INVESTIGATION OF SULFUR-TOLERANT CATALYSTS FOR SELECTIVE SYNTHESIS OF HYDROCARBON LIQUIDS FROM COAL-DERIVED GASES. FINAL TECHNICAL PROGRESS REPORT, SEPTEMBER 19, 1979-OCTOBER 22, 1984
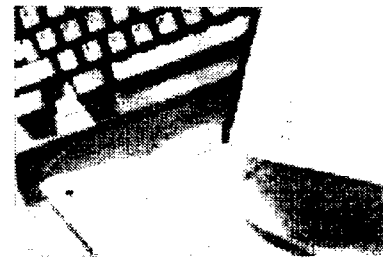
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INVESTIGATION OF SULFUR-TOLERANT CATALYSTS
FOR SELECTIVE SYNTHESIS OF HYDROCARBON
LIQUIDS FROM COAL-DERIVED GASES

Final Technical Progress Report
For Period September 19, 1979 to October 22, 1984

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FORWARD

This report summarizes technical progress during a three-year study (September 19, 1979 to September 18, 1982) conducted for the Department of Energy (DOE) under Contract No. DE-AC01-79ET14809. This contract was extended two years on a no-cost-increase basis to enable Mr. Duane Davis and Mr. Jeffery Rankin to complete their thesis and dissertation work prior to the preparation of this final report. 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: Richard M. Bowman, Duane M. Davis, Glen Witt, Brian Armstrong, and Jeffery L. Rankin. Dr. Bartholomew was the principal author of this report. Nancy Anderson and Geralee Walker provided typing services.

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ABSTRACT

The effects of support and of boron or potassium promoters on the adsorption properties, CO hydrogenation activity/selectivity behavior, and sulfur resistance of iron (and to a lesser extent cobalt) were investigated. Iron catalysts supported on alumina, silica, and silicalite and promoted with potassium were prepared by conventional impregnation techniques. Cobalt and iron borides were prepared by chemical reduction with $NaBH_4$. The adsorptions of CO and H_2 on these catalysts were studied by static adsorption and temperature-programmed desorption techniques. Activity, selectivity, and sulfur-resistance during CO hydrogenation on these catalysts were determined using a laboratory microreactor. The results indicate that support, promoter, and catalyst pretreatment significantly influence adsorption, activity, selectivity, and sulfur resistance behavior of these catalysts. Hydrogen adsorption on these catalysts is highly activated; moreover the degree of activation varies with support, promoter and pretreatment. Specific activities of iron catalysts on different supports vary 40 fold; selectivities of these catalysts for CO_2 and different hydrocarbons also vary significantly with support. Calcination at 473 K of potassium promoted Fe/silica shifts selectivity from conventional Fisher-Tropsch products (C_1-C_{10} hydrocarbons and CO_2) to mainly methane, ethylene and propylene. These and other signficant results are presented and discussed. An account of technical communications and publications is also included.

I. OBJECTIVES AND SCOPE

A. Background

Cobalt and iron catalysts find wide application in the oil, gas and chemical industries, particularly in ammonia synthesis, hydrotreating and hydrocarbon synthesis reactions. They are expected to find even broader application in future energy technologies, especially in production of synthetic fuels from coal.

Although cobalt and iron containing catalysts for synthesis of aliphatic and aromatic hydrocarbons from coal-derived gases (Fischer-Tropsch Synthesis) were developed 2-3 decades ago and are even used on a very limited basis commercially to produce gasoline, their activity, selectivity and stability properties leave much to be desired. Most Fischer-Tropsch (FT) catalysts, for example evidence poor selectivity for highly desirable products such as gasoline (C_6-C_{12}) or chemical (C_2-C_5) feedstocks; that is, the hydrocarbon products range from gases to heavy waxes. Thus, there is clearly a need to find more selective catalysts. Since much of the recent work has been directed at synthesis of gaseous hydrocarbons for chemical feedstocks, there is clearly a need to focus on catalysts selective for the production of liquid aliphatics and aromatics, particularly in the C_6-C_{12} gasoline feedstock range.

With the exception of a few recent studies, previous investigations have emphasized a trial and error (screening) approach to finding the best FT catalysts. Much of the previous work was carried out using large catalyst beds under conditions such that the kinetics were influenced by diffusional resistance, temperature gradients and heat/mass transport effects. Generally, there was relatively little characterization of the physical and chemical properties of the catalysts. Yet recent evidence indicates that FT catalysts are complex, multiphase solids and that structural and chemical promoters and surface additives (including sulfur) can profoundly influence the activity, selectivity and stability of these catalysts (1-3). Moreover, poisoning by sulfur compounds at levels as low as 1 ppm can result in rapid significant losses of activity and dramatic changes in selectivity; yet there has been very little definitive work to characterize the effects of sulfur poisoning. Therefore, the need is evident for a comprehensive, systematic scientific investigation of these phenomena which includes careful characterization of bulk and surface catalytic properties and activity studies under chemical-reaction-controlled conditions.

B. Objectives

This report describes the results of 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 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

Originally 28 catalysts were planned for preparation as part of this study (4). This number was later reduced to 27 (5), then 26 (6) and finally to 18 (see Table 1) as the necessity for focussing the work became evident. Supported catalysts were prepared mainly by impregnation of high purity carriers with aqueous solutions of cobalt and iron nitrates. The Al_2O_3 and SiO_2 supported catalysts were generally dried at 373 K without precalcination and all catalysts were reduced in flowing hydrogen for 36 hours at 725 K. Potassium promoted catalysts were prepared by separating a dried Fe/SiO_2 into several batches and reimpregnating several batches with solutions of KNO_3.

Cobalt and iron borides were prepared by chemical reduction with $NaBH_4$ according to special techniques recently developed in this laboratory for preparation of supported cobalt and nickel borides (1,2). This approach involved a nonaqueous, low temperature reduction of the metal nitrate or metal nitrate/support with sodium borohydride followed by washing, drying and high temperature reduction in hydrogen.

The catalysts prepared in this study were characterized by a number of different techniques including H_2 and CO chemisorption, temperature-programmed desorption chemical analysis, x-ray diffraction, TEM, and Moessbauer Spectroscopy. Metal dispersions were measured using hydrogen adsorption at and were checked in selected cases using x-ray line broadening. X-ray diffraction scans were used to establish the various catalytic phases. The extent of reduction to the metallic state and bulk oxidation states were determined by oxygen titration and Moessbauer spectroscopy. Characterization experiments are summarized in Table 2. Experiments to determine the effects

Table 1

Catalyst Preparation Plans[a] (Task 1)

Metal-Suppport Combination	Unpromoted	Promoted	Additive Pretreatment		No. Catalysts
		K_2O	S	B	
Fe (unsupported)	x		x	x	3
Co (unsupported)	x			x	2
Co/SiO$_2$	x(2)[c]			x	3
Fe/SiO$_2$	x(2)[c]	x	x(2)[b]	x	6
Fe/Al$_2$O$_3$	x				1
Fe/ZSM-5	x				1
Fe/Silicalite	x				1
Fe/C	x				1
				Total	18

[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.

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
b. H_2, CO and CO_2 Adsorption Measurements on K_2O Promoted Catalysts	Determine effects of promoters reactant adsorption	Fe/SiO_2
c. Moessbauer Spectroscopy	Determine effects of support and promoter on state of metal reduction	Fe-B, Fe/SiO_2, Fe/Al_2O_3
2-Activity/Selectivity Measurements	Effects of support	Fe, Fe/SiO_2 Fe/Al_2O_3, Fe/ZSM-5, Fe/Silicalite, Co, Co/SiO_2, Co/ZSM-5
	Effects of metal	Co, Fe
	Effects of metal loading	3 and 15% Fe/SiO_2
	Effects of Promoter	K_2O promoted Fe/SiO_2
	Effects of Sulfiding	Fe, Fe/SiO_2 (unpromoted and K_2O-promoted); and Co/SiO_2
	Effects of Boriding	Fe and Fe/SiO_2, Co and Co/SiO_2
3-In situ H_2S Deactivation	Effects of support	Fe, Fe/SiO_2

Effects of metal	Co/SiO$_2$ and Fe/SiO$_2$
Effects of metal loading	3 and 15% Fe/SiO$_2$
Effects of Promoter	K$_2$O promoted Fe/SiO$_2$
Effects of Sulfiding	Fe, Fe/SiO$_2$ (unpromoted and K$_2$O-promoted)
Effects of Boriding	Borided Fe

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[a]Co/ZSM-5, Fe/ZSM-5 and Fe/Silicalite samples were obtained from the Pittsburgh Energy Technology Center.

of promoters and sulfur poisoning on the adsorption of CO and H_2 were also included.

Task 2:   Activity/Selectivity Measurements

The experimental plan in Table 2 also summarizes the catalysts to be tested and the purpose of their study.   The conditions selected for the activity/selectivity measurements were 475-525 K, 1 atm, $H_2/CO = 2$ and space velocities in the range of 100 to 1,500 h^{-1}.   Originally, there were plans to test selected catalysts at high presure; however, there was not sufficient time to conduct these tests during this contract period; nevertheless, high pressure tests are planned in followup studies.   The space velocity was adjusted in each test so that the CO conversion at 525 K was in the range of 5-10% in order that intrinsic activities could be obtained in the absence of diffusional influences.   Catalyst samples were 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 were minimized thermal gradients in the catalyst bed.   Samples were reduced in situ for 36 hours and then conditioned under the reaction conditions for a period of 24 hours during which time chromatograph samples were carried out intermittently.

Task 3:   In situ H_2S Poisoning Measurements

The catalysts studied for sulfur tolerance are listed in Table 2 along with the purpose for investigation.   Activity measurements were made as a function of time during reaction at 500 or 525 K, 1 atm, $H_2/CO = 2$ and space velocities of 200 to 1000 hr^{-1} with 0.5 to 5 ppm H_2S in the reactant mixture.   The analysis of hydrocarbons was made intermittently using chromatography over a period of 24-48 hours.   Catalysts were housed in a Pyrex differential tubular reactor cell.   ·

To ensure reproducibility in both activity and poisoning experiments, chromatographic samples were analyzed repeatedly until consistent results were obtained.   Duplicate samples of the same catalyst were tested in selected instances.

II. EXECUTIVE SUMMARY

The effects of support and of boron or potassium promoters on the adsorption properties, CO hydrogenation activity/selectivity behavior, and sulfur resistance of iron (and to a lesser extent cobalt) were investigated. The accomplishments are best described according to Task:

Task 1. Catalyst Preparation and Characterization. Over 30 catalysts were prepared and characterized. Supported catalysts were generally prepared by impregnation to incipient wetness of the dried support with nitrate salts. Metal borides were prepared by reduction with $NaBH_4$ at 283 K of cobalt or iron nitrates in ethanol or isopropanol followed by washing in methanol or water. H_2 and CO (and in selected cases CO_2) adsorption uptakes of these catalysts were measured by static chemisorption methods. The kinetics of H_2 adsorption on selected catalysts were studied by temperature-programmed adsorption. Extents of reduction of most of these catalysts in the reduced state were determined by oxygen titration at 673 K and/or by Moessbauer spectroscopy.

Hydrogen adsorption on cobalt and iron catalysts is activated. The degree of activation and the binding energy of hydrogen with the metal increase with increasing calcination temperature and increasing potassium content. Based on Moessbauer and chemical analyses, washing iron borides in water hydrolyzes the small boride crystallites to large particles of iron oxide.

Task 2: Activity /Selectivity Measurements. Activity/selectivity data were obtained in a laboratory single-pass, differential reactor at 1 atm, 473-523 K, and conversions less than 10%. Products were routed directly through heated lines to a chromatograph, separated with glass capillary and packed columns, and analyzed by thermal conductivity and flame ionization detectors.

Specific activities and selectivities of silica-supported cobalt and iron compare favorably with those reported earlier for similar catalysts. Specific activities of cobalt and iron borides vary considerably with preparation; however, they are generally about as active as their unborided counterparts. Cobalt borides are much more active and stable than iron borides; moreover, they are highly selective for gasoline range hydrocarbons at 1 atm. The specific activity and selectivity of iron catalysts vary significantly with support and promoter. The differences may be a result of differences in dispersion and extent of reduction. Specific activities of Fe/silica and Fe/K/silica decrease with increasing precalcination temperature and with increasing potassium content; there is also a striking increase in the C_2-C_4 fraction and olefin/paraffin ratio with increasing K content of catalysts precalcined at 473 K. Indeed, the product distribution for 15% Fe/3% K/silica precalcined at 473 K consists of only methane, ethylene and propylene. The unusually high selectivity for light olefins and the unusually low activation energy of 32 kJ/mol suggest that CO hydrogenation occurs on this catalyst by a mechanistic route distinct from FT synthesis.

Task 3: In Situ H_2S Poisoning Measurements. A cobalt/silica and four iron catalysts (unsupported Fe, Fe/silica, Fe/K/silica, FeB) were exposed to 0.5-8 ppm H_2S either in situ or in pure hydrogen before reactor testing.

Catalyst activity and selectivity were monitored as a function of sulfur coverage at 500-525 K and 1 atm.

All of the iron catalysts except FeB lose activity rapidly in the presence of ppm levels of H_2S independent of support and promoter. Monolayer surface sulfides are formed at H_2S concentrations lower than 2 ppm; bulk sulfides are formed at concentrations above 2 ppm. FeB is extremely sulfur resistant, losing only 5% activity after several days exposure to 8 ppm; upon exposure to 0.5 ppm for 2-3 days, the activity increases 40-50%! The product distribution of Co/silica is changed in favor of heavier hydrocarbons during exposure to H_2S; the product distribution of iron/silica is not affected.

Technical Communications and Miscellaneous Accomplishments.

The PI and his students published or submitted 6 papers, presented 15 papers and 5 seminars, visited 24 laboratories, and received 45 visitors. Five students (1 Ph.D. and 2 M.S. students) were supported by this contract.

III. DETAILED DESCRIPTION OF TECHNICAL PROGRESS

A. Task 1: Catalyst Preparation and Characterization

1. Catalyst Preparation

Altogether, over 30 catalysts were prepared as part of the contract study. Catalyst codes, compositions and preparation methods are listed for 26 of these catalysts in Table 3. Silica- and Silicalite-supported catalysts were prepared by multiple impregnations with aqueous solutions of cobalt or iron nitrates or with iron nitrate and potassium nitrate to incipient wetness, followed by drying at 373 K overnight, although a few catalysts were dried/calcined at 473 K prior to reduction in order to determine effects of calcination pretreatment. After drying/calcination, catalysts were generally reduced at 723 K for 36 hours, since it was determined that shorter reduction periods were insufficient for reaching maximum extents of reduction of the catalysts (5).

