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METAL BORIDE CATALYSTS FOR INDIRECT LIQUEFACTION

Quarterly Technical Progress Report for the Period
December 1, 1983—February 29, 1984

By
Calvin H. Bartholomew

April 12, 1984
Date Published

Work Performed Under Contract No. FG22-82PC50816

Brigham Young University
Provo, Utah

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Brigham Young University
Provo, Utah 84602

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PREPARED FOR THE UNITED STATES
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FOREWORD

This report summarizes technical progress during the sixth quarter (December 1, 1983 to February 29, 1984) of a three-year study conducted for the Department of Energy (DOE) under Contract No. DE-FG22-82PC50816. 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: Dean Gessel, Jay Wang, Chang Wang, and Brian Armstrong. Dr. Bartholomew was the principal author. Valerie Evans provided typing services.

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ABSTRACT

During the sixth quarter four boron-promoted cobalt catalysts were prepared by a new boriding process using diborane gas as the boriding agent. These catalysts were characterized by chemical analysis, BET, H_2 chemisorption, and x-ray diffraction. Temperature-programmed desorption spectra of H_2 were obtained for a sodium-promoted cobalt boride and a sodium-promoted Co/SiO_2 . Four cobalt catalysts (unsupported, boron-promoted, sodium-promoted, and doubly-promoted) were tested for CO hydrogenation activity and selectivity at 1 atm and 3-4 temperatures in the range of 190-240°C. About 10% of the surface of cobalt boride consists of reduced metallic cobalt. The addition of sodium to cobalt increases its binding energy with H_2 and its activation energy for H_2 adsorption. Boron does not affect the activity of cobalt; sodium decreases it by a factor of 10. Cobalt boride produces lighter hydrocarbon products relative to cobalt; sodium-promoted cobalt produces heavier products, more alcohols, and more CO_2 .

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 3-4 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, aromatics, and alcohols particularly in the C_6 - C_{12} gasoline feedstock range.

Two classes of catalyst show promise for selective production of chemicals and gasoline range products: (i) Fe, Co, or Ru combined with a ZSM-5 class zeolite for production of aromatic gasoline liquids and olefins (1-4) and (ii) iron nitrides (5-7) or cobalt and iron borides (8-10) for production of high octane aliphatics and alcohols. There are, nevertheless, improvements in the selectivity and stability properties of these catalysts, especially the nitrides and borides, which need to be made (7,10). Such improvements are most likely to occur as the result of a careful, systematic investigation, giving attention to methods of preparation, effects of different supports, and careful characterization of the adsorption and chemical/physical properties of the catalyst. It may also be possible to combine the highly desirable properties of these two catalyst types.

B. Objectives

This report describes recent progress in a quantitative, systematic investigation of unsupported and supported cobalt and iron metal boride catalysts for Fischer-Tropsch synthesis, the objectives of which are:

1. Determine the intrinsic activity/selectivity properties of stoichiometric unsupported cobalt and iron borides and the effects of preparation, i.e. boron and alkali metal contents on these properties.
2. Determine the effects of support (including shape selective supports) on the activity/selectivity and chemical/thermal stability properties of cobalt and iron borides.

3. Determine the optimum reaction conditions (especially temperature and pressure for the production of alcohols, olefins and gasoline-diesel range products on selected cobalt and iron boride catalysts.

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:

1. Preparation and characterization of unsupported and supported cobalt and iron borides. Supports will include SiO_2 , Al_2O_3 , and ZSM-5.
2. Measurement of CO hydrogenation activity/selectivity properties over a range of reaction conditions and as a function of time.
3. In situ characterization of iron boride catalysts using Moessbauer spectroscopy to identify phase composition and structure as a function of time during reaction.

The experimental approach for each of these tasks is described below:

Task 1: Catalyst Preparation and Characterization. Boride catalysts to be prepared as part of this study are listed in Table 1 along with details of the proposed preparation techniques.

Unsupported cobalt and iron borides will be prepared using borohydride reduction techniques, some of which were developed previously in this laboratory (8-11). Development of dry reduction techniques similar to that used by Bonny et al. (12) will also be attempted. The solvent phase preparations will involve adding a nitrate salt of either cobalt or iron to an ethanolic solution of the boron-containing reducing agent at 0-25°C followed by washing of the metal-boride precipitate in either methanol or water. Three different reducing agents, NaBH_4 , KBH_4 and NH_3BH_3 will be investigated, to determine if alkali metal impurities are affecting the catalytic properties. The dry reduction will involve heating a dry mixture of a chloride salt of cobalt or iron and the reducing agent (NaBH_4 or NH_3BH_3) to 300-400°C in H_2 (the actual reaction temperature will be determined by TGA).

