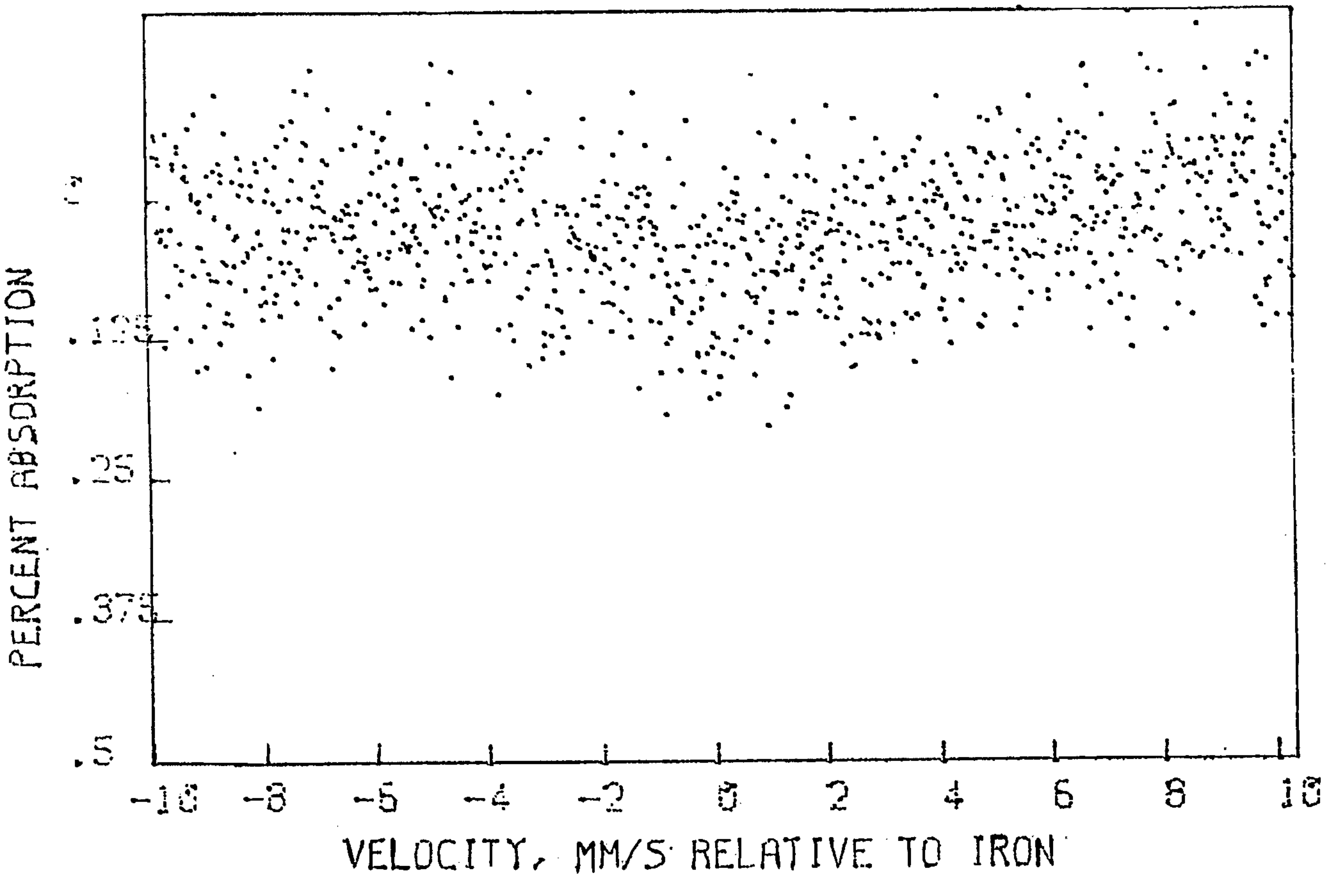

Figure 10. Moessbauer Spectrum of Fresh 200°C Calcined Fe/SiO_2 (C-7) Catalyst

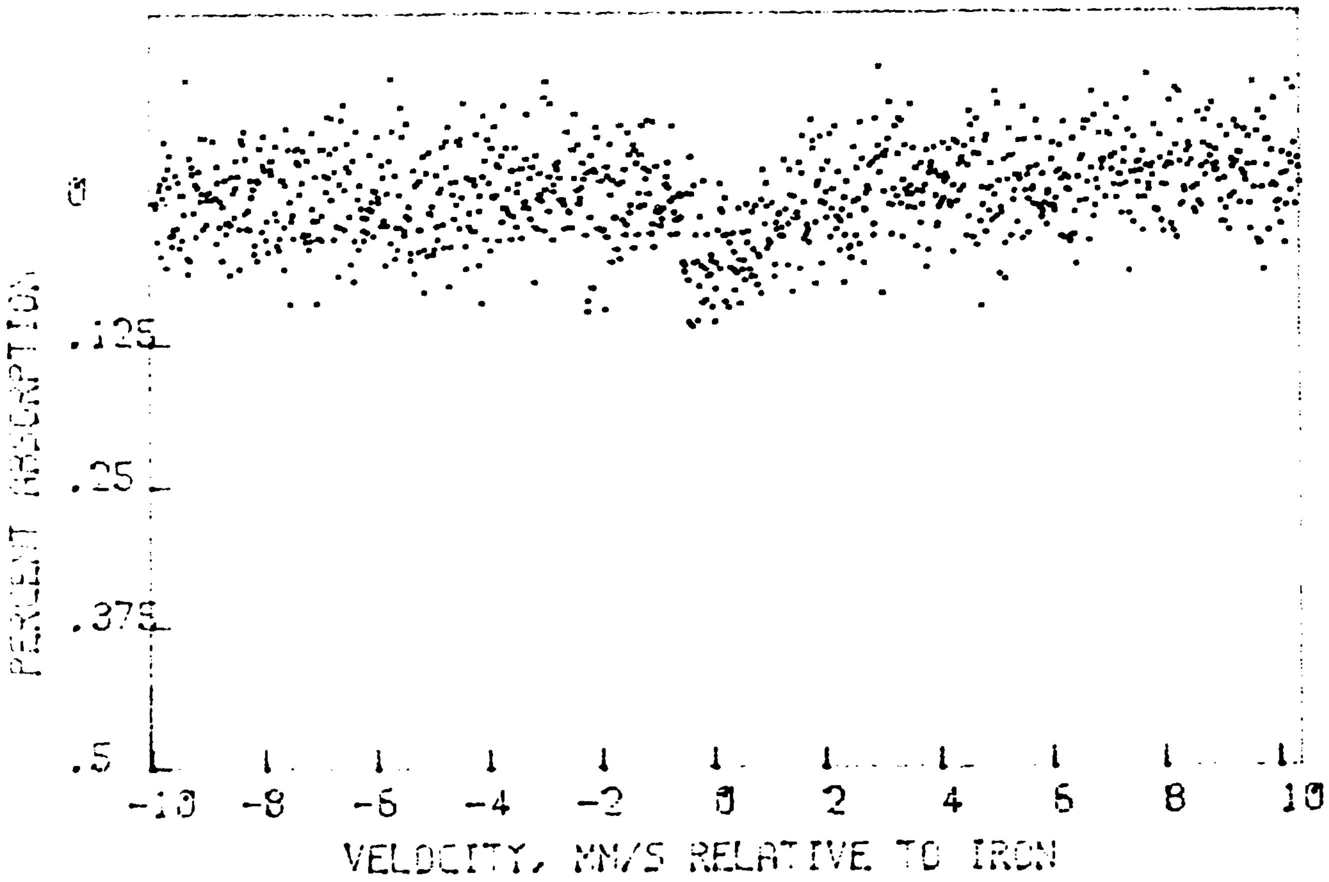

Figure 11. Moessbauer Spectrum of Reduced 200°C Calcined Fe/SiO$_2$ (C7) Catalyst