The Fe/Al_2O_3 catalyst was prepared according to Vannice (7) , Carter and Savini (8) by heating a mixture of iron nitrate and alumina to 100°C, at which temperature the nitrate melt was able to penetrate the pores of the support. Preparation by aqueous impregnation was unsuccessful as it resulted in hard lumps of nonporous material.

Cobalt and iron metal borides were prepared by reduction with $NaBH_4$ at 10°C of cobalt or iron nitrates in ethanol or isopropanol solution. The resulting fine black precipitate was washed with methanol and/or water. Unfortunately, the methanol wash did not remove all of the sodium impurities (see Table 3), while washing in water caused hydrolysis of iron boride to iron oxide (see Moessbauer results in section on Catalyst Characterization).

2. Catalyst Characterization

Adsorption Measurements.   Since H_2 adsorption on cobalt and iron catalysts is activated (9) , hydrogen uptakes were measured at 298 K after cooling for 673 to 298 K in a measured quantity of hydrogen. Hydrogen, CO and CO_2 adsorption uptakes, extents of reduction and dispersions of cobalt and iron catalysts and of cobalt and iron metal borides are summarized in Tables 4 and 5. From the data in Table 4, it is evident that (i) Co/SiO_2 catalyst have higher dispersions relative to Fe/SiO_2 catalysts, (ii) hydrogen adsorption on cobalt and iron catalysts is highly activated, i.e. subject to kinetic limitations as evidenced by increasing quantity adsorbed with increasing temperature (the effect was particularly dramatic for 3% Fe/SiO_2 (Fe-S-107) and 9% Co/ZSM-5 where adsorption capacity increased from 1.6 and 0 μmoles/g to 15 and 123 μmoles/g respectively as adsorption temperature was increased from 25-100%), (iii) hydrogen uptake, dispersion, and extent of reduction vary significantly with support among iron catalyst (e.g., Fe/Al_2O_3 has the lowest extent of reduction and highest dispersion), (iv) hydrogen and carbon monoxide adsorption capacities and extent of reduction decrease while CO_2 adsorption capacity increases with increasing potassium content in the $Fe/K/SiO_2$ system, and (v) calcination at 473 K causes a further decrease in the extent of reduction and in hydrogen and CO adsorption capacities of $Fe/K/SiO_2$ catalysts.

Table 3

Summary of Catalysts Prepared

Code	Catalyst/Composition	Preparation Method
Co-S-101	3% Co/SiO$_2$	Impreg., dried 373 K
Co-S-102	15% Co/SiO$_2$	" "
Co-S-103	3% Co/SiO$_2$	" "
Fe-100	100% Fe	Nitrate decomp. at 473 K
Fe-S-100	3% Fe/SiO$_2$	Impreg, dried 373 K
Fe-S-101	15% Fe/SiO$_2$	" "
Fe-S-102	15% Fe/SiO$_2$	" "
Fe-S-103	3% Fe/SiO$_2$	" "
Fe-S-105	15% Fe/SiO$_2$	" dried/calcined at 473 K
Fe-S-107	3% Fe/SiO$_2$	" , dried at 373 K
Fe-A-100	15% Fe/Al$_2$O$_3$	Impregnated with nitrate metal at 373 K; calc. 473 K
Fe-C-100	15% Fe/Carbon	Nonaqueous deposition
Fe-L-100	15% Fe/Silicalite	Impregnated, dried 373 K
FeK-S-100	15% Fe/3% K/SiO$_2$	Impreg., " "
FeK-S-101	15% Fe/3% K/SiO$_2$	Impreg., " "
FeK-S-102	15% Fe/3% K/SiO$_2$	Impreg.; dried/calc. 473 K
FeK-S-103	15% Fe/1% K/SiO$_2$	" "
FeK-S-104	15% Fe/3% K/SiO$_2$	" , dried 373 K
FeK-S-105	15% Fe/0.2% K/SiO$_2$	" , dried/calc. 473 K
CoB-102	83.3% Co/3.0% B/3.1% Na	NaBH$_4$ redn in EtOH; MeOH wash
CoB-A-101	CoB/Al$_2$O$_3$	NaBH$_4$ redn in Isoprop.; MeOH wash
CoB-S-100	CoB/SiO$_2$	NaBH$_4$ redn
CoB-S-101	12% Co/0.8% B/1.8% Na/SiO$_2$	NaBH$_4$ redn in Isoprop.; MeOH wash
FeB-101	76% Fe/1.6% B/0.2% Na	NaBH$_4$ redn in EtOH; MeOH/H$_2$O wash
FeB-S-101	FeB/SiO$_2$	" ; MeOH wash
FeB-S-105	11.9% Fe/0.12% B/0.56% Na/SiO$_2$	" ; MeOh/H$_2$O wash

Table 4

H$_2$, CO, and CO$_2$ Adsorption Uptakes of Cobalt and Iron Catalysts After 36 Hours of Reduction

Catalyst Code	Catalyst/ Composition	H$_2$ Uptake[a] (μmol/g)			CO Uptake[a] at 198K (μmoles/g)		CO$_2$ Uptake[b] at 298K (μmoles/g)		% Reduction[c]	% Dispersion[d]
		673 → 298 K		298 K						
		TOT	Irrev	TOT	TOT	Irrev	TOT	Irrev		
Co-S-101	3% Co/SiO$_2$			13		25			71	7.2
Co-S-102	15% Co/SiO$_2$			52		90			35	12
Co-S-103	3% Co/SiO$_2$			19		56			18	41
Co-S-104	15% Co/SiO$_2$	69	54	62	140	86				
Co-s-105	3% Co/SiO$_2$	21	11	17	38	23				
PETC-B1	9% Co/ZSM-5	125[g]		0		48				
Fe-100[f]	100% Fe	15.5	11	8.2	41	28				
Fe-S-100	3% Fe/SiO$_2$			3.5[e]		2.7[e]				
Fe-S-101	15% Fe/SiO$_2$			3.5[e]		4.7[e]				
Fe-S-102	15% Fe/SiO$_2$		16		12				79	1.5
Fe-S-103	3% Fe/SiO$_2$			2.4		1.2			23	3.9
Fe-S-105[f]	15% Fe/SiO$_2$	57	49.5	12	38	21	17	4.5	90	4.7
Fe-S-107	3% Fe/SiO$_2$	15	13	1.6						
Fe-A-100[f]	15% Fe/Al$_2$O$_3$	30	27	6.8	60	15			30	7.5
Fe-C	15% Fe/Carbon	12	11	3.8	34	11			60	1.5
Fe-L-100	15% Fe/Silicalite	27	23	3.9	55	21			91	2.2
Fe-Z-100 (PETC)	15% Fe/ZSM-5	36	31	7.6	94	36			74	3.6

Table 4 (Cont.)

H_2 CO, and CO_2 Adsorption Uptakes of Cobalt and Iron Catalysts After 36 Hours of Reduction

Catalyst Code	Catalyst/ Composition	H_2 Uptake[a] (µmol/g) 673 → 298 K		298 K	CO Uptake[a] at 198K (µmoles/g)		CO_2 Uptake[b] at 298K (µmoles/g)		% Reduction[c]	% Dispersion[d]
		TOT	Irrev	TOT	TOT	Irrev	TOT	Irrev		
FeK-S-100	15% Fe/3% K			9.1		4.9		6.6	42.5	1.7
FeK-S-101	15% Fe/3% K	23								
FeK-S-102[f]	15% Fe/3% K	23.5	16		3.4	2.0	122	24	65	1.7
FeK-S-103[f]	15% Fe/1% K	29	21		7.3	5.1	71	14	81	2.1
FeK-S-104	15% Fe/3% K	31	22		9.3	3.6	118	16	70	2.3
FeK-S-105[f]	15% Fe/0.2% K	54.5	54		30	18	30	16	93	4.0

[a]Total uptake was determined after high temp. evacuation; irreversible is the amount remaining after evacuation at 298 K.
[b]Same definitions as a; CO_2 uptakes were determined at 190, 298, and 343 K; data at 298K are most accurate.
[c]Determined from O_2 titration at 673 K assuming formation of Co_3O_4 or Fe_2O_3.
[d]Fraction of metal atoms exposed determined from total H_2 uptakes after cooling in H_2 from 673 K.
[e]Reduced only 12 hours at 725 K.
[f]Precalcined at 473 K; all others at 373 K.
[g] Adsorption at 373 K.

Table 5

Chemisorption Data for Cobalt and Iron Boride Catalysts

Catalyst Code	Catalyst		Total H2 Uptake (μmol/g)	CO uptake (μmol/g)		%D	CO/H	
				total	irreversible		total	irreversible
CoB-A-102	CoB	a	47.5	45.2	32.6	3.4	0.48	0.34
	CoB	b	260	45.2	32.6	3.4	0.09	0.06
CoB-A-101	CoB/Al$_2$O$_3$	a	59	--	66	--	--	0.50
CoB-S-100	CoB/SiO$_2$	a	6.2	--	4.1	--	--	0.33
CoB-S-101	CoB/SiO$_2$	a	21.2	59.9	24.4	7.0	1.4	0.58
"	CoB/SiO$_2$	b	20.8	59.9	24.4	7.0	1.4	0.56
"	CoB/SiO$_2$	c	42.4	59.9	24.4	7.0	0.70	0.29
FeB-101	FeB	a	5.56	12.0	1.85	0.39	1.10	0.17
	FeB	b	9.52	12.0	1.85	0.39	0.63	0.10
FeB-102	FeB	a	4.1	--	1.85	--	--	0.22
FeB-S-101	FeB/SiO$_2$	a	6.4					
FeB-S-105	FeB/SiO$_2$	a	7.75	17.3	3.6	1.4	1.2	0.23
"	FeB/SiO$_2$	b	8.54	17.9	3.6	1.4	1.01	0.21

[a] Chemisorption at 298 K

[b] H$_2$ Chemisorption at 373 K

[c] H$_2$ Chemisorption performed by cooling from 673 K to room temperature in H$_2$.

Temperature-programmed desorption studies of the Fe/SiO$_2$ and Fe/K/SiO$_2$ systems revealed that the extent of activation for H$_2$ adsorption and the binding energy of hydrogen on iron both increase with increasing temperature of precalcination and with addition of potassium. The change in extent of activation is illustrated in Figs. 1-4 by the larger spectrum areas obtained after cooling from the reduction temperature in H$_2$ and the absence of adsorption at low temperatures for catalyst precalcined or promoted with potassium. The desorption peaks are shifted to higher temperatures or higher energy binding states for the same catalyst (see Figs. 1-4). This shift is particularly dramatic for the Fe/K/SiO$_2$ catalyst calcined at 473 K; in this case, no desorption occurs below about 600 K, a temperature characteristic of the CO hydrogenation reaction. Details regarding the TPD work are described in a recently published paper (10) and a paper in preparation (11).

Moessbauer Spectroscopy and X-ray Measurements. The study of Fe/SiO$_2$ and Fe/K/SiO$_2$ catalysts by Moessbauer spectroscopy was useful in determining (i) effects of washing on metal boride catalysts, (ii) phases present in dried, calcined, reduced and reaction-aged catalysts, and (iii) the effects of potassium promotion and precalcination on the composition of the reduced catalyst.

Fig. 5 shows spectra of FeB-101 before and after washing with water. The double spectrum before washing is characteristic of small particles of FeB and/or Fe$_2$O$_3$. However, the complex 6-line spectrum after washing in water is indicative of the presence of large particles of Fe$_2$O$_3$ and Fe$_3$O$_4$. In other words, the evidence suggests that washing in water hydrolyzes the small particles of FeB to large particles of iron oxide.

Moessbauer spectra of reduced Fe/SiO$_2$ and Fe/K/SiO$_2$ catalysts are shown in Figure 6. The spectrum for the unpromoted catalyst consists predominantly of the characteristic 6-line spectrum for reduced α-Fe metal but also contains a small central peak assignable to either superparamagnetic α-Fe$_2$O$_3$ or Fe$_3$O$_4$. As potassium level is increased, the central peak becomes more prominant and a new peak appears at about +2 mm/sec. These central peaks can be assigned to mixtures of small particles of α-Fe$_2$O$_3$ and Fe$_3$O$_4$. Areas under the central and 6-line peaks determined from peak width and intensity parameters derived from least-squares minimization are listed in Table 6 together with calculated percent reductions of iron to the zero-valent state determined from O$_2$ titration. Extents of reduction determined from oxygen titration of the reduced samples are generally in good agreement with those derived from Moessbauer spectroscopy. It is evident the extent of reduction decreases with increasing potassium content and with increasing temperature of precalcination.