Supported catalysts will be prepared in similar fashion. However, the solvent phase reduction will involve adding the dried, Co or Fe nitrate-impregnated support to a solvent containing the reducing agent, in which the Co or Fe nitrate is insoluble. Alternatively, a dry mixture of the Co or Fe chloride-impregnated support and the reducing agent will be heated to 300-400°C. Nitrate or chloride salts and catalyst supports of highest available purity will be used, e.g. Cab-O-Sil SiO_2 and Conoco Dispal Al_2O_3 .

All chemically reduced samples will be washed with methanol, ethanol, and/or water to remove alkali salt impurities, dried in H_2 at 25-50°C and reduced at 250-300°C (the reduction temperature to be determined by TPD), all in the absence of air.

Table 1. Catalyst Preparation Plans (Task 1)

<u>Catalyst/Support</u>	<u>Reducing Agent</u>	<u>Preparation Technique</u>
Fe ₂ B	NaBH ₄ KBH ₄ NH ₃ BH ₃	Ethanollic reduction ^a " " " "
FeB	NaBH ₄ NH ₃ BH ₃	Dry reduction ^b " "
FeB/SiO ₂	NaBH ₄ or NH ₃ BH ₃	Solvent phase reduction ^c
FeB/Al ₂ O ₃	" "	Dry reduction of impregnated support ^d
FeB/ZSM-5 ^e	" "	Solvent phase or dry reduction of impregnated support
Co ₃ B	NaBH ₄ NH ₃ BH ₃	Ethanollic reduction ^a " "
CoB	NaBH ₄ or NH ₃ BH ₃	Dry reduction ^b
CoB/SiO ₂	" "	Solvent phase ^c or dry ^d reduction
CoB/Al ₂ O ₃	" "	of impregnated support
CoB/ZSM-5 ^e	" "	

^aChemical reduction in ethanolic solution (normally nitrate salt of Co or Fe is added to solution of boride salt) followed by washing in methanol or water, drying in H₂ at 25-50°C, and reduction at 250-300°C, all in the absence of air.

^bDry mixture of Co or Fe chloride and boride salt is heated in H₂ to 300-400°C followed by washing in methanol or water, drying in H₂ at 80-100°C, and reduction at 250-300°C, all in the absence of air.

^cChemical reduction of dried, impregnated nitrate salt of Co or Fe on support similar to (a) using solvent in which nitrate salt is insoluble; otherwise the same as (a).

^dDry mixture of Co or Fe chloride (or carbonyl)-impregnated support and boride salt is heated to 300-400°C; otherwise the same as (b).

^eTime permitting, a study will be made of silicalite and NaY zeolite supported materials as well. Dry reduction of ion-exchanged materials will be attempted.

The catalysts prepared in this study will be characterized by a number of different techniques including H_2 chemisorption, x-ray diffraction, electron microscopy, temperature programmed desorption/reduction and chemical analysis. Metal dispersions will be measured for all fresh and used catalysts by hydrogen adsorption at 298 K (9,10,13) and will be checked in selected cases using x-ray line broadening and transmission electron microscopy (see Table 2). Total H_2 adsorption uptakes will be measured using a recently developed technique from this laboratory which involves exposing the catalyst to H_2 (after evacuation) at the reduction temperature followed by cooling to 25°C. This avoids complications due to activated adsorption. In addition, BET measurement will be conducted on the unsupported materials. X-ray diffraction scans and Moessbauer spectroscopy will be used to establish the nature and extent of catalytic phases in selected catalysts. The extent of reduction to the metallic state and bulk oxidation states will be determined by temperature programmed reduction (14) and Moessbauer spectroscopy (10,11,15-17). Thermal stability will be determined for selected catalysts using TGA to high temperatures (400-500°C) preceded and followed by pulse adsorption measurements. Chemical stability will be determined using TPD of H_2 to high temperature accompanied by mass spectrometer analysis for volatile boron products. All samples will be chemically analyzed to determine transition metal and boron contents. Moessbauer experiments to determine chemical stability are outlined under Task 3.

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 a general comparison of activity/selectivity properties are 180-225°C, 1 atm, $H_2/CO=2$ and space velocities in the range of 200-1,000 h^{-1} . Approximately 4-5 of the most promising catalysts (based on tests at 1 atm) will be tested at higher pressures (10 and 25 atm) and over a range of temperature (180-250°C) and as a function of time during reaction over a 48 hour period. The space velocity will be adjusted in each test so that the CO conversion at 180°C is in the range of 5-10% in order that intrinsic activities in the absence of diffusional influences may be obtained. 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 relatively high space velocities will minimize thermal gradients in the catalyst bed. Samples will be reduced in situ for 2 hours and then conditioned under the reaction conditions for a period of 6-8 hours during which time chromatograph samples will be taken intermittently. From previous investigations (9,10,18-21) it is clear that in the case of small samples (especially borides) 6-8 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.