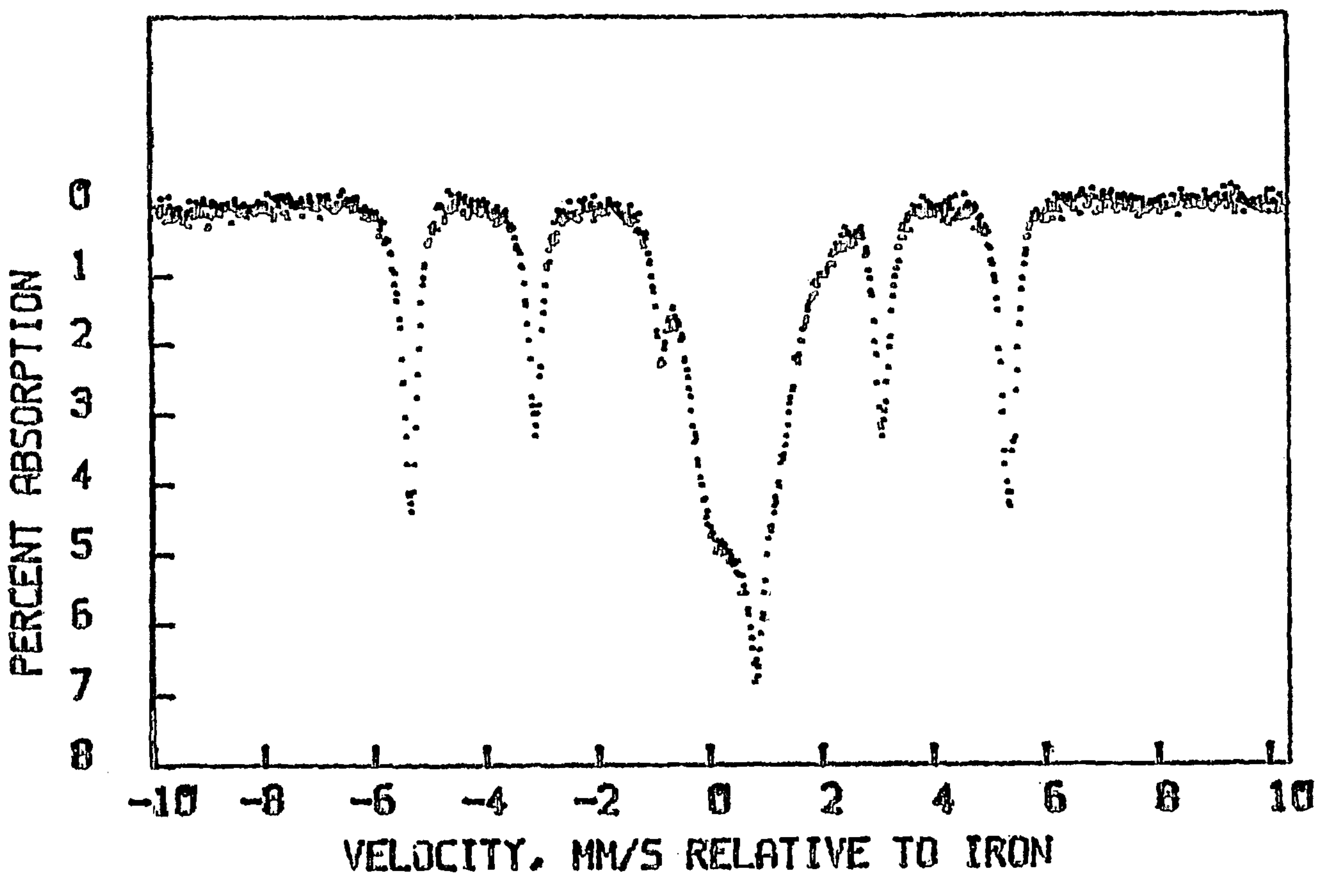

Figure 12. Moessbauer Spectrum of Fe B-101 Reduced 36 hrs. at 673 K.

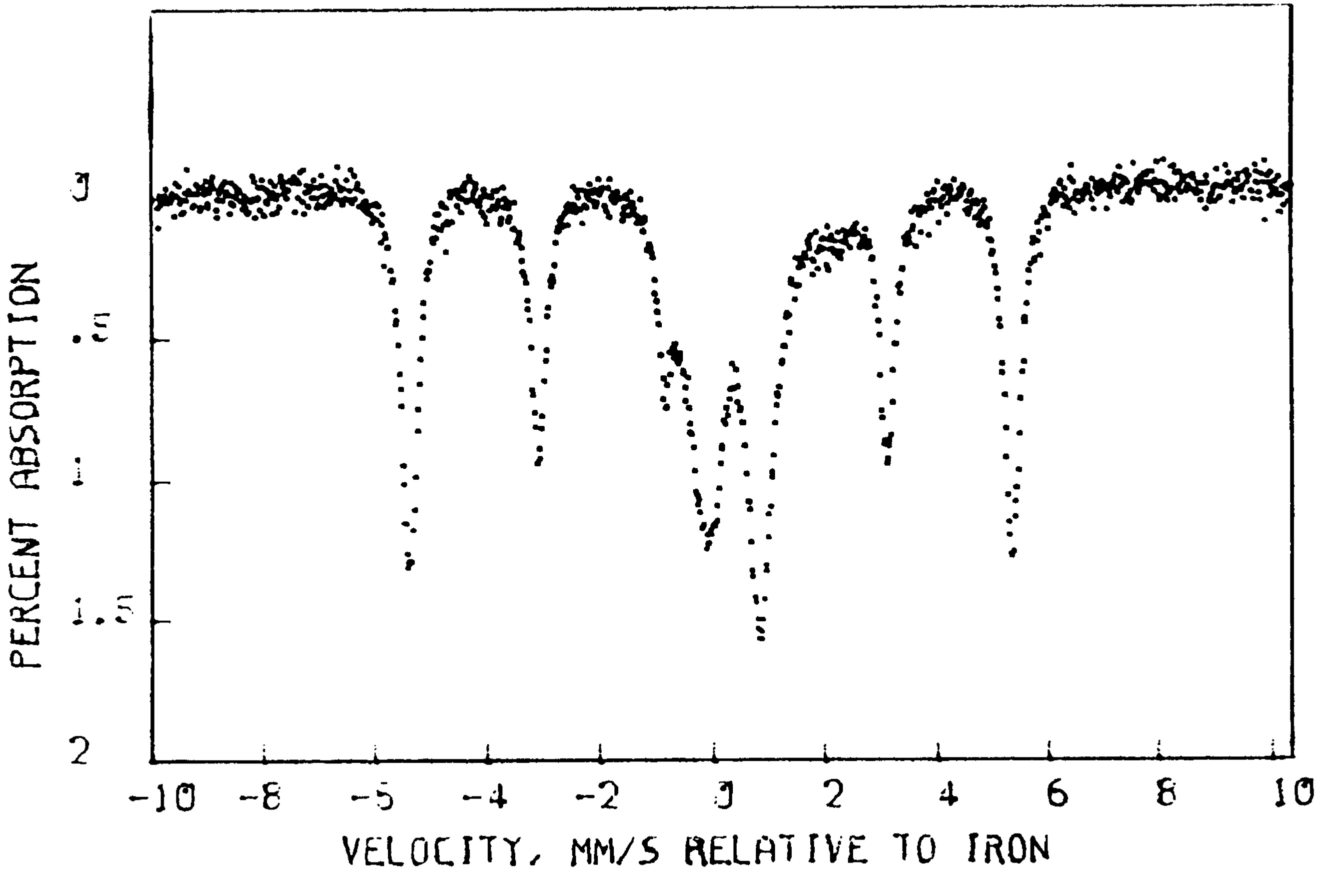

Figure 13. Moessbauer Spectrum of Fe B-S-105 Reduced 36 hrs. at 673 K.