Metal crystallite diameters calculated from x-ray diffraction line broadening and H$_2$ uptakes assuming H/Fe = 1 are also listed in Table 4. The values determined for the unpromoted catalyst of 30 nm and 26 nm are in good agreement. However, large discrepancies in the crystallite diameters of the promoted catalyst are evident, probably due to the suppression of H$_2$ adsorption by K$_2$O or potassium silicate on promoted Fe.
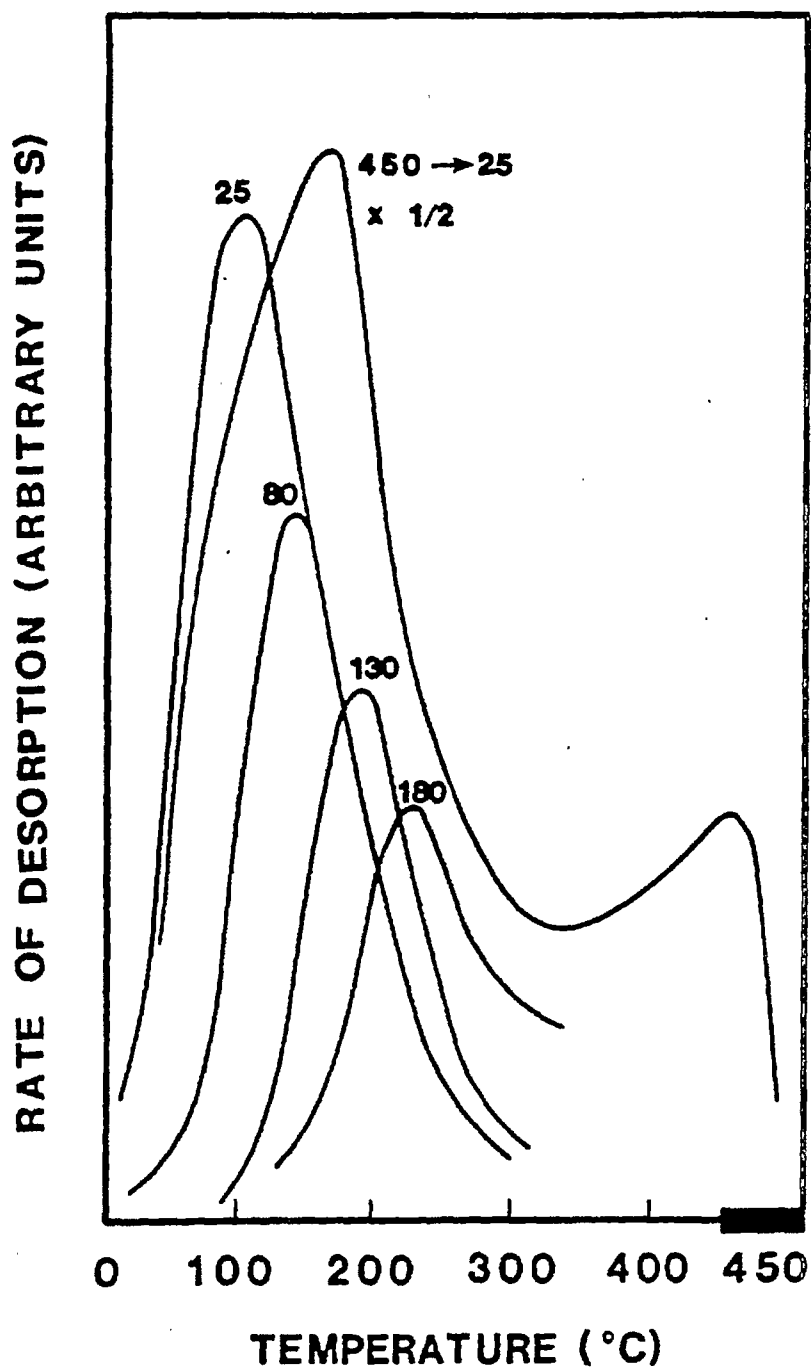
Figure 1. Temperature programmed desorption spectra of H_2 from 15% Fe/SiO$_2$ (dried at 60-80°C prior to reduction) as a function of temperature.
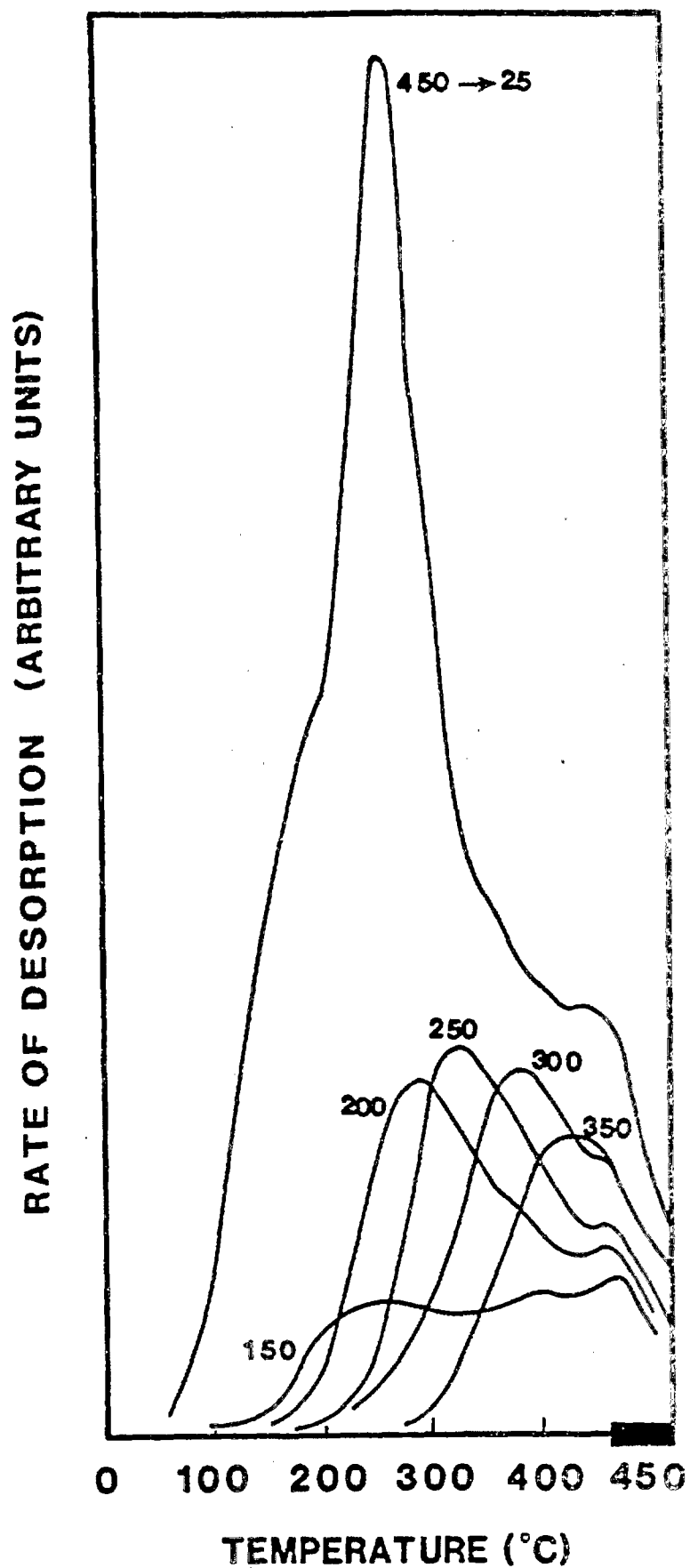
Figure 2. Temperature-programmed desorption spectra of H_2 from
15% Fe/SiO_2 (dried at $100°C$) as a function of temperature.
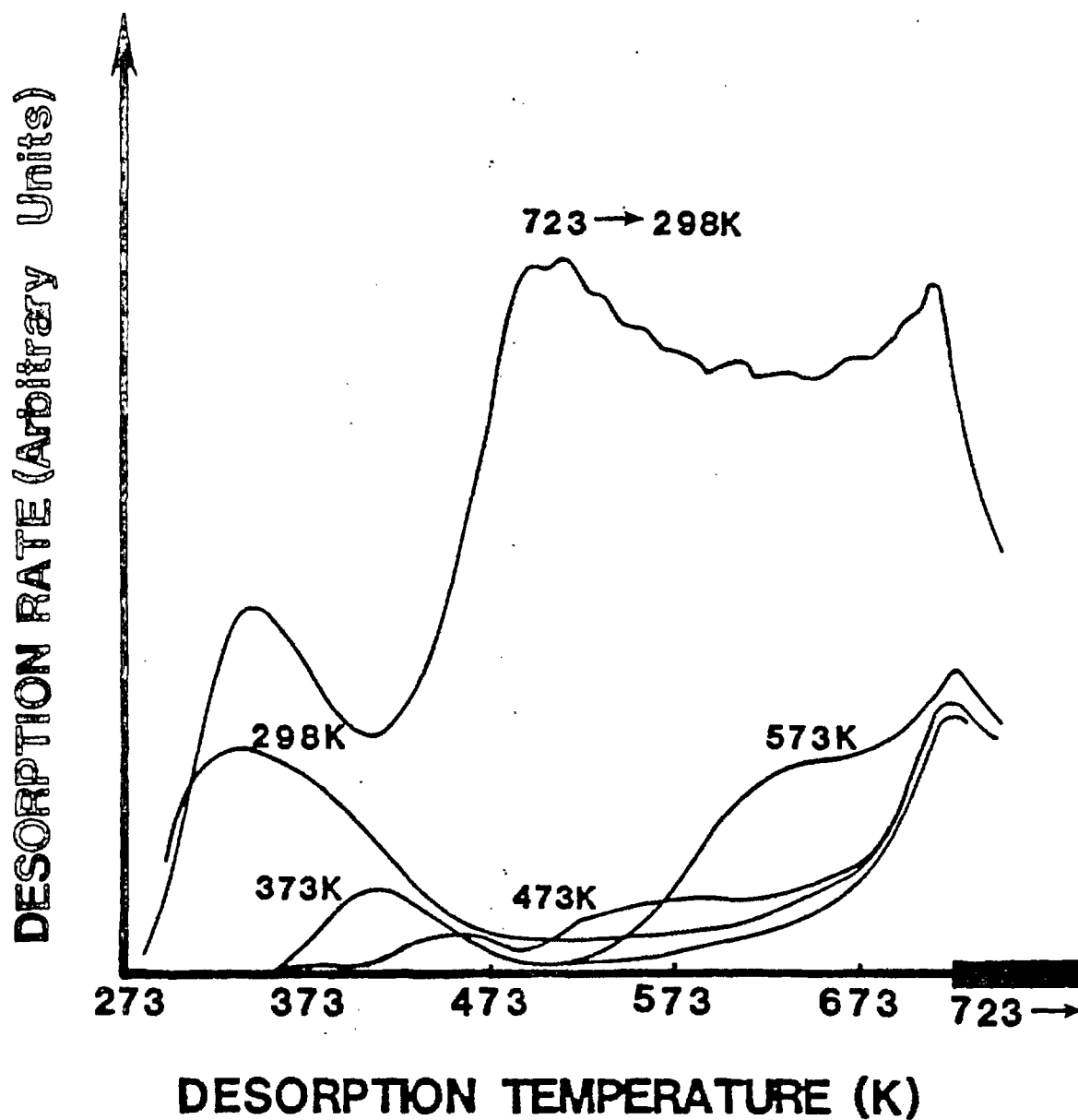
Figure 3. Temperature programmed spectra of H_2 from 15% Fe/3% K/SiO$_2$ (predried·at 373 K) as a function of adsorption temp-erature.
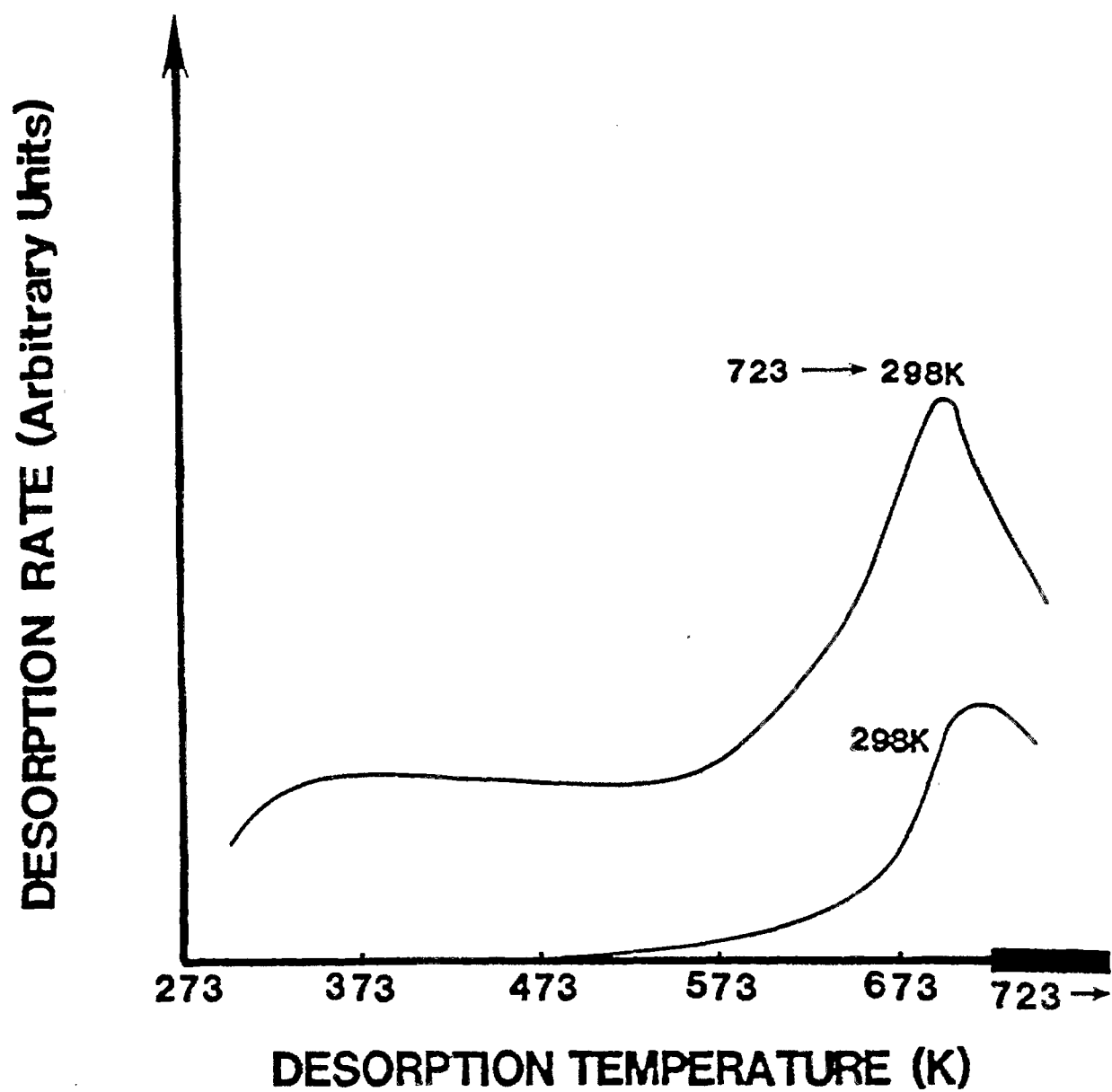
Figure 4. Temperature-programmed desorption of H_2 from 15%
Fe/3% K/SiO$_2$ (calcined at 473 K) as a function of
adsorption temperatures.
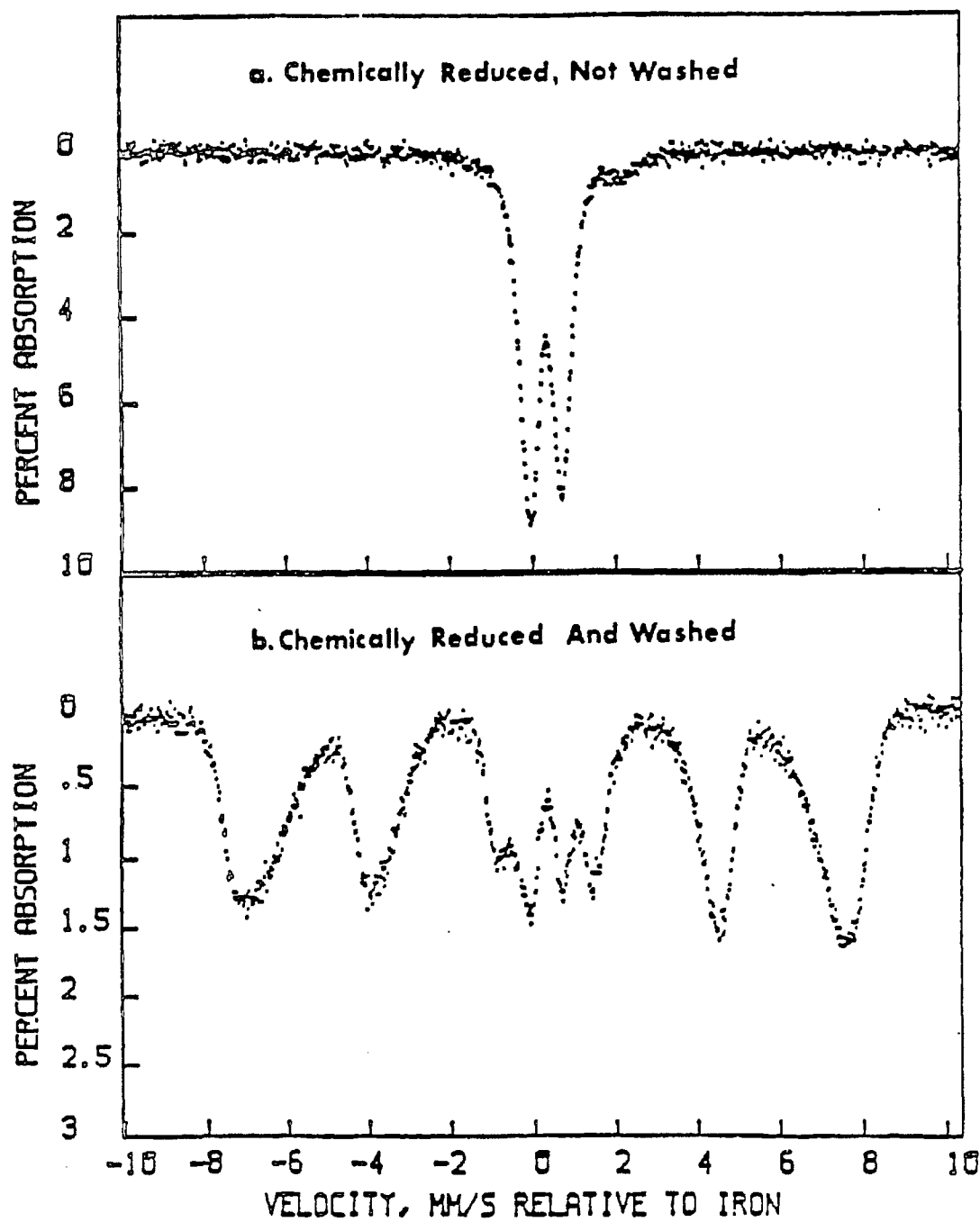
Figure 5.   Moessbauer Spectra of Unsupported Iron Boride
at Different States of Preparation
a.   Chemically reduced before washing
b.   Chemically reduced and washed with MeOH/water