Most of the activity/selectivity tests will be carried out in a tubular, differential reactor system described earlier (9,10). This system is capable of 25-1,000°C, 1-30 atm operation and is equipped with mass flow meters, and an HP-5834 chromatograph with TCD and FID detection. A tubular reactor suitable for testing of powdered samples and traps for hydrocarbon liquids are presently available. The analysis of gaseous phase hydrocarbons from 1 atm runs will be conducted using a capillary column as previously described (10,11,22). Liquid and aqueous phase samples collected in high pressure runs will be analyzed using a mass spec./GC available in the BYU Chemistry department.

Table 2. Experimental Plan

<u>Task</u>	<u>Experiment and Purpose of Study</u>	<u>Catalysts</u>
1. Catalyst Characterization	a. H ₂ adsorption measurements to determine active site concentrations	All catalysts in Table 1
	b. BET measurements	All unsupported catalysts
	c. TEM, x-ray, TPR and Moessbauer to determine extent of reduction, particle size, and phase composition of reduced and used catalysts. TPD and TGA to determine thermal and chemical stability.	Selected catalysts
2. Activity/Selectivity	a. Activity/selectivity comparison to determine effects of preparation and support	All catalysts in Table 1
	b. Effects of temperature and pressure (180-250°C, 1-25 atm)	4-5 selected catalysts based on A/S comparison
	c. Activity stability tests (48 hrs)	Same 4-5 catalysts as in b
3. <u>In situ</u> Moessbauer Measurements	a. Determination of phase composition of chemically and H ₂ reduced catalysts	All iron boride catalysts in Table 1
	b. Determination of chemical stability under reaction conditions (48 hr period)	2-3 selected iron boride catalysts

Task 3: In Situ Moessbauer Spectroscopy Characterization. Catalysts to be investigated during reaction using Moessbauer spectroscopy and the purposes for study are summarized in Table 2. All of the iron boride catalysts will be analyzed in reduced form by Moessbauer spectroscopy to determine phase composition and the structure of the most abundant phases. Based on the results of the activity/selectivity comparisons and the analysis of fresh catalysts, 3-4 selected catalysts will be analyzed as a function of time during reaction in controlled atmosphere cells to determine the chemical stability of iron boride phases towards carbide formation.

As a technique to facilitate the unambiguous identification of important catalytic phases in each catalyst, the proposed Moessbauer experiments will include the determination of spectra for model compounds i.e. unsupported FeB, Fe₂B, Fe₃B, and Fe₃C. These spectra and any available literature data will be compared with the spectra for the working catalyst to enable the latter spectra to be more easily decomposed. Since there are no reported investigations of iron boride catalysts using Moessbauer spectroscopy, the proposed investigation should provide valuable new data on the structures of the bulk catalytic phases.

II. SUMMARY OF PROGRESS

A. Task 1: Catalyst Preparation and Characterization

Four cobalt boride catalysts were prepared by exposure of reduced cobalt to 1% B_2H_6/H_2 at $350^\circ C$ for 48 hours. The resulting catalysts contained about 10% boron consistent with a stoichiometry of Co_2B . The XRD pattern of a cobalt boride prepared by this technique indicated the presence of CoB, Co_3B , and Co metal phases. No loss of surface area was observed for Co-B-109 after 30-40 hours of reaction. From comparison of BET and H_2 adsorption surface areas, the surface of Co-B-109 is estimated to consist of about 10% reduced cobalt metal. TPD spectra of sodium-promoted CoB and Co/SiO_2 indicate that sodium increases the binding energy and activation energy for H_2 adsorption on cobalt.

B. Task 2: Activity/Selectivity Measurements

Specific CO hydrogenation activities and selectivities of Co, CoB, CoB/Na, and $Co/Na/SiO_2$ catalysts were obtained at 1 atm, $H_2/CO = 2$, and 3-4 reaction temperatures in the range of $190-240^\circ C$. The specific activities of Co, CoB, and CoB/Na are about the same; the specific activity of $Co/Na/SiO_2$ is a factor of 10 less. CoB produces lighter hydrocarbons relative to cobalt; $Co/Na/SiO_2$ produces heavier hydrocarbons, more CO_2 , and significant quantities of alcohols. The product distribution of CoB/Na depends on reduction time and temperature; after severe reduction ($350^\circ C$, 16 hrs) the catalyst produces less gasoline hydrocarbons.