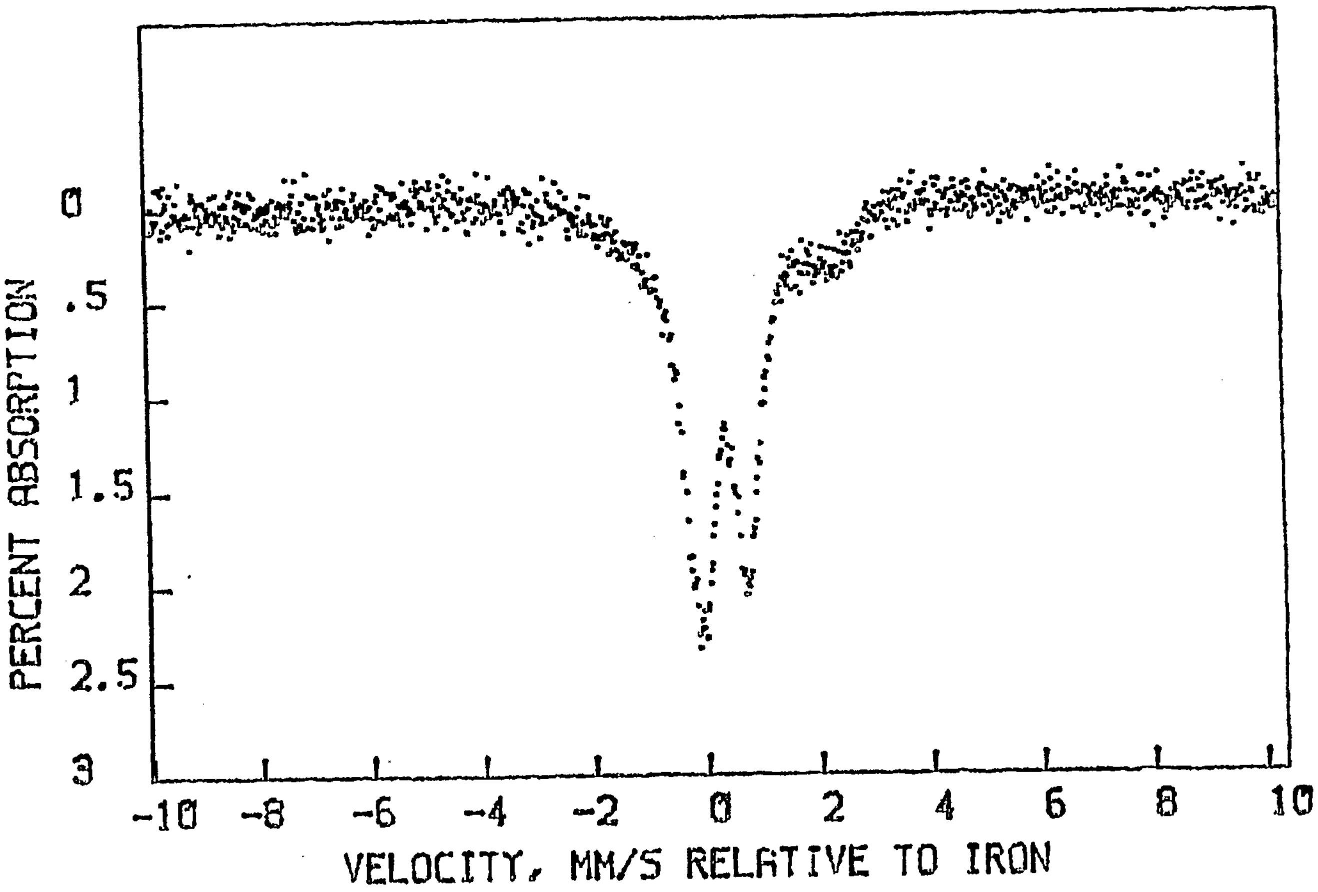

Figure 14. Moessbauer Spectrum of Chemically Reduced Unwashed Fe B-103.