PERCENT ABSORPTION

VELOCITY, MM/S RELATIVE TO IRON

15% Fe/SiO$_2$
precalcined at 473K

a.

15% Fe/0.2%K/SiO$_2$
precalcined at 473K

b.

15% Fe/1%K/SiO$_2$
precalcined at 473K

c.

15% Fe/3% K/SiO$_2$
precalcined at 473K

d.

15% Fe/3% K/SiO$_2$
precalcined at 373K

e.
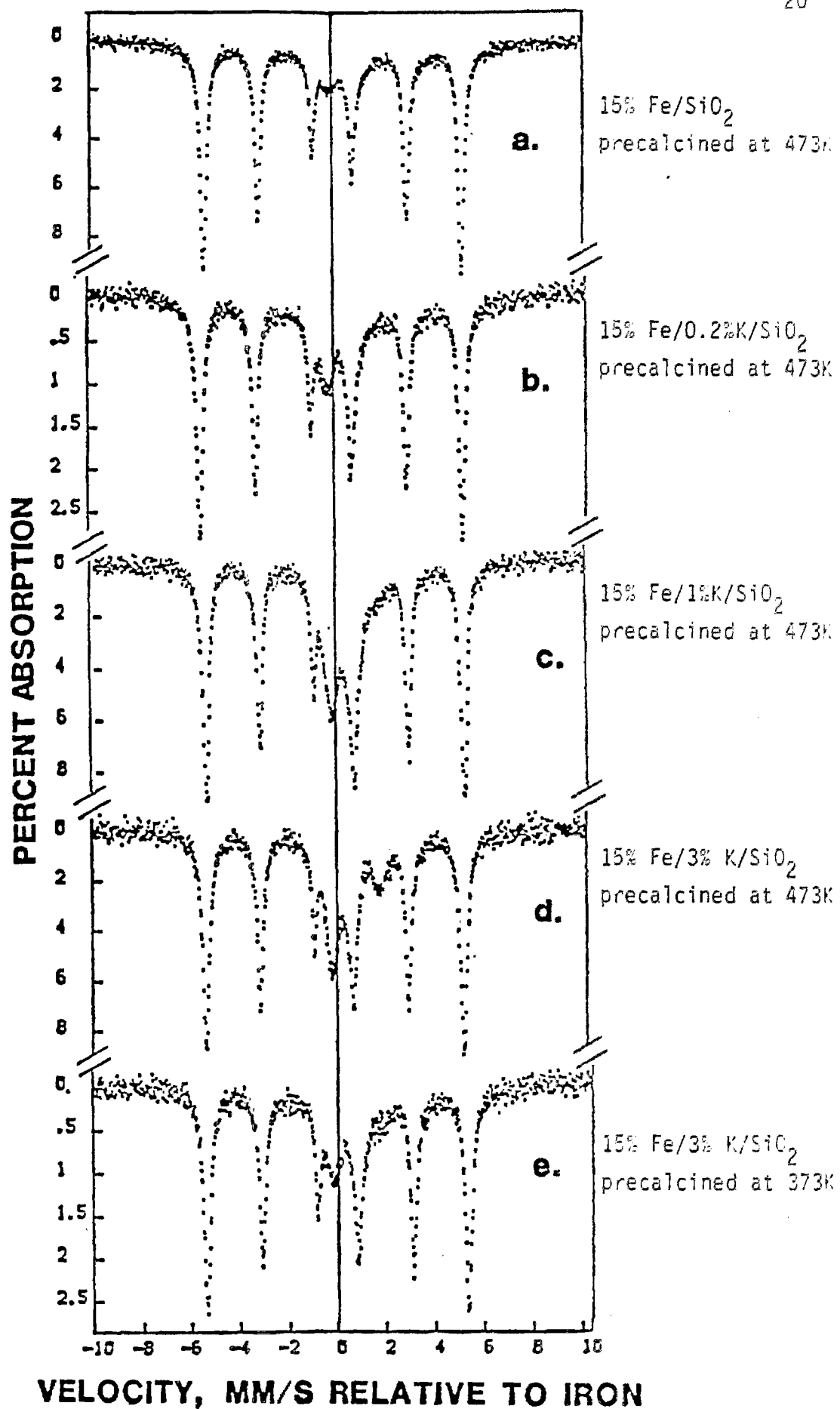
Figure 6. Moessbauer Spectra of reduced Fe/SiO$_2$ and Fe/K/SiO$_2$

TABLE 6

Dispersion and Phase Analysis of K-Promoted Fe/SiO_2 Catalysts

Catalyst	Calcination Temperature (K)	%D[a]	H_2 Chemisorption[a] d^s (nm)	Crystallite Size XRD d^v (nm)	Reduced Catalyst Moessbauer Spectrum Areas Fe^{3+}	Fe^{2+}	Fe^0	% Reduction Moessbauer[c]	O_2 Titration[d]
15% Fe/SiO$_2$	473	4.7	26	30	9.7	0	90.3	90.3	89.9
15% Fe/0.2% K/SiO$_2$	473	4.4	28		10.7	16.3	73.6	79.0	92.6
15% Fe/1% K/SiO$_2$	473	2.6	47		14.1	25.6	60.3	68.8	81.0
15% Fe/3% K/SiO$_2$	473	2.7	46	18	25.5	14.7	59.8	64.7	65.2
15% Fe/3% K/SiO$_2$	373	3.3	37	15	22.6	4.9	72.5	74.2	70.1

[a]Percent of Fe atoms exposed to surface based on total H_2 uptake.

[b]Based on Total H_2 Uptake.

[c]% Redn. $= \sum_i$ [3 - (oxidn. state ith phase)][wt. % ith phase]/3

[d]Based on formation of Fe_2O_3 at 723 K.

B. Task 2: Activity/Selectivity Properties

1. Activity/Selectivity Measurements

Activity/selectivity tests were performed in a single-pass, differential, fixed bed microreactor system described earlier (4) at 1 atm total pressure, a H_2/CO feed ratio of 2, and temperatures of 473-523 K. Conversions were limited to 10% or less to ensure measurements of surface reaction rates in the absence of mass and heat transfer disguises. Products were separated and analyzed using a Hewlett-Packard gas chromatograph (Model 5830A) equipped initially with a 12 m and later with a 30 m methyl silicone-coated capillary column and flame ionization detector. Fixed gases were separated and analyzed using a 1/8 in x 10 ft packed column of Chromosorb 102 and a thermal conductivity detector. The capillary column and ionization detector were calibrated for over 120 hydrocarbons and oxygenates ranging in carbon number from 1 to 25.

A complete correlation of retention times of hydrocarbons in the 12 m capillary column was worked out and reported earlier (6). It shows 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.

Feed flowrates were monitored to ±0.1% using mass flow controllers (Brooks Instruments). Mass balances over the reactor closed within 1-2%.

2. Activity/Selectivity Data

Specific activities in the form of CO turnover numbers (number of CO molecules converted per site per second) obtained during the first three years of study are listed in Table 7. Corresponding selectivity data are listed for the same catalysts in Table 8. Cobalt silica catalysts were found to be more active than iron/silica catalysts. The specific activities, selectivities and activation energies of these silica-supported cobalt and iron compare favorably with those reported earlier for similar catalysts (12,13). Specific activities of cobalt and iron borides vary considerably with preparation; however, generally the cobalt borides are more active and stable.

Specific activities and selectivities of cobalt and iron boride catalysts determined in a master's thesis study by Davis (14) are listed in Tables 9 and 10. It is evident from Table 9 that cobalt and iron borides are generally about as active as the corresponding unpromoted cobalt and iron catalysts. However, the activation energies for CoB-S-101 and CoB-102 samples having a relatively higher boron content (see Table 3) and which were not washed in water are about twice those of the other catalysts. This suggests that a different rate-determining step or mechanism is operative on the cobalt borides of high boron content. The selectivities of the metal borides varied with support and washing technique; it was probably influenced by the relative levels of boron and sodium present in the sample (see Table 3). For example, FeB-S-105 which contained 0.6% sodium and only 0.1% B exhibited a higher methane make than 15% Fe/SiO_2 (Fe-S-102), while FeB-101 which contained

TABLE 7

CO Turnover Numbers for Supported Iron and Cobalt Catalysts

Catalyst Code	H_2/CO Ratio	Reaction Temperature (K)	Turnover Number[a] ($N_{CO} \times 10^3$)	Activation Energy (kJ/gmole)
Fe-S-102	2	460	0.64	92
	2	483	2.5	
	2	498	3.9	
	1	449	0.19	99
	1	483	1.4	
	1	498	2.5	
Fe-S-103	2	448	0.72	83
	2	483	3.2	
	2	498	7.0	
	1	448	0.79	81
	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	152
	2	473	1.7	--
CoB-102	1	458	0.28	140
	1	470	0.64	
	1	485	1.6	
CoB-S-100	1	504	16	79
	1	520	29	
FeB-102	1	483	8.0	81
	1	493	15	
	1	503	23	
	1	513	25	
	1	523	42	
CoB-S-101	2	468	1.5	154
	2	486	6.3	
	2	499	21	

[a]Number of CO molecules converted per H adsorption site per second.

TABLE 8

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

Catalyst Code	Selectivity (wt.% of carbon product)					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	--

[a] $H_2/CO = 2$
[b] $H_2/CO = 1$

Table 9

Activities and Activation Energies for

Unpromoted and Boron Promoted

Cobalt and Iron Catalysts

Catalyst Code	Catalyst	Temp(K)	Turnover Number ($N_{CO} \times 10^3$)	Activation Energy (kJ/g mole)
Fe-S-102	15% Fe/SiO$_2$ [b]	483	2.5	92.5
FeB-S-105	FeB/SiO$_2$ [a]	483	3.8	82
FeB-101	FeB [a]	483	8.1	81
Co-S-105	10% Co/SiO$_2$ [c]	498	7.5	69
CoB-S-101	CoB/SiO$_2$	486	6.3	150
"	CoB/SiO$_2$ [a]	504	16	79
CoB-102	CoB	485	1.6	140

[a] These catalysts were washed in water.

[b] Data from this study (see Table 7).

[c] Data from Ref. 15.

Table 10

Product Selectivities for Iron Boride Catalysts at 498 K and Cobalt Boride Catalysts at 483 K

Catalyst Code	Catalyst		CH_4	C_2-C_4	C_{5+}	CO_2	Alcohols
Fe-S-102	15% Fe/SiO$_2$	c	0.12	0.23	0.02	0.56	0.07
FeB-S-105	FeB/SiO$_2$	a	0.26	0.19	0	0.55	0
FeB-101	FeB	a	0.17	0.44	0.23	0.10	0.06
Co-S-105	10% Co/SiO$_2$	d	0.27	0.24	0.34	0.04	0.11
CoB-S-101	CoB/SiO$_2$	a	0.31	0.26	0.31	0.06	0.06
"	CoB/SiO$_2$	b	0.07	0.20	0.72	0.01	0.00
CoB-102	CoB	b	0.15	0.24	0.50	0.07	0.04

[a] Washed in water.

[b] Washed only in methanol.

[c] Data from this study (see Table 8).

[d] Data from Ref. 15.

relatively less sodium (0.2%) and more boron (1.6%), produced more C_2-C_4 and C_{5+} products and less CO_2 relative to the 15% Fe/SiO_2. Selectivities of CoB-S-101 and CoB-102 washed only in methanol were significantly different than for 10% Co/SiO_2 (Co-S-105), i.e. these former catalysts produced less methane and higher C_{5+} gasoline fractions. On the other hand, the selectivity of the CoB-S-101 sample washed in water and which had a lower boron content was almost the same as that of Co/SiO_2. X-ray data obtained for the methanol-washed cobalt borides provided evidence for the presence of stoichiometric Co_3B (14). The investigation of cobalt and iron borides is being continued under a separate three year contract (16).