C. Task 3: Moessbauer Spectroscopy Studies

No runs were made this quarter. The spectrometer's old 6800 computer was replaced with a new Radio Shack color computer (68 K) with dual disk drives.

D. Technical Communication and Miscellaneous Accomplishments

During the past quarter Dr. Bartholomew presented a talk at the Chicago Catalysis Club (January 9) dealing with oxygen adsorption on molybdenum catalysts and visited Amoco Oil Company. Members of the BYU Catalysis Laboratory attended the Emmett Lectures presented at the University of Utah (January 9-13) by Professor Albert Vannice and the Ninth Symposium of the Rocky Mountain Fuel Society held February 22-24 in Salt Lake City.

III. DETAILED DESCRIPTION OF TECHNICAL PROGRESS

A. Task 1: Catalyst Preparation and Characterization

1. Catalyst Preparation. Four cobalt boride catalysts (CoB-107 to CoB-109) were prepared by boriding of a reduced, unsupported cobalt catalyst with a diborane in hydrogen gas. The details of this procedure are as follows:

- a. $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was calcined for 16 hours at 200°C .
- b. The resulting cobalt oxide (identified by x-ray diffraction as Co_3O_4 , was subjected to hydrogen reduction at heating rate of $2^\circ\text{C}/\text{min}$ up to 350°C with a 1 hour hold at 200°C , and then held at 350 for 16 hours. The hydrogen space velocity was 2000 h^{-1} .
- c. After reduction, 1% $\text{B}_2\text{H}_6/99\% \text{H}_2$ was passed through the sample held at 350°C at a flow rate of 100-120 cc/min for 48 hours.

Using this technique it was possible to prepare cobalt boride catalysts free of impurities such as alkali metals, typically introduced in chemical reductions using sodium or potassium borohydride (22-26).

2. Catalyst Characterization. Hydrogen chemisorption uptake data were obtained for 4 cobalt catalysts. Three cobalt boride catalysts prepared by the new boriding technique and a sodium-promoted cobalt catalyst were submitted for chemical analysis. The BET surface area of CoB-109 was also measured after reaction. The results of these measurements are summarized in Table 1.

The unsupported cobalt (prepared in a companion study, Ref. 27) and the sodium-promoted Co/silica (preparation described in the last quarterly report, Ref. 26) were reduced in flowing hydrogen at 250°C for 15 hours using a temperature schedule similar to that for the cobalt boride catalysts. In preparation for the chemisorption measurements, the catalysts were evacuated to 3×10^{-5} Torr at 240°C after which a known quantity of hydrogen gas was permitted to enter the cell. With the gas pressure maintained at 40 cm Hg, the temperature was lowered to 25°C , after which the adsorption isotherm measurements were carried out. A very similar procedure was used in the adsorption measurements involving sodium-promoted cobalt boride catalysts reduced at 350°C .

The hydrogen adsorption uptake data in Table 3 for CoB-109R indicate that no loss of cobalt surface area occurred during reaction, since the hydrogen uptakes for fresh and reaction-exposed catalyst are the same within experimental error. Assuming an inverse site density for the cobalt sites in the CoB catalyst of $8.9 \times 10^{-2} (\text{nm})^2/\text{atom}$ (Ref. 27), the calculated cobalt surface area for CoB-109R is $1.4 \text{ m}^2/\text{g}$. Comparison of this cobalt area with the BET surface area of $16.2 \text{ m}^2/\text{g}$ leads to the conclusion that about 9% of the surface consists of sites which adsorb hydrogen; presumably the other 91% is composed of boron atoms which do not adsorb hydrogen.

Temperature-programmed desorption spectra of hydrogen were obtained for CoB-102 (containing 2% sodium) and Co/Na-S-100 as a function of adsorption temperature (see Figure 1 and 2). The results indicate that sodium (and

Table 3. Chemical Compositions, H₂ Adsorption Uptakes, and BET Surface Areas of Cobalt Catalysts

<u>Catalyst Code</u> <u>Number</u>	<u>Chemical Analysis Wt.%</u>			<u>Co/B Atomic</u> <u>Ratio</u>	<u>H₂ Uptake</u> <u>(μmoles/g)</u>	<u>BET</u> <u>(m²/g)</u>
	<u>Co</u>	<u>B</u>	<u>Na</u>			
Co-103	100				26.8	
CoB-107	90.1	9.83		1.68		
CoB-108 ^a	85.7	9.79		1.61		
CoB-109 ^b	87.7	11.9		1.35	11.5 ^d	
CoB-109R ^c	88.9	10.1		1.61	13.6 ^d	16.2
Co/Na-S-100	~12		~2		56.2	

^aCatalysts exposed to air.