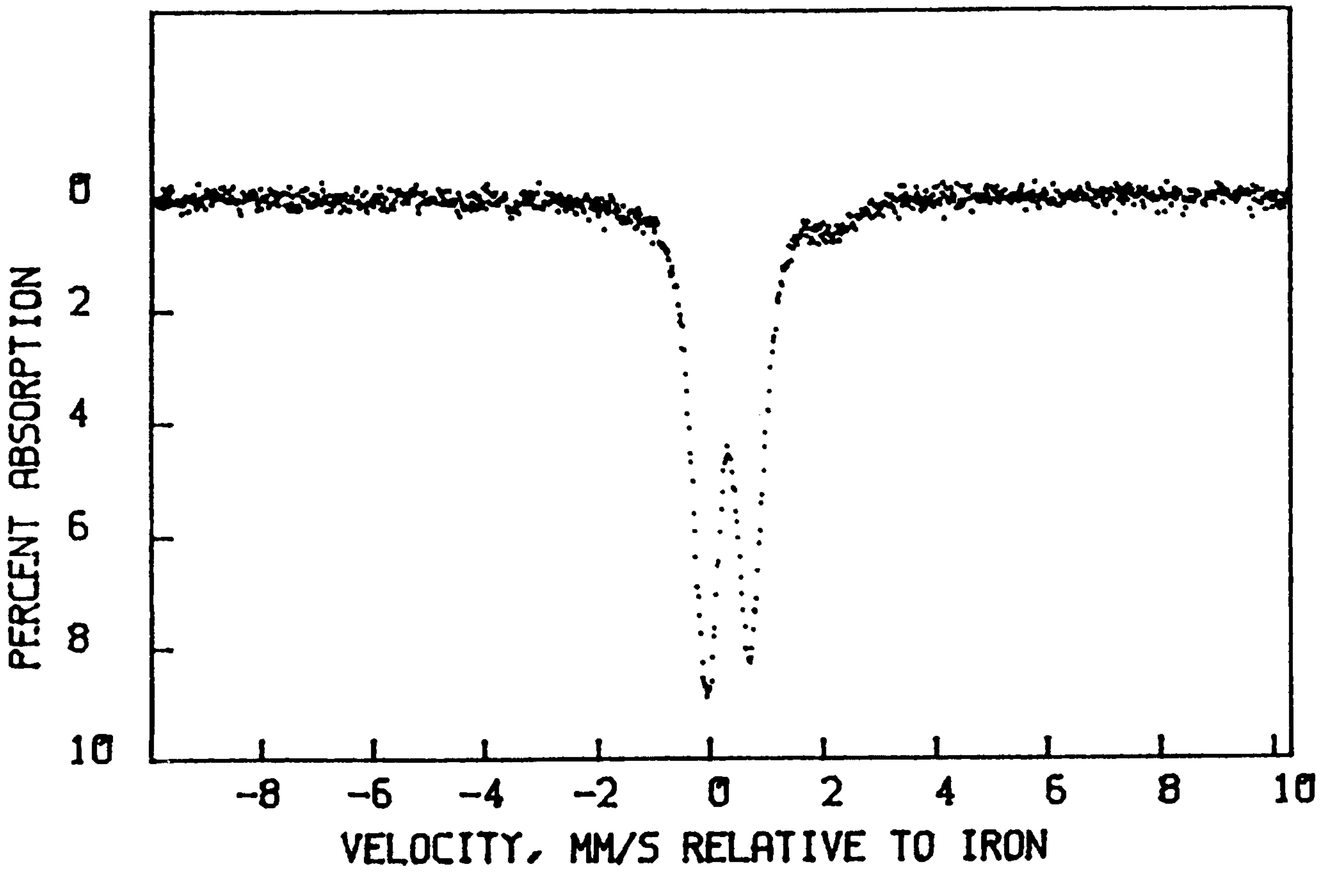

Figure 15. Moessbauer Spectrum of Chemically Reduced and Washed FeB-103.

caused by the boron promoter. Figures 14 and 15 show spectra for freshly chemically reduced (washed and unwashed) unsupported Fe-B catalysts. Again two unidentified peaks appear along with the characteristic doublet for small particles of Fe_2O_3. X-ray and low temperature Moessbauer studies are needed to resolve the unidentified peaks.

From BET measurements of boron-promoted iron and cobalt catalysts (unsupported) BET surface areas of 67.3 m^2/g and 90.9 m^2/g were obtained. Activated H_2 adsorption was also noted in the case of unsupported CoB. At 100°C an uptake of 194.4 μmol/g was obtained, compared to 47 μmol/g at 25°C.

3. Future Plans

During the next quarter, efforts will be made to complete the characterization on all catalysts particularly the zeolite-supported, nitrided and sulfided catalysts.

B. Task 2: Activity/Selectivity Properties

1. Chromatographic Analysis

A complete correlation of retention times of hydrocarbons in our capillary column system was worked out. Figure 16 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

New gas sampling valves were obtained and installed. By maintaining the new valves at 573 K, sample size is much more constant.

2. Experimental Measurements

Two silica-supported iron catalysts derived from $Fe(CO)_5$ (C6 and C7) were tested in H_2/CO mixture of ratio 2 to 1 at 498 K. Data were also obtained for CoB/SiO_2 (CoB-S-101). Reaction data are summarized in Tables 4-6 for these and previously tested catalysts. Figure 17 shows the product distribution for CoB-S-101 as a function of carbon number and Figure 18 shows its activity versus time.

Catalysts C6 and C7 both produced very little methane and high yields of C_2-C_4 hydrocarbons. Unfortunately, much of the C_5+ products were in the C_{18}-C_{22} wax range. Deactivation of the catalysts was significant. That is, after five hours of operation the C6 sample lost 41% of its initial activity, while C7 lost 73% of its initial activity. Nevertheless, initial activities were significantly greater and hence steady-state activities were comparable to conventional iron supported on silica. The C6 and C7 catalysts were significantly more selective for C_2-C_4 and C_{5+} hydrocarbons and less selective for CH_4 and CO_2.

CoB/SiO_2 (CoB-S-101) is clearly very active with a turnover frequency at 500 K comparable with that of Co/SiO_2. Moreover, its activity increases

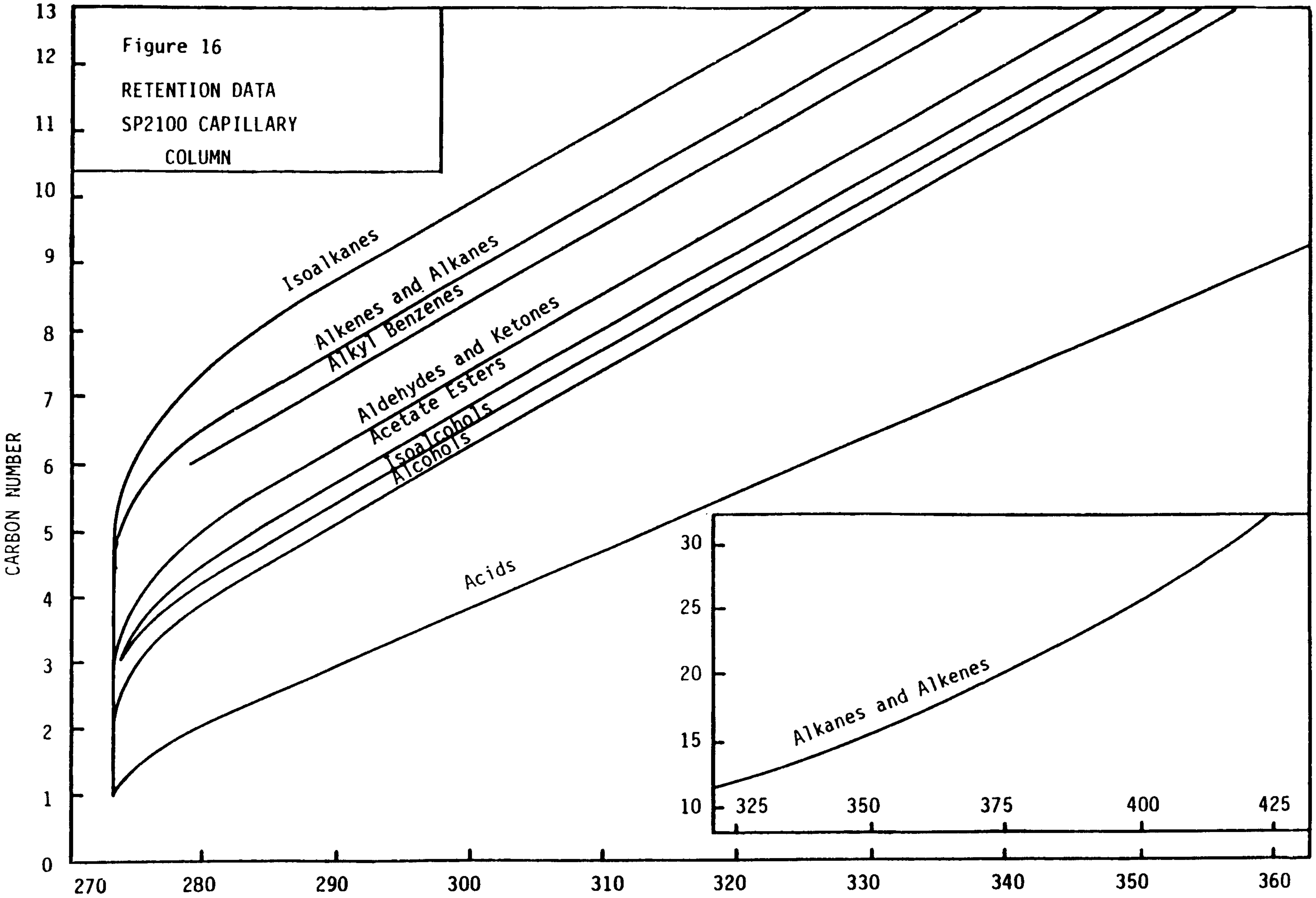

Figure 16. AVERAGE ELUTION TEMPERATURE (K)