The effects of support, potassium promoter and precalcination pretreatment on the adsorption and CO hydrogenation activity/selectivity properties were investigated in the dissertation work of Rankin (17). The activity/selectivity measurements from this study are summarized in Tables 11-14 and in Figures 7-9. The specific activity and activation energy for iron in CO hydrogenation vary significantly with support (see Table 11); indeed specific activities vary among these catalysts by a factor of 40 while activation energies range from 54-132. These differences in activity may be due to (i) structure sensitivity (18,19) since these catalysts vary in their degree of dispersion and since two recent studies show that specific activity decreases with increasing dispersion (18,19) and (ii) differences in the relative distributions of metal, oxide, and carbide phases due to differences in the degree of interaction with the support. For example, the interaction of iron with alumina is strong and hence the catalyst contains a large fraction of the iron as oxides even after reduction for 36 hours at 723 K.

The selectivities of these same iron catalysts are likewise influenced by the differences in support (see Table 12). Indeed, hydrocarbon product distributions, CO_2 selectivities and propagation probabilities vary a great deal among these catalysts. For example, the Fe/C catalyst produces mainly CO_2 and a small C_2-C_4 fraction while unsupported iron, Fe/SiO_2 and Fe/Al_2O_3 produce a wide spectrum of C_1-C_{10} hydrocarbons and relatively little CO_2. Fe/ZSM-5 and Fe/Silicalite produce negligible quantities of olefins while a large fraction of the hydrocarbons produced by Fe/C are olefinic.

The data in Tables 13 and 14 and in Figures 7-9 illustrate the effects of potassium and precalcination temperature on specific activity and selectivity of Fe/SiO_2 catalysts. From Table 13 it is evident that specific activities of both 15% Fe/SiO_2 and 15% Fe/3% K/SiO_2 catalysts decrease as precalcination temperature is increased from 373 to 473 K. For catalysts calcined at 473 K, activity and activation energy decrease with increasing K content. Interesting corresponding modifications in product selectivity are also observed (see Table 14 and Figs. 7-9). For example, methane and olefin/paraffin ratios of Fe/SiO_2 and $Fe/K/SiO_2$ increase as the precalcination temperature is increased. What is most interesting is the decrease in C_{5+} fraction and increase in C_2-C_4 fraction and olefin/paraffin ratio with increasing K content of catalysts precalcined at 473 K. Indeed the product distributions of Fe/SiO_2 (precalcined at 473 K) and of Fe/3% K/SiO_2 (precalcined at 373 K) are typical of FT catalysts (see Figs. 7-8), i.e. involve products ranging from C_1-C_{10} hydrocarbons. Moreover, a plot of ln [mole fraction] versus carbon number is linear for both these catalysts, i.e. is consistant with Anderson-Schulz-Flory kinetics. However, the product distribution for 15% Fe/3% K/SiO_2 precalcined at 473 K (Fig. 9) consists of

Table 11

Effect of Support on Fe Catalyst Activity

(2/1 H_2/CO, 1 atm, 498 K)

Catalyst Code	Catalyst	N_{CO}[a] $(\times 10^3)$ (sec^{-1})	Activation Energy E_A (kJ/gmole)
Fe-100	Unsupported Fe	4.0	132
Fe-S-105	15% Fe/SiO$_2$	0.36	110
Fe-A-100	15% Fe/Al$_2$O$_3$	0.21	99
Fe-C-100	15% Fe/C	0.11	54
Fe-Z-100	15% Fe/ZSM-5	1.8	110
Fe-L-100	15% Fe/Silicalite	0.86	116

[a] Molecules CO reacted per site per second (based on total H_2 uptake)

Table 12

The Effect of Support on Selectivity of Fe Catalysts
(2/1 H_2/CO, 1 atm, 498 K)

Catalyst	Carbon Selectivity (9%)					$\dfrac{Olefin^a}{Paraffin}$	% Branching[b]	H_2/CO Usage	Propagation Probability α
	C_1	C_2-C_4	C_{5+}	C_{OH}	CO_2				
Unsupported Fe	16.8	35.6	27.8	2.9	17.0	0.61	14.1	1.76	0.47
15% Fe/SiO_2	24.7	42.9	20.6	4.4	7.4	1.19	25.5	2.11	0.51
15% Fe/Al_2O_3	17.7	28.4	32.8	1.3	19.9	0.72	13.6	1.67	0.57
15% Fe/C	0.7	4.3	0.5	--	94.5	2.28	--	0.82^c	0.38
15% Fe/ZSM-5	17.5	36.4	29.3	2.3	14.5	0.12	81.2	1.89	0.48
15% Fe/Silicalite	19.5	49.1	18.4	4.4	8.6	0.08	58.4	2.13	0.45

[a] C_2-C_4 fraction.

[b] C_6 fraction.

[c] Influenced by CO_2 from support.

TABLE 13

Effects of K-Level and Calcination Temperature on the CO Hydrogenation Activity of Fe/K/SiO$_2$ (H$_2$/CO=2, 1 atm, 523 K)

Code	Catalyst	Calcination Temp (K)	N_{CO} x 10^3 (s^{-1})[a]	Activation Energy[b] (kJ/mol)
Fe-S-102	15% Fe/SiO$_2$	373	11	93
Fe-S-105	15% Fe/SiO$_2$	473	1.6	110
FeK-S-105	15% Fe/0.2% K/SiO$_2$	473	0.27	104
FeK-S-103	15% Fe/1.0% K/SiO$_2$	473	0.12	72
FeK-S-102	15% Fe/3% K/SiO$_2$	473	0.063	32
FeK-S-104	15% Fe/3% K/SiO$_2$	373	5.9	124

[a] CO turnover frequency - molecules CO reacted per H adsorption site per second.

[b] Activation energy for CO conversion determined from CO turnover frequencies in the temperature range 473-523 K.

TABLE 14

Effects of Potassium Level and Calcination Temperature on Selectivity of K-Promoted Fe/SiO$_2$ Catalysts
(H$_2$/CO = 2, 1 atm)

Catalyst	Calcination Temperature (K)	Reactor Temperature (K)	Carbon Selectivity[a] (wt.%)					Olefin[b] Paraffin	H$_2$/CO[c] Usage
			C$_1$	C$_2$-C$_4$	C$_{5+}$	C$_{OH}$	CO$_2$		
15% Fe/SiO$_2$[d]	373	498	16.0	27.0	3.0	7.0	47.0	0.33	--
15% Fe/SiO$_2$	473	473	25.0	43.3	21.8	4.1	5.8	1.1	2.1
		498	24.7	42.9	20.6	4.4	7.4	1.2	2.1
		523	21.5	41.8	19.8	3.0	13.9	1.2	1.9
15% Fe/0.2% K/SiO$_2$	473	473	13.2	56.4	0	0	30.4	8.2	1.25
		498	7.9	31.9	11.8	0.1	48.3	1.2	0.68
		523	6.2	25.2	24.0	0.6	44.1	3.5	0.77
15% Fe/1% K/SiO$_2$	473	473	13.8	60.7	0	0	25.6	321	1.4
		498	13.5	48.8	2.8	0	34.9	11	1.09
		523	10.5	29.8	15.1	0.1	44.6	2.9	0.80
15% Fe/3% K/SiO$_2$	473	473	20.3	77.3	0	0	2.4	>400	2.15
		498	20.2	75.6	0	0	4.2	>400	2.1
		523	16.0	53.9	2.2	0	28.0	9.8	1.4
15% Fe/3% K/SiO$_2$	373	473	13.0	27.5	43.3	1.8	14.4	1.5	1.8
		498	13.1	27.7	40.7	0.8	17.7	2.0	1.7
		523	12.0	25.9	31.3	1.9	28.9	2.2	1.3

[a]Fraction of converted CO appearing as a specified product in wt.%.

[b]C$_2$ - C$_4$ fraction.

[c]Moles of H$_2$ used per mole of CO converted.

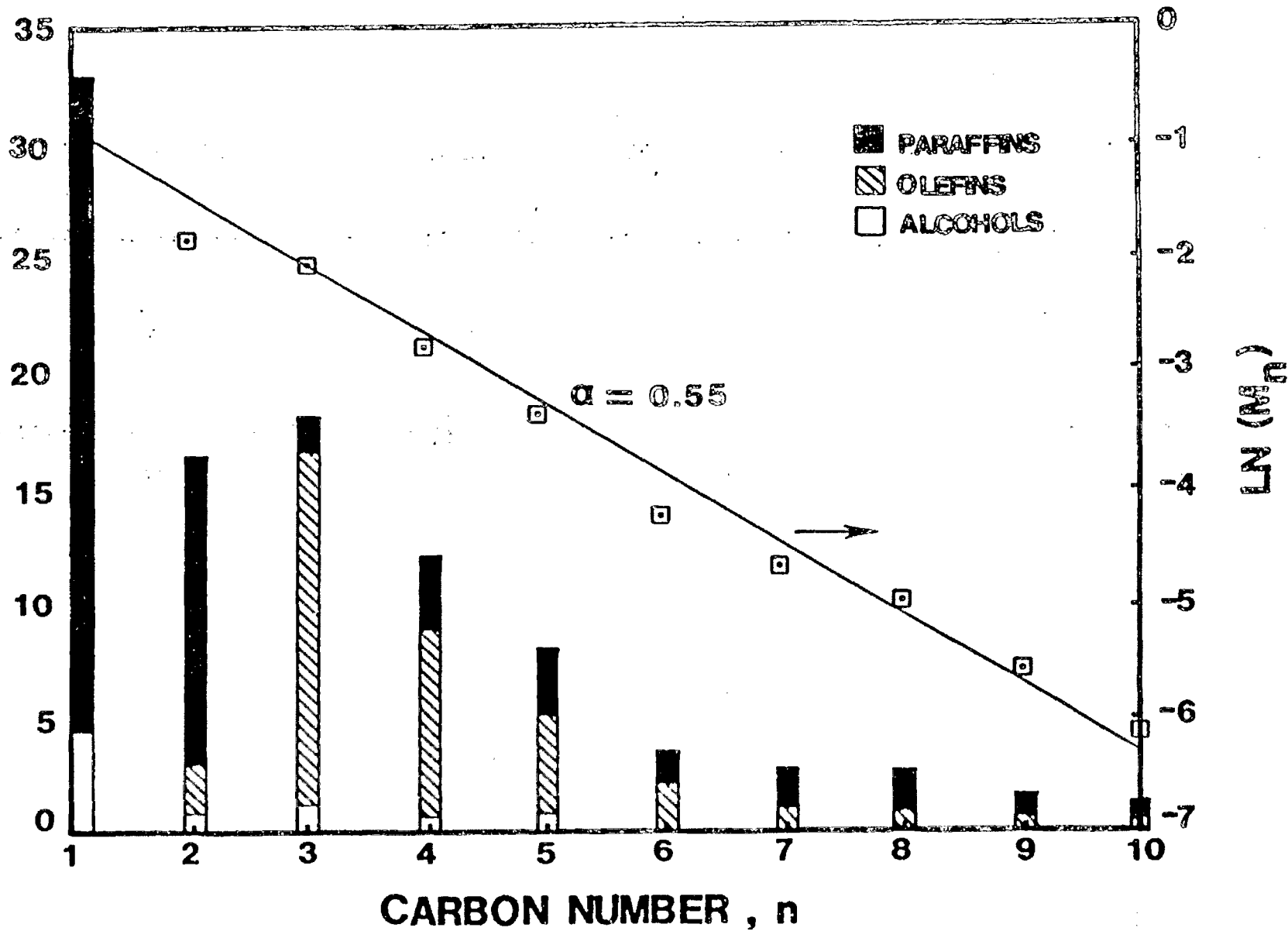[d]Data obtained earlier using a 12 m glass capillary column.

Figure 7. Hydrocarbon Product Distribution and Schulz-Flory Plot. 15% Fe/SiO$_2$
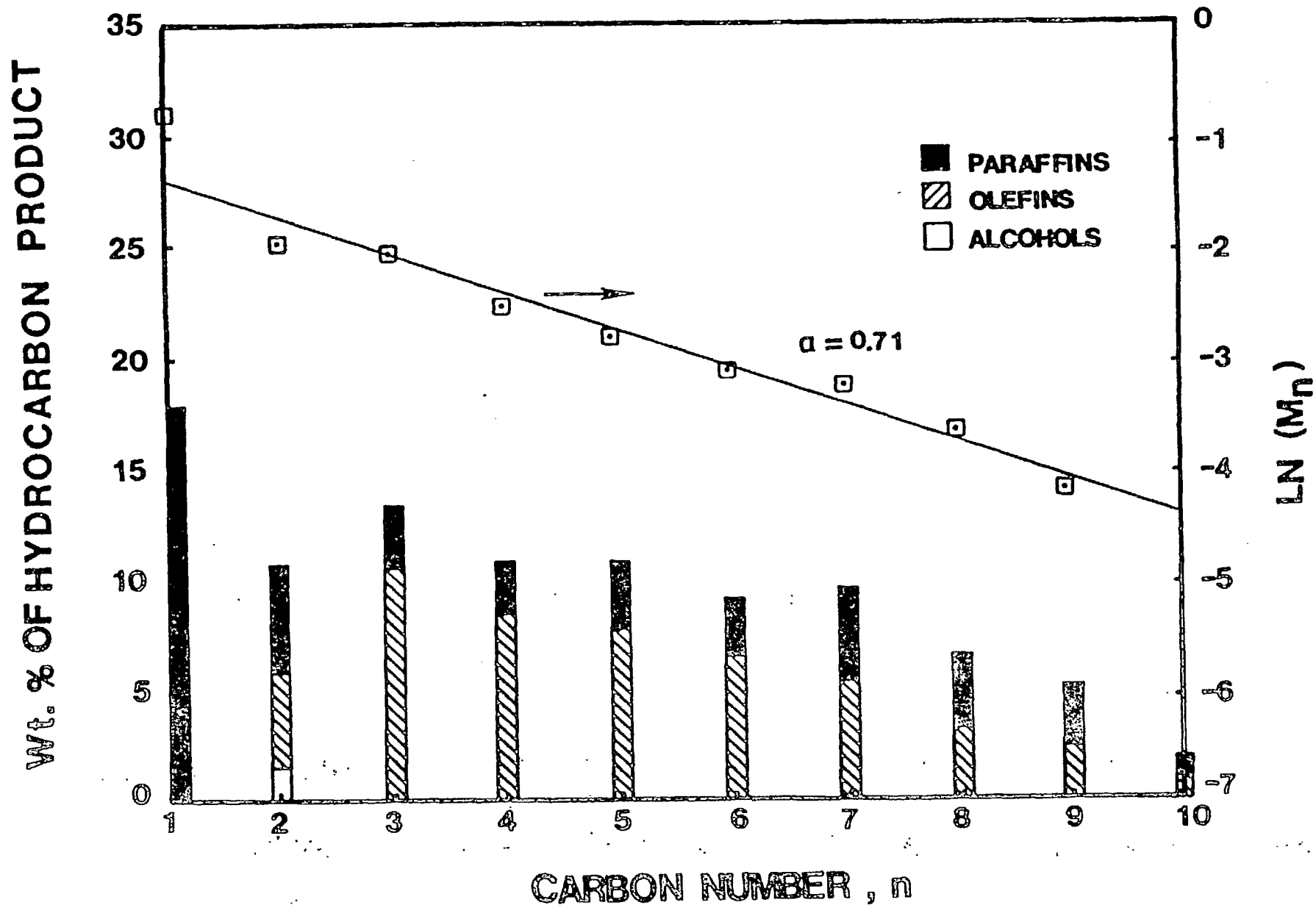(Calcined 473 K); 498 K, H$_2$/CO = 2, 1 atm.

Figure 8.   Hydrocarbon Product Distribution and Schulz-Flory Plot.   15% Fe/3% K/SiO$_2$
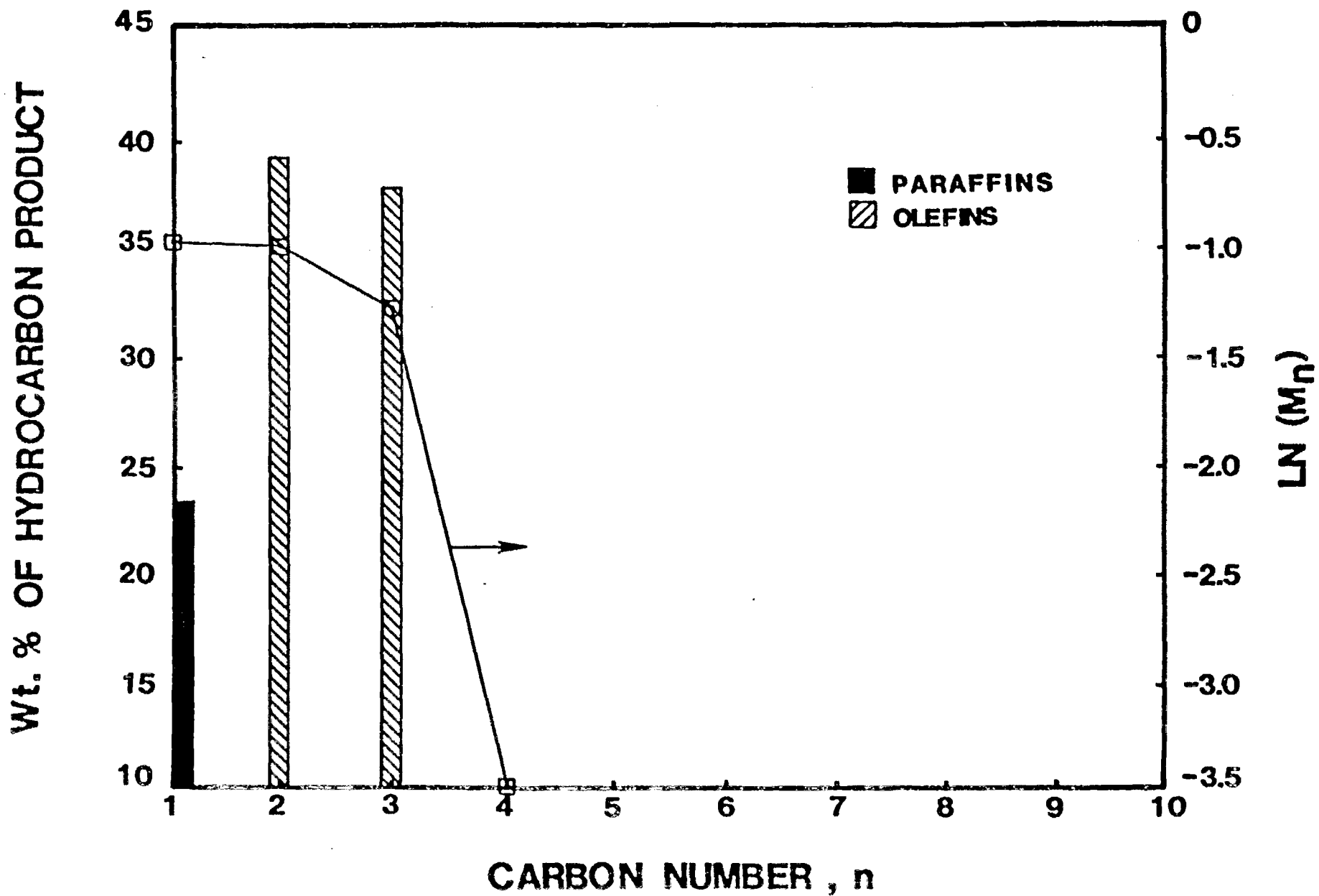(Calcined 373 K); 498 K, H$_2$/CO = 2, 1 atm.)

Figure 9.   Hydrocarbon Product Distribution and Schulz-Flory Plot.   15% Fe/3% K/SiO₂
(Calcined 473 K); 498 K, H₂/CO = 2, 1 atm.)

only methane, ethylene and propylene; in this case the distribution is clearly not Anderson-Schulz-Flory. This fact and the unusually low activation energy of 32 kJ/mole (Table 13) suggest that CO hydrogenation occurs on this catalyst by a mechanistic route distinct from FT synthesis. The evidence (11) suggests that this behavior is due to highly activated hydrogen adsorption leading to a deficiency of hydrogen on the surface; the lower activity and activated adsorption may be caused by the presence of potassium silicate or other such combination of support and promoter on the surface as a result of the precalcination treatment. This possibility is currently being investigated in a followup study in this laboratory.

C. Task 3: In Situ H_2S Poisoning Measurements

A master's thesis study of sulfur poisoning of a cobalt/silica and four iron catalyst (unsupported, silica-supported, K-promoted and borided) was conducted by Mr. Richard Bowman (20). The results of this study were reported at the National AIChE Meeting (21) and at an ICC Post Congress Symposium in Germany (22) and will be published in Applied Catalysis (23).

The laboratory reactor system and experimental procedures were described in an earlier report (5). The catalysts were exposed to 0.5-8 ppm H_2S either in situ (during reaction) or before reactor testing in pure hydrogen (presulfiding treatment). Catalyst activity and selectivity were monitored as a function of sulfur coverage after the catalyst had been conditioned in the reaction mixture 24 hours.

The results of in situ poisoning experiments are shown in Figures 10-12. Plots of normalized activity (activity at time t divided by initial activity) for Fe/SiO_2 versus sulfur coverage at different H_2S concentrations are shown in Fig. 10 during reaction at 500 K, 1 atm and $H_2/CO = 2$. The more rapid decline at 0.6 and 1.8 ppm suggests that monolayer surface sulfides are formed below about 2 ppm H_2S while bulk sulfides are formed at higher H_2S concentrations. Similar normalized activity profiles are shown in Figure 11 for in situ poisoning in 2 ppm H_2S of unsupported iron, Fe/SiO_2 and $Fe/K/SiO_2$. There is a large decline in activity with increasing sulfur coverage which is apparently independent of support and promoter in these catalysts; indeed about 50% of the activity is lost for a nominal sulfur coverage of only 0.04-0.08 atoms of sulfur per surface atom of iron. In presulfiding experiments with Fe/SiO_2, 4-8 times as much sulfur was required for the same extent of deactivation. In other words, there appears to be a synergestic deactivation effect during in situ sulfur poisoning which cannot be accounted for by adsorption of sulfur atoms alone.

While silica-supported or potassium-promoted iron was not significantly more resistant to sulfur poisoning, the iron boride catalyst clearly was. Indeed, only about 5% of its activity was lost during exposure for several days to 8 ppm H_2S. A most striking result was obtained upon exposure of the same catalyst (different sample) to 0.5 ppm H_2S: the activity increased by 40-45% after 2-3 days exposure! We don't really know the reason for this behavior, but it is clearly something worth additional investigation.

The in situ deactivation data were fitted to a model developed previously for sulfur poisoning in a fixed bed (24). Deactivation parameters and
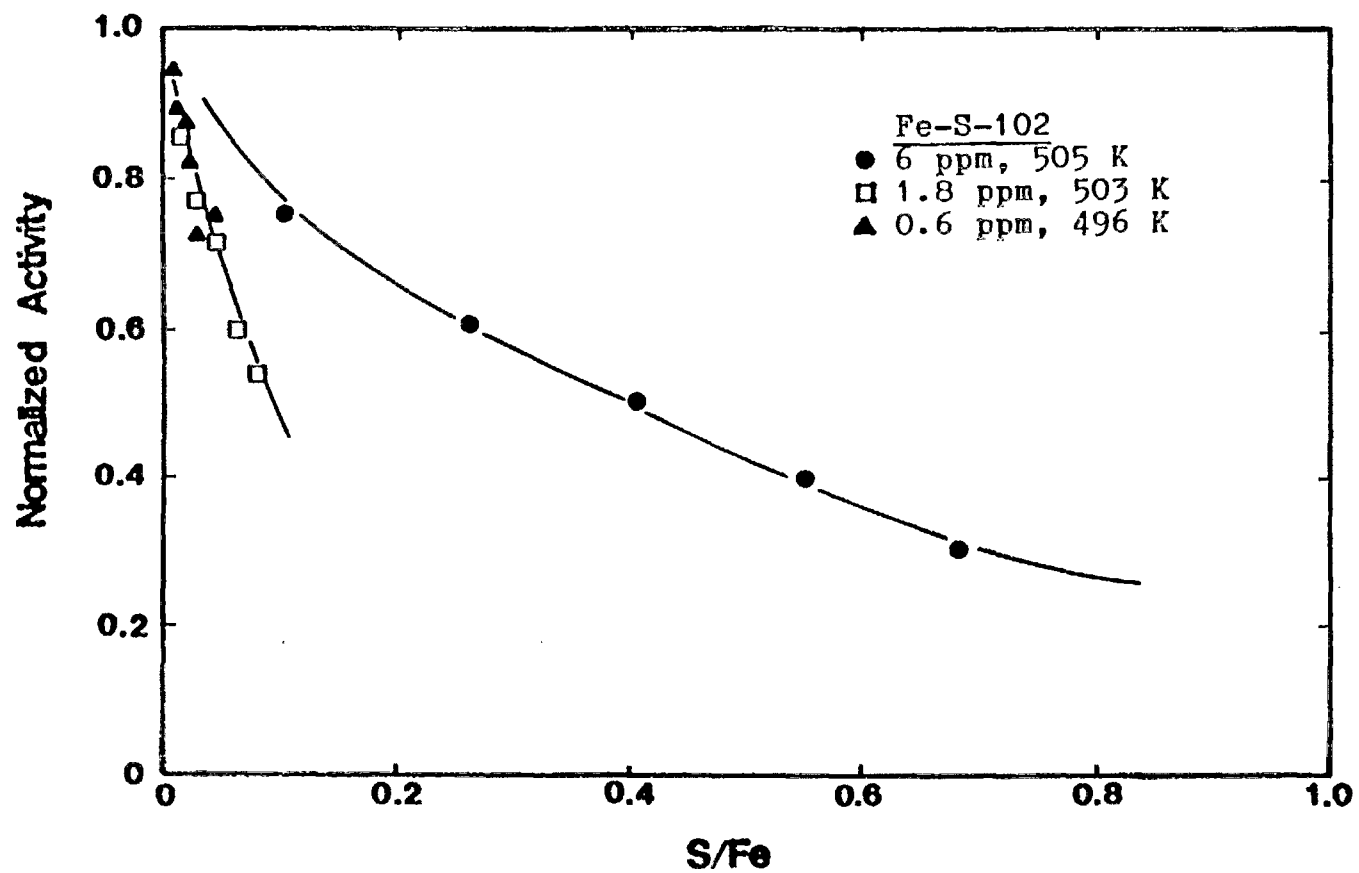
Figure 10.   Normalized Activity of Fe-S-102 at 0.6, 1.8, and 6.0 ppm
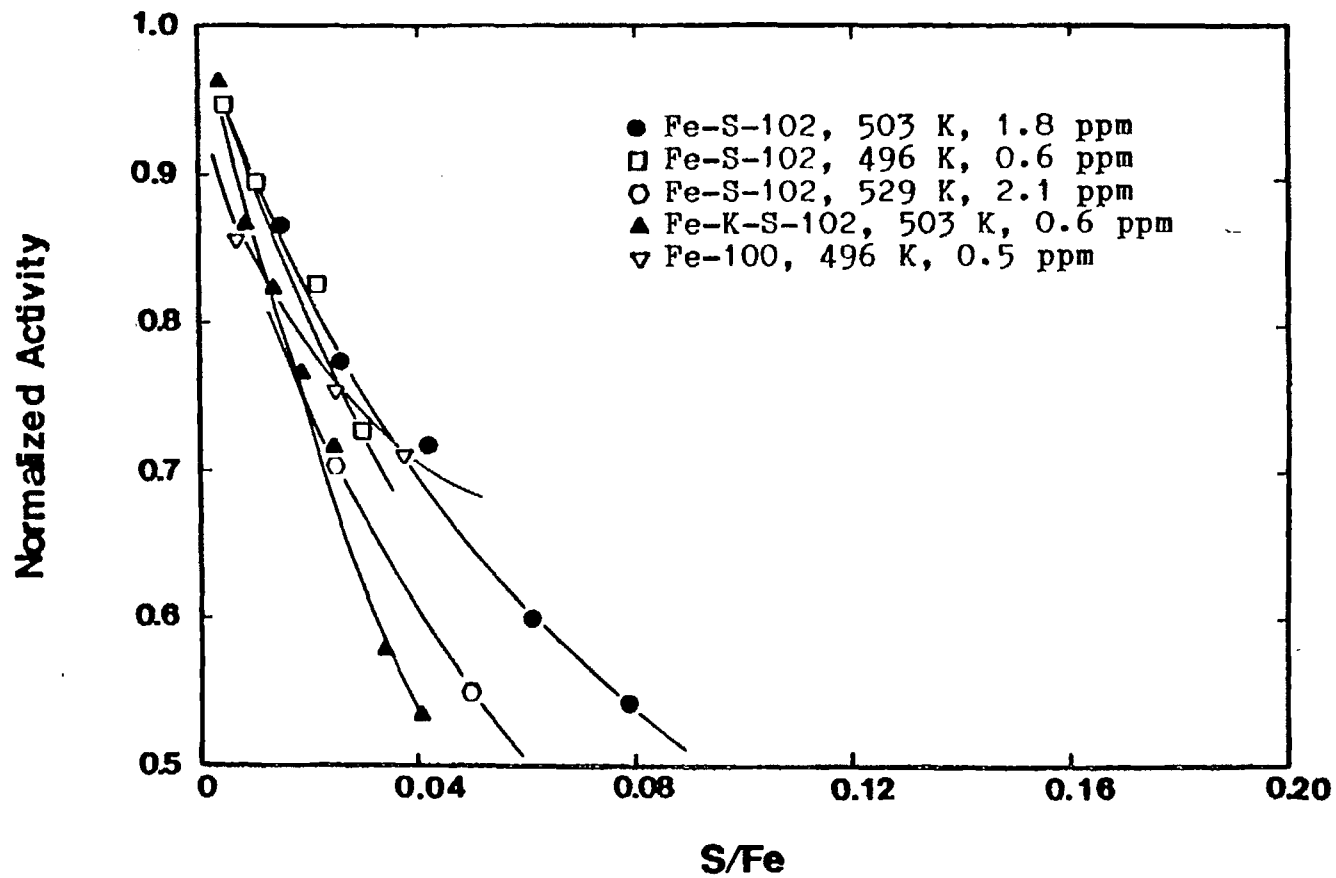H_2S, 496-505 K, and H_2/CO = 2 as a Function of
Sulfur to Iron ratio