TABLE 4

CO Turnover Numbers for Supported Iron and Cobalt Catalysts

Catalyst Code	H_2/CO Ratio	Temperature (K)	Turnover Number (N_{CO} x 10^3)	Activation Energy (kJ/g mole)
Fe-S-102	2	460	0.64	92.5
	2	483	2.5	
	2	498	3.9	
	1	449	0.19	99.3
	1	483	1.4	
	1	498	2.5	
Fe-S-103	2	448	0.72	82.8
	2	483	3.2	
	2	498	7.0	
	1	448	0.79	80.8
	1	473	2.3	
	1	498	7.0	
FeK-S-100	2	498	6.6	--
FeB-S-101	2	498	0.33	--
Co-S-101	2	463	5.9	
CoB-102	2	453	0.31	151.6
	2	473	1.7	--
CoB-102	1	458	0.28	139.6
	1	470	0.64	
	1	485	1.55	
CoB-S-100	1	504	16.49	79.1
	1	520	29.46	
FeB-102	1	483	8.05	81.4
	1	493	14.58	
	1	503	22.92	
	1	513	25.42	
	1	523	42.24	
CoB-S-101	2	468	1.48	153.9
	2	486	6.28	
	2	499	20.62	
C6	2	498	18	--
C7	2	498	10	--

TABLE 5

Product Selectivities for Iron Catalysts at 498 K and Cobalt Catalysts at 473 K

Catalyst Code	Selectivity					Ave. Molecular Weight Hydrocarbon Product
	CH_4	C_2-C_4	C_5+	CO_2	Alcohols	
Fe-S-102[a]	0.16	0.27	0.03	0.47	0.07	27.77
Fe-S-102[b]	0.12	0.23	0.02	0.56	0.07	28.68
Fe-S-103[a]	0.25	0.33	0.04	0.30	0.08	26.27
Fe-S-103[b]	0.20	0.31	0.03	0.36	0.10	27.54
FeK-S-100[a]	0.08	0.19	0.03	0.65	0.05	30.26
FeB-S-100[a]	0.26	0.19	0	0.55	0	20.25
Co-S-101[a]	0.27	0.24	0.34	0.04	0.11	31.21
CoB-S-102[a]	0.15	0.24	0.50	0.07	0.04	40.25
FeB-102[b]	0.17	0.44	0.23	0.10	0.06	--
CoB-S-100[b]	0.31	0.26	0.31	0.06	0.06	--
CoB-103[b]	0.18	0.16	0.20	0.40	0.06	--
CoB-S-101[a]	0.07	0.20	0.72	0.01	0.00	--
C6	0.02	0.17	0.76	0.06	--	--
C7	0.01	0.47	0.50	0.03	--	--

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[a] $H_2/CO = 2$

[b] $H_2/CO = 1$

TABLE 6

Product Distributions for CoB/SiO_2 (CoB-S-101)

	226°C			213°C		
	wt.% P^a	wt.% O^b	O/P^c	wt.% P	wt.% O	O/P
C_1	8.88	--	--	6.56	--	--
C_2	2.12	--	--	1.52	--	--
C_3	4.82	--	--	3.73	--	--
C_4	1.43	3.71	2.59	3.93	--	--
C_5	4.13	1.62	0.39	2.15	2.29	1.07
C_6	4.99	1.19	0.24	2.82	1.63	0.58
C_7	7.02	0.91	0.13	4.54	1.32	0.29
C_8	9.78	0.57	0.06	7.34	1.02	0.14
C_9	13.17	0.48	0.04	10.82	0.93	0.09
C_{10}	13.61	0.29	0.02	13.20	0.71	0.05
C_{11}	9.70	0.40	0.04	9.33	0.63	0.07
C_{12}	5.85	0.18	0.03	7.19	0.35	0.05
C_{13}	2.97	0.07	0.02	4.75	0.22	0.05
C_{14}	0.15	--	--			
C_{15}	0.42	--	--			
C_{16}	0.77	--	--			
C_{17}	0.61	--	--			
C_{18}	0.59	--	--			
C_{19}	0.29	--	--			
C_{20}	0.09	--	--			

	195°C		
	wt.% P	wt.% O	O/P
C_1	6.90	--	--
C_2	0.0	--	--
C_3	9.13	--	--
C_4	9.11	--	--
C_5	5.69	4.14	0.73
C_6	5.95	3.31	0.56
C_7	6.08	1.30	0.21
C_8	6.47	0.66	0.10
C_9	6.46	--	
C_{10}	5.22	--	
C_{11}	5.15	--	
C_{12}	5.69	--	
C_{13}	6.80	--	
C_{14}	10.02	--	
C_{15}	0.61	--	
C_{16}			
C_{17}			
C_{18}			
C_{19}			
C_{20}			

Table 6 (cont.)

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[a] Weight percent paraffin in product.
[b] Weight percent olefin.
[c] Olefin to paraffin ratio (wasn't possible to determine for C_2 and C_3).