36

Figure 11. Normalized Activity of Fe-S-102 Fe-K-S-102, and Fe-100 at H_2S concentrations below 2 ppm, $H_2/CO = 2$
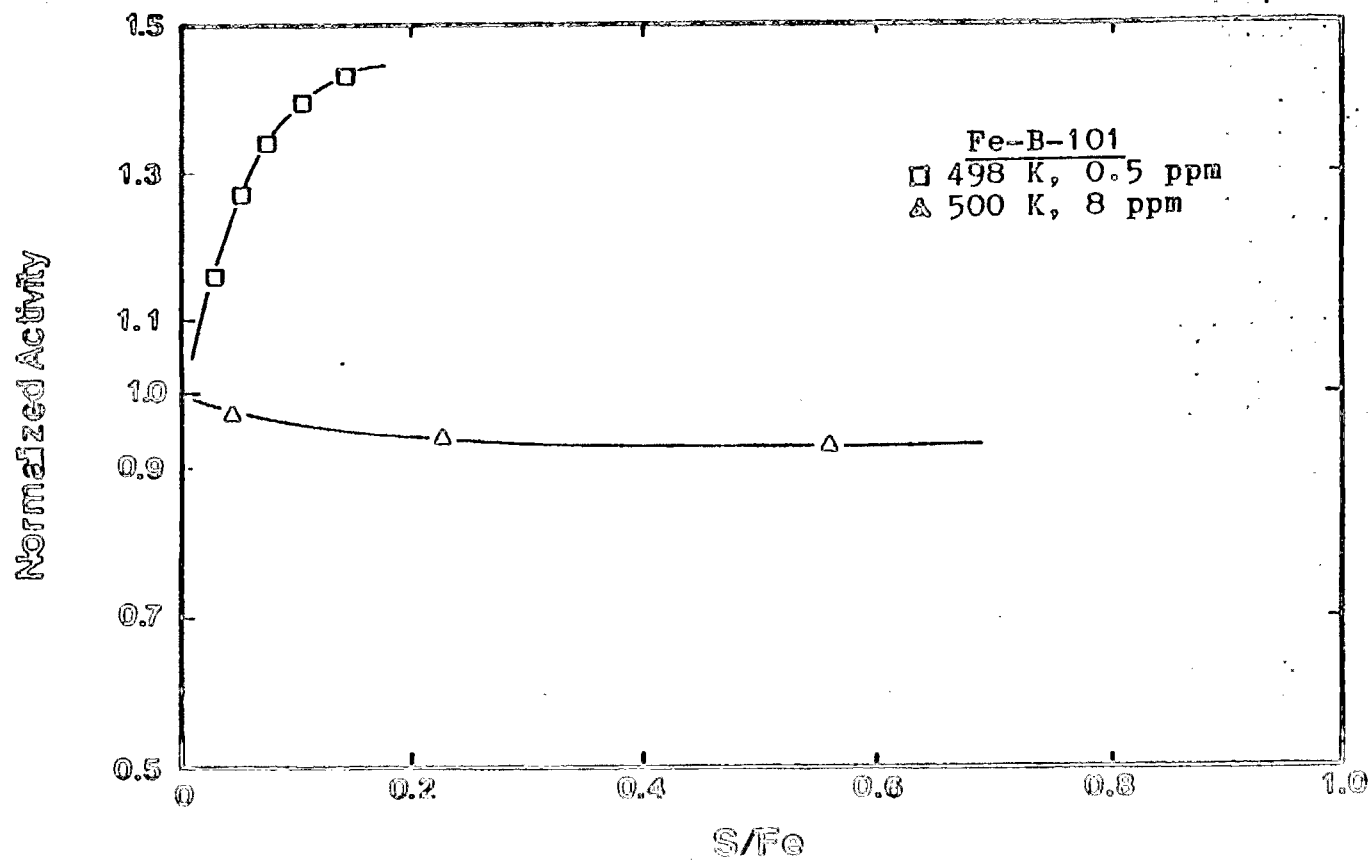
Figure 12. Normalized Activity of Fe-B-101 at 0.5 and 8 ppm, 500 K, $H_2/CO = 2$ as a Function of Sulfur to Iron Ratio

estimates of catalyst life obtained from this model are summarized in Table 15. It is estimated that FeB-101 has a catalyst life which is 10-100 times greater than for the other catalysts. The deactivation rate constant is an intrinsic measure of resistance to poisoning by sulfur. The significantly lower value for FeB-101 confirms its intrinsic resistance to poisoning; this could be due to a modification in the way sulfur affects nickel ensembles on a FeB surface. The sulfur adsorption site density S_0 is a measure of sulfur adsorption capacity. In the case of Fe-B-101, the large S/M_s value of 19 indicates that 19 times as much sulfur is taken up by this catalyst as there are sulfur adsorption sites. In other words, the superior life of FeB-101 is due in large part to its ability to absorb and adsorb sulfur. Apparently then, the boron acts as a getter to extend the life of iron FT sites in the catalyst.

Figure 13 shows the effects of continuous sulfur exposure during reaction in a fixed bed on the carbon product selectivities (fractions of converted CO appearing as different products) of Co/SiO_2. The product distribution of the partially poisoned catalyst shows a marked shift towards higher molecular weight products. This effect is maximized at about 50% activity and 50% sulfur coverage but then appears to diminish as the sulfur coverage approaches saturation and the catalyst activity diminishers. At nearly complete sulfur coverage and nearly zero activity the selectivities for different hydrocarbons are approximacely the same as in the fresh catalyst. CO_2 selectivity, however appears to decrease at the same rate as the rate of CO conversion. In other words, the water gas shift reaction is preferentially poisoned on Co/SiO_2. No such shift toward higher selectivity for higher molecular weight hydrocarbons with increasing sulfur coverage was observed for Fe/SiO_2 and $Fe/K/SiO_2$ catalysts.

D. Technical Communications and Miscellaneous Accomplishments

Technical communications were an important part of this contract work. Table 16 summarizes publications in connection with this contract. Altogether 6 papers were published, sumitted or are in preparation. Thirteen papers were presented at national and regional meetings while 5 seminars were presented at universities and companies (see Table 17). The principal investigator visited 24 laboratories and received 45 visitors (see Tables 18 and 19).

Probably the most important aspect of this contract work was the education and training of undergraduate and graduate chemical engineering students. Table 20 lists the students supported by this contract, while dissertations completed as part of this contract are listed in Table 16.

TABLE 15

Deactivation Rate Parameters for _In Situ_ H_2S Poisoning[a]

Catalyst	H_2 Uptake[b] ($\mu mol/g$)	H_2S Conc. (ppm)	s_0[c] ($\mu mol/g$)	S/M_s[d]	k, Deact. Rate[e] Const. x 10^3 (h^{-1} ppm^{-1})	Catalyst Life (days)
Co-S-102	68	6	57	0.42	9.1	14
Fe-S-102	57	0.6	12	0.10	34	3.2
		6	63	0.55	4.8	17
Fe-K-S-102	23	0.5	9.0	0.20	8.3	4.7
		6	73	1.6	1.1	36
Fe-100	15	0.5	13	0.43	22	6.6
FeB-101	9.5	8	366	19	0.4	371

[a] In a flowing stream of 67% H_2, 33% CO, 0.5-0.6 or 4-6 ppm H_2S at 500 K, 1 atm, conversions of 2-30%.

[b] Total H_2 adsorption uptake after cooling in H_2 from 673 to 300 K.

[c] Sulfur adsorption site density; calculated assuming that 10^6 ppm = 2 x 10^{20} sites/g for supported catalysts (5 x 10^{19} sites/g for FeB and 10^{20} sites/g for Fe-100).

[d] Atoms of sulfur adsorbed during reaction relative to available H_2 adsorption sites.

[e] Based on -da/dt = kna where a = normalized activity and n = H_2S concentration in ppm.

[f] Calculated from the Bartholomew-Wise deactivation model (Refs. 14-17) assuming final activity is one-half initial activity, and assuming n = 1 ppm H_2S and a space velocity of 500 h^{-1}.
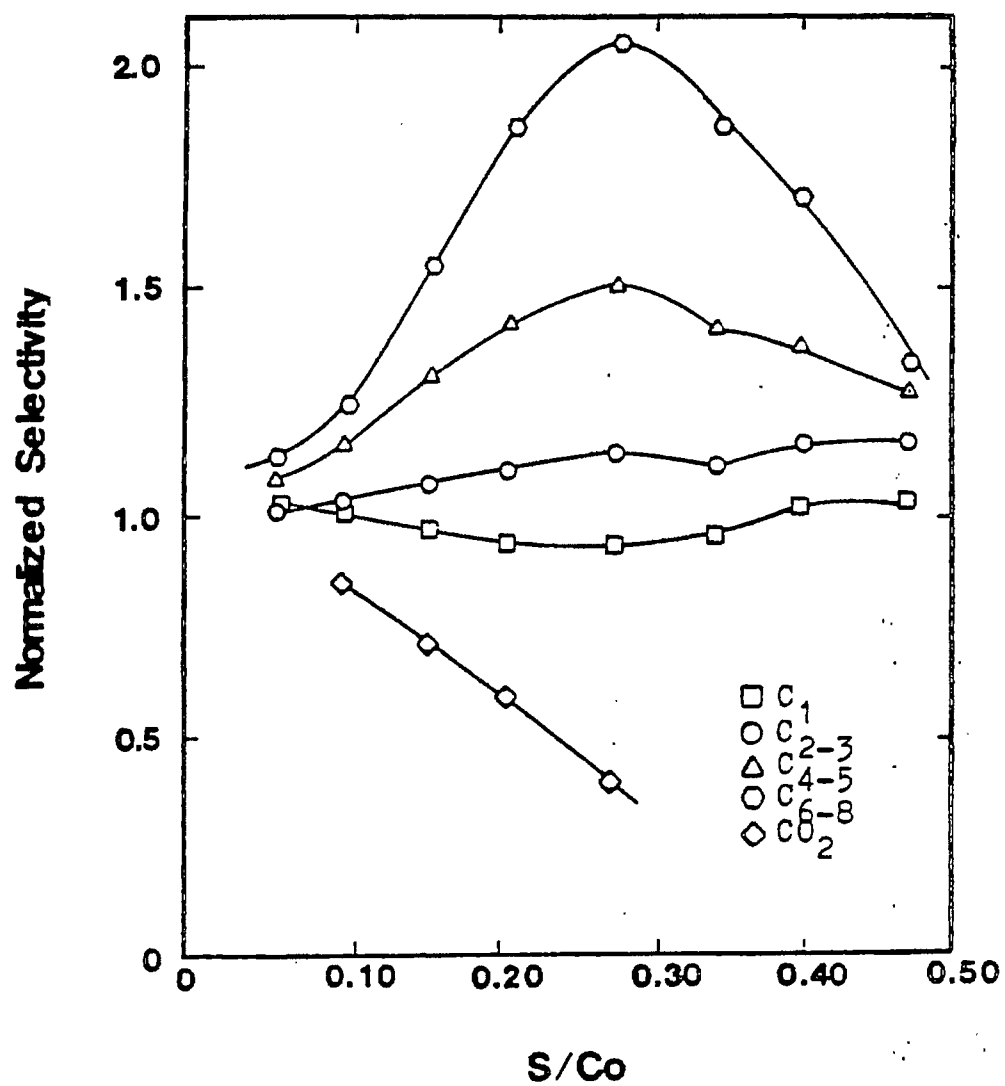
Figure 13. Normalized Selectivity of Co-S-102 as a
Function of Sulfur to Cobalt Ratio
(6 ppm H_2S, 500 K, H_2/CO = 2)

Table 16   Publications in Connection
With This Contract

Journal Publications

1. G.D. Weatherbee, J.L. Rankin, and C.H. Bartholomw, "Activated Adsorption of H_2 on Iron: Effects of Support, Potassium Promoter, and Pretreatment," Appl. Catal. <u>11</u>, 73 (1984).

2. C.H. Bartholomew and R.M. Bowman, "Sulfur Poisoning of Cobalt and Iron Fischer-Tropsch Catalysts," Appl. Catal., accepted, 1984.

3. J.L. Rankin and C.H. Bartholomew, "Effects of Potassium and Calcination Pretreatment on the Adsorption and Chemical/Physical Properties of Fe/SiO_2," paper in preparation, 1984.

4. J.L. Rankin and C.H. Bartholomew, "Effects of Calcination on the CO Hydrogenation Activity/Selectivity Properties of Potassium-Promoted Iron/Silica," paper in preparation, 1984.

5. J.L. Rankin and C.H. Bartholomew, 'Effects of Support on the Adsorption and Chemical/Physical Properties of Iron," paper in preparation, 1984.