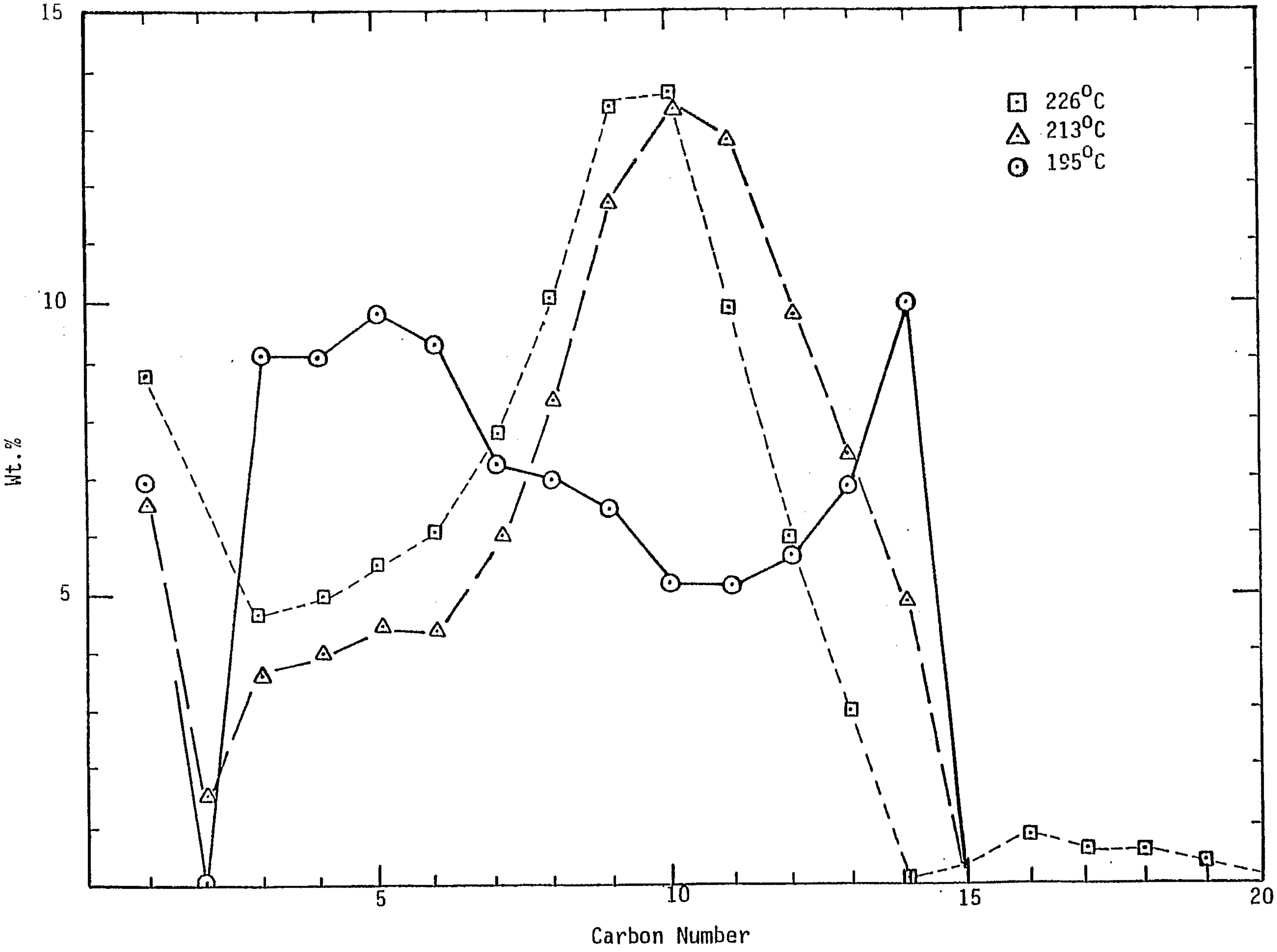

Figure 17. Product Distribution for CoB-S-101 at 1 atm, $H_2/CO = 2/1$.

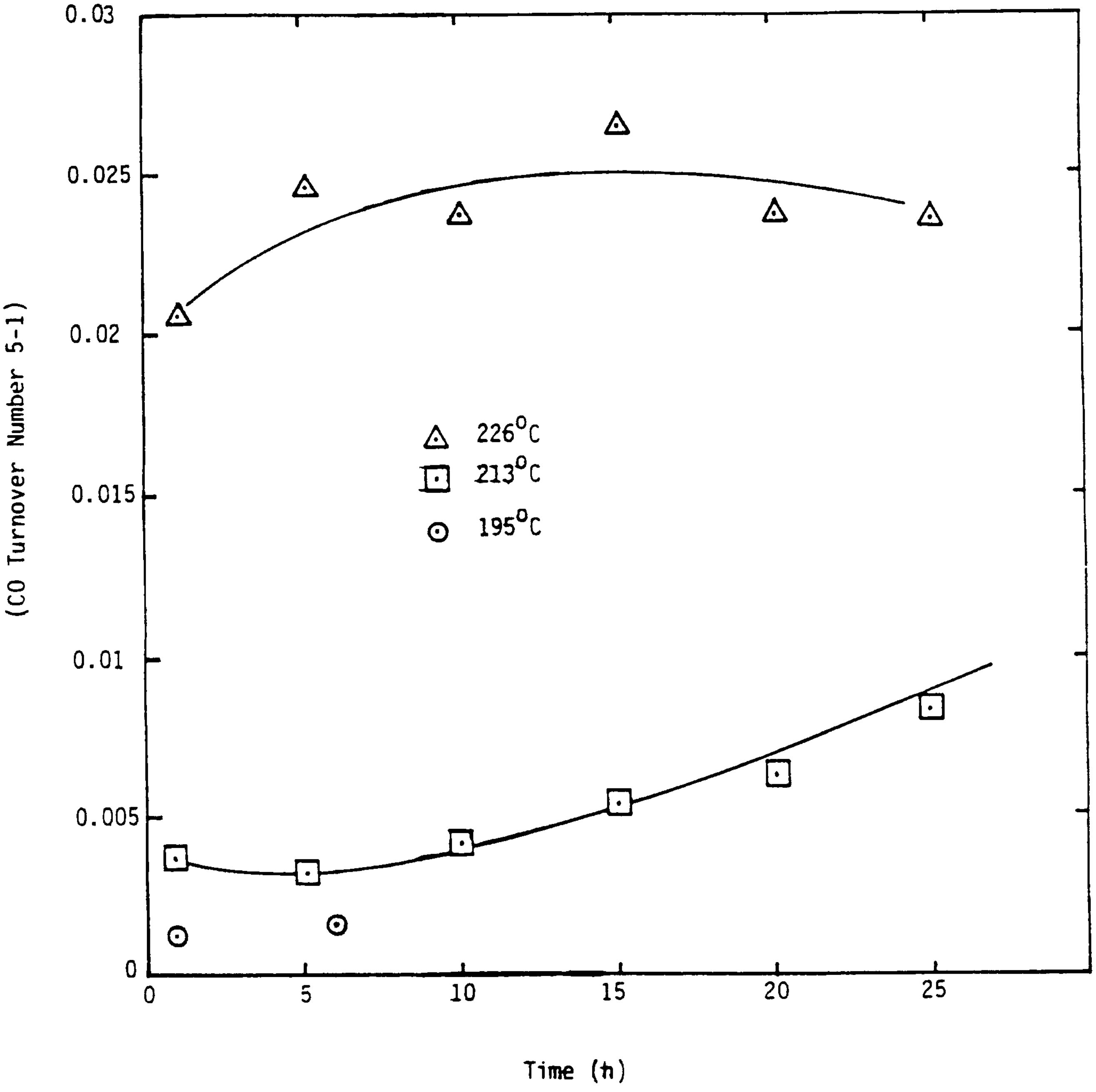

Figure 18. Turnover Number vs. Time for CoB-S-101 (15% CoB/SiO$_2$).

rather than decreases with time. More importantly, its selectivity for C_{5+} gasoline range products is on the order of 70%, a value significantly better than predicted by Schultz-Flory and better than any previously tested catalysts. For example, under comparable conditions, Co/SiO_2 produces 30% C_{5+} gasoline range products. Moreover, the selectivity of CoB/SiO_2 for C_4 olefins is very high (C_2 and C_3 olefins could not be resolved).

It was also observed 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.

C. Task 3: In Situ H_2S Poisoning Measurements

In situ deactivation tests were completed on several catalysts this year. 15% iron on silica (Fe-S-102) was tested at 473, 498 and 523 K in either 1-2 ppm or 5-6 ppm H_2S in the reactant stream. Figure 19 shows the normalized activity of Fe/SiO_2 versus sulfur coverage data at different H_2S concentrations. The Fe/SiO_2 catalyst is most rapidly deactivated by lower H_2S concentrations, i.e., the two Fe/SiO_2 samples exposed to 2 ppm H_2S deactivated much more rapidly than samples exposed to 4-8 ppm H_2S (see Fig. 5). The two samples exposed to 2 ppm H_2S also exhibited a slight shift to lighter molecular weight products as deactivation occurred. In both cases the selectivity of the catalyst to C_{6+} hydrocarbons decreased as poisoning occurred. This was not observed with those samples exposed to higher concentrations of H_2S. The samples tested at 250°C also evidenced significant changes in product distribution with increasing severity of poisoning. For example, the ratio of C_2H_4 to C_2H_6 formed increased greatly as the catalysts deactivated. This was mainly due to the more rapid decrease in C_2H_6 production.

Figure 20 shows normalized activity plotted as a function of sulfur to surface metal ratio (based on metal surface area measured by H_2 adsorption) for other catalysts tested to date in 4-6 ppm H_2S. The unsupported iron boride catalyst is by far the least affected by sulfur. In fact, it loses only 5-6% activity after exposure to sufficient sulfur to completely deactivate most of its available sites. The potassium promoted iron catalyst is significantly more resistant than its unpromoted counterpart under similar conditions. Fe/SiO_2 is apparently more sulfur resistant than Co/SiO_2.

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 Activity 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."

The principal investigator and several students attended the Seventh Annual Symposium of the Rocky Mountain Fuel Society Feb. 19-20, 1982. Dr.

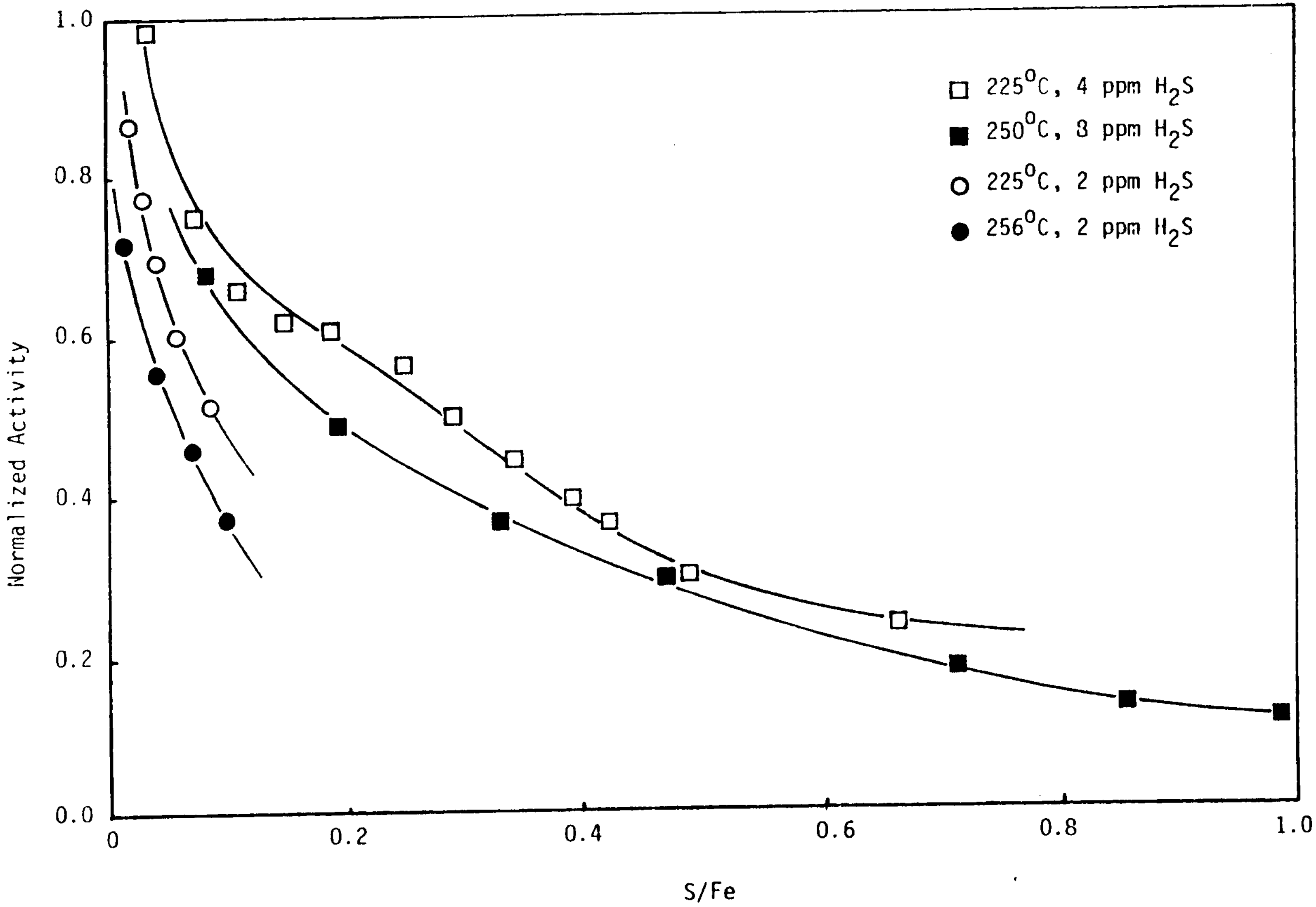

Figure 19. Normalized Activity versus Sulfur Coverage (atoms of adsorbed S/Fe surface atom) for 15% Fe/SiO_2 (at 1 atm, $H_2/CO = 2$).