6. J.L. Rankin and C.H. Bartholomew, "Effects of Support on the Activity and Selectivity of Iron in CO Hydrogenation," paper in preparation, 1984.

Theses and Dissertations

1. R.M. Bowman, "Sulfur-Poisoning of Iron and Cobalt Fischer-Tropsch Catalysts," M.S. Thesis, Brigham Young University, Aug. 1983.

2. D.M. Davis, "Cobalt Boride and Iron Catalysts for the Fischer-Tropsch Synthesis," M.S. Thesis, Brigham Young University, Dec. 1983.

3. Rankin, J.L., "The Effects of Support and Potassium Promoter on the Adsorption and CO Hydrogenation Activity and Selectivity of Iron," Ph.D. Dissertation, Brigham Young University, in final preparation, 1984.

Table 17

Technical Meeting, Papers, and Presentations in
Connection With This Contract

Technical Meeting Papers

1. C.H. Bartholomew and J.R. Katzer, "Sulfur Poisoning of Nickel in CO Hydrogenation," Presented at the International Conference on Catalyst Deactivation, Antwerp, Belgium, October 13-15, 1980.

2. C.H. Bartholomew, "Investigation of Catalysts for Selective Synthesis of Hydrocarbon Liquids from Coal-Derived Gases," Presented at the DOE University Contractors Conference on Coal Liquefaction, October 21-22, 1980.

3. J.L. Rankin and C.H. Bartholomew, "Investigation of Sulfur-Tolerant Catalysts for Selective Synthesis of Hydrocarbon Liquids from Coal-Derived Gases," DOE Contractors Conference on Indirect Liquefaction," Pittsburgh, PA, May 20, 1981.

4. J.L. Rankin and C.H. Bartholomew, "Investigation of Activity/Selectivity Properties of Iron and Cobalt Fischer-Tropsch Synthesis Catalysts," Micro ACS Meeting, Provo, UT, March 27, 1982.

5. J.L. Rankin and C.H. Bartholomew, "Fischer-Tropsch Synthesis on Promoted and/or Supported Iron and Cobalt Catalysts," Annual Meeting of the AIChE, Los Angeles, CA, November 14-19, 1982.

6. C.H. Bartholomew and R.M. Bowman, "Sulfur Poisoning of Cobalt and Iron Fischer-Tropsch Catalysts," Annual Meeting of the AIChE, Los Angeles, CA, November 14-19, 1982.

7. D.M. Davis and C.H. Bartholomew, "Boron-Promoted Iron and Cobalt Catalysts for Fischer-Tropsch Synthesis," Eighth Symposium of the Rocky Mountain Fuel Society, Salt Lake City, UT, February 24-25, 1983.

8. C.H. Bartholomew, "Metal Boride Catalysts for Indirect Liquefaction," University Coal Research Contractors Conference, Pittsburgh, PA, October 18-20, 1983.

9. J.L. Rankin and C.H. Bartholomew, "Effects of Support and Promoters on the Activity and Selectivity of Iron FT Catalysts," Ninth Symposium of the Rocky Mountain Fuel Society, Salt Lake City, February 22-24, 1984.

10. J.L. Rankin and C.H. Bartholomew, "Effects of Potassium on the Activity and Selectivity of Iron FT Catalysts," Micro ACS Meeting of the Central Section of the ACS, Provo, March 24, 1984.

11. C.H. Bartholomew, and R.M. Bowman, "Sulfur Poisoning of Cobalt and Iron Fischer-Tropsch Catalysts," ICC Post-Congress Symposium on Characterization of Activity, Selectivity and Deactivation of Solid Catalysts, Bochum, Germany, July 9-11, 1984.

12. J.L. Rankin and C.H. Bartholomew, "Effects of Pretreatment and Support on the Activity and Selectivity of Potassium-Promoted Iron," 188th National Meeting of the ACS, Philadelphia, August 27-31, 1984.

13. C.H. Bartholomew and J.L. Rankin, "Effects of Pretreatment and Support on the Activity and Selectivity of Potassium-Promoted Iron," 1984 Annual Meeting of the AIChE, San Francisco, Nov. 25-30, 1984.

Presentations at Universities and Companies

1. C.H. Bartholomew, "Metal Boride Catalysts in CO Hydrogenation," Process Sciences and Engineering, Pittsburgh Energy Technology Center, Oct. 31, 1979.

2. C.H. Bartholomew, "Metal Boride Methanation Catalysts," Dept. Chem. Eng., University of Delaware, April 10, 1980.

3. C.H. Bartholomew, "Metal Boride Catalysts in CO Hydrogenation," Department of Chemistry, University of Utah, May 19, 1981.

4. C.H. Bartholomew, "H_2 and CO Adsorptions on Co/ZSM-5 Catalysts," Presented to the Process Science and Engineering Division, Pittsburgh Energy Technology Center, Oct. 9, 1981.

5. C.H. Bartholomew, "Sulfur Poisoning and Carbon Deposition," Ashland Oil Co., Nov. 19, 1981.

Table 18

Laboratories Visited by the Principal Investigator
During contract Period

1. Process Sciences &   Dr. Richard Schehl   Oct. 31, 1979
   Engineering Division
   Pittsburgh Energy
   Technology Center

2. Cornell University   Prof. Robert Merrill   Feb. 14, 1980

3. Dept. of Chem. Eng.   Dr. Glen Schraeder   April 9-12, 1980
   Univ. of Delaware   Dr. James Katzer

4. Catalytica Associates   Dr. Robert Garten   April 15, 1980
                                   Dr. Ralph Dalla Belta
                                   Dr. Richards Levy

5. Lawrence Berkeley Lab   Dr. Heinz Heineman   April 16, 1980
   Univ. of California

6. Refinery Research   Dr. Kess Alley   Summer 1980
   Science & Technology   Dr. Dennis McArthur
   Union Oil Research   Dr. David Mears
   Brea, California

7. Petrochemical Institute   Prof. G.F. Froment   Oct. 16, 1980
   of Technology   Dr. P. Govind Menon
   University of Ghent

8. Institute of Physical   Prof. H. Knoezinger   Oct. 17, 1980
   Chemistry
   University of Munich

9. Laboratory of Coal Science,   Prof. Francis Hanson   Dec. 11, 1980
   Synthetic Fuels and Catalysis
   University of Utah

10. Department of Chemistry   Prof. Edward Eyring   May 19, 1981
    Laboratories
    University of Utah

11. Harvey Technical Center   Dr. John Mooy   Aug. 12, 1981
    ARCO Petroleum Co.
    Harvey, IL

12. Process Sciences and   Dr. Udaya Rao   Oct. 9, 1981
    Engineering Division

13. Ashland Oil Co.	James (Don) Carruthers Steven M. Kovach Jim Palmer Bill Hettinger	Nov. 19, 1981
14. Phillips Petroleum Co. (with Mr. Duane Davis)	Edward Sughrue Marvin Johnson Jack Gillary George Parks Dee Johnson	May 3-4, 1982
15. Dept. Chem. Eng. University of Washington	Charles Sleicher Barbara Krieger	July 28, 1982
16. Dept. Chem. Eng. University of Colorado	John Falconer	April 21, 1983
17. Dept. of Chemistry Colorado School of Mines	Scott Cowley	April 22, 1983
18. Dept. Fuels Engineering University of Utah	Frank Hansen Frank Massoth Joseph Shabtai	May 19, 1983
19. Dept. Chem. Eng. Montana State University	John Sears Wanen Scarrah Doug Smith Daniel Shaffer	Nov. 17, 1983
20. Amoco Oil Company	Mike Baird John Peri	Jan. 10, 1984
21. Topsoe Catalyst Co.	Henrik Topsoe Rostrup-Nielsen	June 28-29, 1984
22. Institute of Solid State and Radiochemistry	Frigyes Solymosi	July 12, 1984
23. Institute of Isotopes Budapest	Zoltan Poal	July 13, 1984
24. Monsanto Co.	Barry Haymore Bob Friedeman	Sept. 21, 1984

Table 19

Visitors and Speakers, BYU Catalysis Laboratory
During Contract Period

Dr. Robert Ference Technical Specialist	Catalyst Development Climax Molybdenum Co. of Michigan	Oct. 1-2, 1979
Prof. M. Albert Vannice Associate Professor	Dept. of Chemical Eng. Penn. State U.	Oct. 2, 1979
Professor Robert Merrill	Dept. of Chemical Eng. Cornell Univ.	Oct. 8, 1979
Dr. P. Govind Menon	Lab. for Petrochem. Eng. State University of Gent Belgium	Oct. 26, 1979
Dr. Perry Maxfield	Department of Chemistry Brigham Young University	Nov. 6, 1979
Dr. Richard Pannell	Catalysis Research Gulf Res. & Dev. Co.	Feb. 26, 1980
Dr. Howard Evans	IBM Corp. Boulder, Colorado	Feb. 27, 1981
Prof. John Falconer	Univ. Colorado	Mar. 12, 1981
Dr. Tony Perotta	Catalysis Research Gulf Res. & Dev.	Mar. 26, 1981
Dr. Richard Pannell	Catalysis Research Gulf Res. & Dev.	April 2, 1981
Mr. Peter Hughes Ms. Nellie Arsilla Mr. Charles Davis Ms. Linda Hook	Advanced Reactor Systems Department General Electric	March 5, 1981
Mr. Thomas Clough Dr. John Sibert Mr. Gary Myers	ARCO, Technology Coordination	May 13, 1981
Dr. Jaques Coenen	Kathlieke Universiteit Netherlands	June 29, 1981
Dr. Jens Rostrup-Nielsen	Haldor Topsoe Denmark	Aug. 25, 1981
Dr. Eric Moorehead	Union Oil Research Brea Calif.	Nov. 5, 1981

Prof. Robert J. Madix	Dept. Chem. Eng. Stanford University	Feb. 3, 1982
Dr. Richard Pannell	Gulf Research Pittsburgh	May 17, 1982
Dr. Roger Baetzold Dr. John Monnier	Eastman Kodak	May 18, 1982
Dr. Azza Elattar	Texaco	May 19, 1982
Dr. Yang Ki Hong	University of Utah	June 22, 1982
Dr. J. Grimblot	Universite des Sciences de Lille (France)	Aug. 17, 1982
Dr. Richard Pannell	Gulf Research Pittsburgh	Dec. 30, 1982
Dr. John Sibert Dr. Saul Akitus	Corporate Technology Atlantic Richfield Co.	Feb. 15, 1983
Prof. John Butt	Dept. Chem. Eng.	March 9-10, 1983
Dr. Carol Hemminger	Union Oil Research Brea, California	March 24, 1983
Prof. Alexis T. Bell	Dept. Chem. Eng. Univ. California Berkely	April 8, 1983
Dr. Barry Haymore	Monsanto Co.	April 14-15, 1983
Dr. Jay Labinger	Corporate Technology Atlantic Richfield Co.	April 26, 1983
Dr. Yang Ki Hong	University of Minnesota	May 13, 1983
Mr. Robert Wade	Ventron Division Hercules Corporation	May 18, 1983
Dr. Nag	Dept. Fuels Eng. University of Utah	May 27, 1983
Prof. Bohdan W. Wojciechowski	Dept. Chem. Eng. Queens University Kingston, Ontario	Nov. 3-4, 1983
Prof. James Dumesic	Dept. Chem. Eng. University of Wisconsin Madison	March 8, 1984
Prof. Tim Cale	Dept. Chem. Eng. Arizona State University	June 14, 1984

Dr. Hutch Harnsberger	Harnsberger Assoc.	July 27, 1984
Prof. Scott Cowley	Colorado School of Mines Golden, CO	July 31-Aug. 14, 1984
Prof. Hans Schultz	University of Karlesruhe Germany	Aug. 6-7, 1984
Prof. Zolton Paal	Institute of Isotopes Budapest, Hungary	Sept. 27, 1984
Dr. Wayne Goodman	Surface Chemistry Res. Sandia Laboratory	Oct. 4-5, 1984

Table 20
Students Supported by Contract

Name	Degree	Comments
Glen Davis	--	Accepted position with Signetics, Orem, UT
Evan Witt	B.S.	Accepted position with Amoco
Richard M. Bowman	M.S.	Finished M.S. in Spring 1983, accepted position with Exxon
Duane M. Davis	M.S.	Finished M.S. in Fall 1983, accepted position with National Semiconductor
Jeffery L. Rankin	Ph.D.	Accepted faculty position at Rutgers Fall 1984; presently completing dissertation

IV. CONCLUSIONS

1. Hydrogen adsorption on cobalt and iron catalysts is activated. The degree of activation and the binding energy of hydrogen with the metal increase with increasing calcination temperature and increasing potassium content. Hydrogen uptakes are best measured by cooling from the reduction temperature in a measured amount of hydrogen.

2. Relatively high surface area, active metal boride catalysts can be prepared by $NaBH_4$ reduction at 283 K. It is necessary to wash the resulting black precipitate to remove sodium impurities. Unfortunately, washing in ethanol or methanol does not entirely remove the sodium impurities, while washing in water hydrolyzes the small boride crystallites to large particles of iron oxide.

3. Specific activities of cobalt and iron borides vary considerably with preparation; however, they are generally about as active as their unborided counterparts. Sodium-containing cobalt borides are more active and stable than iron borides; moreover, they are highly selective for gasoline-range hydrocarbons at 1 atm.

4. The specific activity and selectivity of iron catalysts vary significantly with support and promoter. The differences may be a result of differences in dispersion and extent of reduction.

5. Specific activities of Fe/silica and Fe/K/silica decrease with increasing precalcination temperature and with increasing potassium content; there is also a striking increase in the C_2-C_4 fraction and olefin/paraffin ratio with increasing K content of catalysts precalcined at 473 K. Indeed, the product distribution for 15% Fe/3% K/silica precalcined at 473 K consists of only methane, ethylene and propylene. The unusually high selectivity for light olefins and the unusually low activation energy of 32 KJ/mol suggest that CO hydrogenation occurs on this catalyst by a mechanistic route distinct from FT synthesis.

6. Fe, Fe/silica, and Fe/K/silica catalysts lose activity rapidly in the presence of ppm levels of H_2S. Monolayer surface sulfides are formed at H_2S concentrations lower than 2 ppm; multilayer sulfides are formed at concentrations above 2 ppm. FeB is extremely sulfur resistant, losing only 5% activity after several days exposure to 8 ppm H_2S; upon exposure to 0.5 ppm for 2-3 days, the activity increases 40-50%! The product distribution of Co/silica is changed in favor of heavier hydrocarbons during the initial exposure to H_2S; the product distribution of Fe/silica is not affected.

V. REFERENCES

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