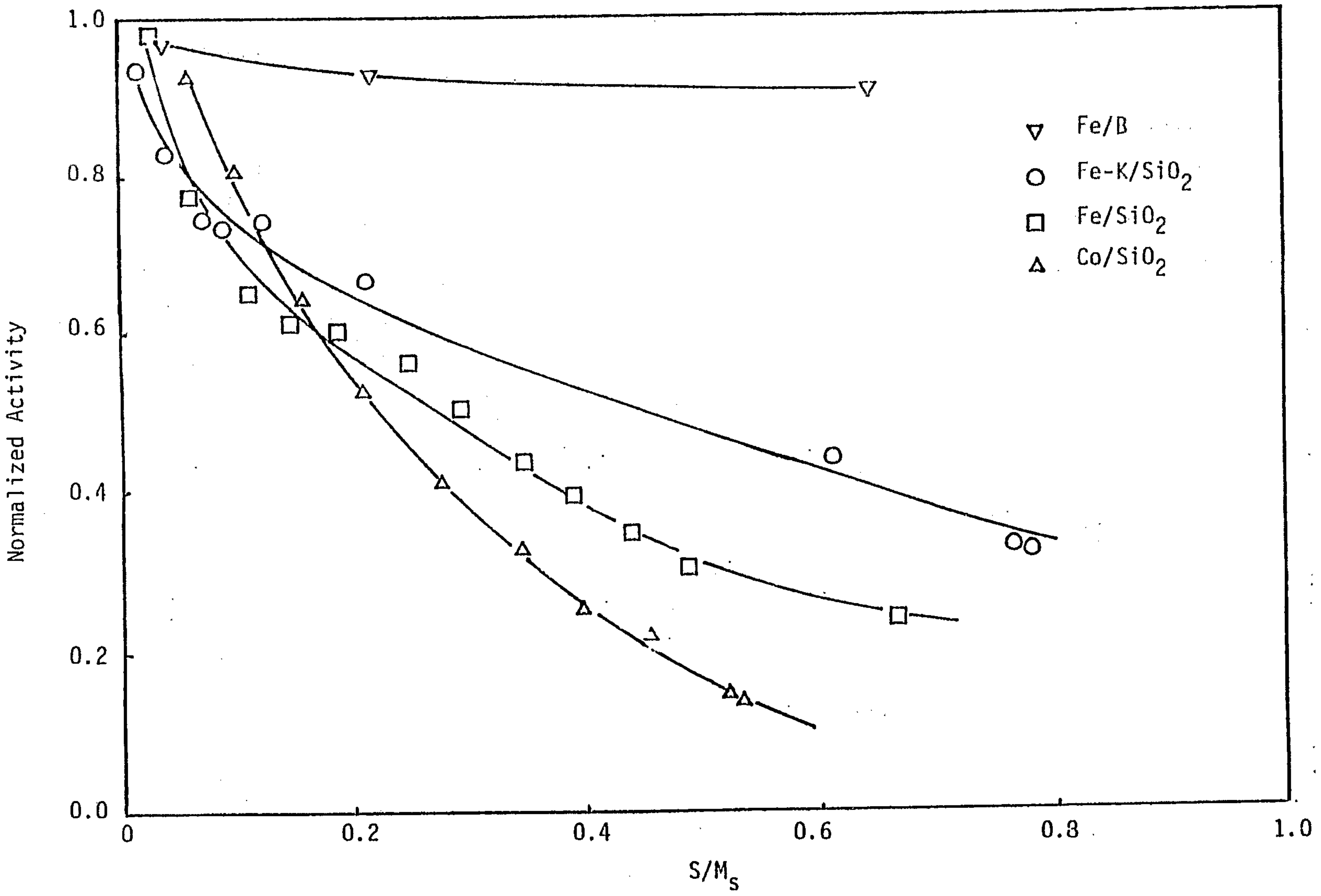

Figure 20. Normalized Activity Versus Sulfur Coverage (atoms of S adsorbed/metal surface atom) during <u>in situ</u> poisoning by 4-6 ppm H_2S (500 K, 1 atm, $H_2/CO = 2$).

Bartholomew chaired a session on fundamental research, while Mr. Travis Bodrero presented a paper on O_2 adsorption on Mo and NiMo sulfides.

The principal investigator and several students also attended a Micro ACS Meeting held March 27, 1982 on the BYU Campus and sponsored by the Central Utah Section. Mr. Gordon Weatherbee presented a paper on TPD of H_2 from Supported Nickel Catalysts, and Mr. Jeffery Rankin presented a paper on "Promoted and/or Supported Fischer-Tropsch Cobalt and Iron Catalysts." Dr. Bartholomew attended the 183rd National ACS meeting held March 28-April 2, 1982 in Las Vegas where he presented a paper, "CO Hydrogenation on Supported Molybdenum Catalysts," and chaired a session dealing with general topics in Catalysis. There were several good presentations at Las Vegas dealing with Fischer-Tropsch synthesis.

On May 3 and 4, Dr. Bartholomew and Mr. Duane Davis visited Phillips Petroleum Research & Development in Bartlesville, Oklahoma where Mr. Davis presented a seminar on "Cobalt and Iron Boride Catalysts" based on work supported by this contract. This invitation to visit was a result of Mr. Davis receiving a Phillips graduate fellowship during the past year. The visit included a tour of the impressive research and catalyst testing facilities at Phillips.

The P.I. and 5 students, including Mr. Richard Bowman, attended Advances in Catalytic Chemistry II, a symposium held May 18-21 in honor of Heinz Heinemann. Dr. Bartholomew chaired a session dealing with "Heterogeneous CO Hydrogenation" which included several interesting papers, e.g., those by Alex Bell, John Butt and Richard Pannell, directly relating to Fischer-Tropsch synthesis.

On July 28th Dr. Bartholomew visited the Dept. of Chemical Engineering at the University of Washington in Seattle. He also attended the 4th International Conference on the Chemistry and Uses of Molybdenum at which he chaired a session on catalyst characterization and presented an informal seminar on "O_2 Chemisorption on Molybdenum Sulfide Catalysts." On Sept 7-8 Mr. Jeff Rankin presented, by invitation a paper summarizing work on this contract at the Annual DOE Liquifaction Conference held in Pittsburgh. Dr. Bartholomew attended the DOE Coal Liquifaction Contractors Meeting Sept. 22-24, 1982 and presented a paper at the California Catalysis Society meeting held in Irvine, CA on Oct. 14-15.

Our laboratory also hosted several guests during the past year. Dr. Moorehead of Union Oil Research visited the Department of Chemical Engineering and the Catalysis Laboratory on November 5, 1981 and presented a seminar on "The Catalytic Synthesis of Maleic Anhydride". Professor Robert J. Madix of Stanford visited on February 3, 1982 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 March 16th 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.

On March 25th Dr. Bill Weigand of NSF visited to discuss opportunities in the Chemical and Biochemical Processes Program. Dr. Richard Pannell of Gulf Research visited our laboratory on May 17th and reviewed our work in Fischer-

Tropsch synthesis. Drs. Roger Baetzold and John Monnier of Eastman Kodak visited on May 18th and toured our laboratories. On May 19th Dr. Azza Elattar of Texaco also visited and toured our facilities.

Dr. Yang Ki Hong of the University of Utah visited our group on June 22nd. Dr. Hong is an expert in ESCA and Moessbauer spectroscopy. On August 17th Dr. J. Grimblot of the Universite des Sciences de Lille (France) visited our group and talked about ESCA studies of molybdenum catalysts.

Two publications dealing with this contract were submitted to AIChE for presentation at the National Meeting to be held in LA on Nov. 14-18.

The deadline for completing our contract was originally September 18, 1982. However, due to delays in performing the proposed work--mainly due to the complex analysis of hydrocarbons and because our research assistants were required to perform teaching duties during the past 2 years, we applied for and received a no-cost extension to June 18, 1983. We were also pleased to receive notice that we will be awarded a new contract to continue our investigation of the cobalt and iron borides.

IV. CONCLUSIONS

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

2. Controlling H_2 reduction heating rates to less than 2°C/min significantly increases active surface areas of cobalt boride/silica catalysts. H_2 adsorption on cobalt boride catalysts is highly activated; indeed the amount adsorbed on unsupported CoB is 4 times greater at 100°C than at 25°C.

3. CoB/SiO_2 is a very active, stable FT catalyst with unusually high (70%) selectivity for C_{5+} gasoline hydrocarbons. Its butene make is also high.

4. Iron boride catalysts produce abnormally large amounts of hydrocarbons in the C_{17} to C_{20} range.

5. Co/SiO_2 catalysts are significantly better dispersed than Fe/SiO_2 catalysts. It may be possible to achieve dispersions of cobalt as high as 40% at a loading of 3 wt.%, although the extent of reduction to the metal after 36 hours exposure to H_2 at 400°C is low, e.g., 18%.

6. 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 former catalyst.

7. Fe-carbonyl-derived silica-supported catalysts may be prepared with much higher dispersions and extents of reduction than conventional Fe catalysts. Calcining Fe-carbonyl derived catalysts at 500°C greatly increases crystallite size relative to calcination at 200°C. Carbonyl-derived Fe/SiO_2 catalysts are very active and selective for C_2-C_4 and C_{5+} hydrocarbons. Their selectivies for CH_4 and CO_2 products are low. Although they lose 50-75% of their initial activities within 5 hours, their steady state activities are comparable with conventional Fe/SiO_2 catlaysts.

8. FeB is extremely resistant to poisoning by H_2S. After exposure to 4-6 ppm H_2S for sufficient time to deactivate most of the available active sites, it loses only 5-6% of its initial activity. Its activity maintenance in the absence of sulfur is also unusually high compared to conventional Fe catalysts.

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