^bCatalyst not exposed to air.

^cCatalyst after CO hydrogenation reactor run.

^dH₂ adsorption after cooling in hydrogen from 350 to 25°C.

Figure 1. TPD spectra of H_2 adsorbed on CoB/Na (reduced $400^\circ C$) as a function of adsorption temperature.

Figure 2. TPD spectra of H_2 adsorbed on 15% Co/2% Na/ SiO_2 (reduced at 400°C) as a function of adsorption temperature.

perhaps boron) causes the appearance of new high temperature adsorption states and more highly activated adsorption compared to unsupported, unpromoted cobalt (28).

During the next quarter, an unsupported 0.5% sodium, 99.5% cobalt catalyst will be prepared, characterized and tested for activity and selectivity. Another sample of Co/Na-S-100 will be sent for chemical analysis, since the first analysis indicated a composition considerably different than expected based on the amounts of salts added to the impregnating solutions (hence the approximate composition shown in Table 3).

B. Task 2: Activity/Selectivity Measurements

CO hydrogenation activities and selectivities of four catalysts, Co-103 (#1), CoB-109, Co/Na-S-100 (#1), and CoB-102 (#10), were measured at 3 or 4 different temperatures. Data were obtained at the lowest temperature after 28 hours of reaction for CoB-109 and after about 40 hours for the other catalysts; data were obtained at each of the higher temperatures after 10-20 hours of additional reaction. Activity and selectivity data are summarized for these catalysts in Table 4, while representative hydrocarbon product distributions and Anderson-Schulz-Flory plots are presented in Figures 3-10.

From the data in Table 4 it is evident that addition of the sodium promoter lowers the activity of cobalt by a factor of about 10. Boron-promoted cobalt has the same activity as unpromoted cobalt with experimental error. However, CoB-102 prepared by sodium borohydride reduction and which contains both boron and sodium is a factor of two more active than unpromoted cobalt; in other words, there appear to be a synergism in the case of dual promotion. The cobalt boride prepared from gas phase diborane produces significantly lighter products and has a significantly higher methane make compared to unpromoted cobalt. The sodium-promoted cobalt, on the other hand, produces significantly more C₁₂+ liquids and alcohols relative to unpromoted Co/silica (27). The sodium-promoted cobalt boride (CoB-102) reduced 16 hours at 350°C has a product distribution very similar to that of the unsupported cobalt; the former catalyst does produce slightly less methane and slightly more gasoline range hydrocarbons (C₅-C₁₁). This sample of CoB-102 (#10) reduced under relatively severe conditions has a lower gasoline make than observed for the 5 previously tested samples reduced under milder conditions (25,26). Moreover, the Anderson-Schulz-Flory (ASF) plot (Figure 10) is quite linear; corresponding plots of the samples reduced at lower temperatures showed significant deviations on the low side from ASF kinetics. These deviations, which would account in part for the high gasoline yields, may be due to adsorption of high molecular weight liquids on the support or in the sampling system or to effects of structure-sensitivity (29). These possibilities will be checked in future runs after improvements have been made in the sampling system.

During the next quarter, activity/selectivity tests of CoB-102 reduced at 250°C and a newly prepared Co/Na catalyst will be carried out.

Figure 3. Hydrocarbon product distribution for unsupported Co (reduced at 250°C) at 195°C, 1 atm, $H_2/CO=2$.

Figure 4. Anderson-Schulz-Flory plot for Co (reduced at 250°C) at 195°C, 1 atm, $H_2/CO=2$.

Figure 5. Hydrocarbon product distribution for CoB-109 at $T=212^{\circ}\text{C}$, 1 atm, $\text{H}_2/\text{CO}=2$.

Figure 6. Anderson-Schulz-Flory plot for CoB-109 at 212°C, 1 atm, $\text{H}_2/\text{CO}=2$.

Figure 7. Hydrocarbon product distribution (excluding alcohols) for 12% Co/2% Na/SiO₂ at 1 atm, 1950C, H₂/CO=2.

Figure 8. Anderson-Schulz-Flory plot for 12% Co/2% Na/SiO₂ at 195°C, 1 atm, H₂/CO=2.

Figure 9. Hydrocarbon product distribution for CoB/Na (reduced at 350°C) at 195°C, 1 atm, $H_2/CO=2$.

Figure 10. Anderson-Schulz-Flory plot for CoB/Na (reduced at 350°C) at 1950°C, 1 atm, $H_2/CO=2$.

Table 4. Steady-State CO Hydrogenation Activities and Selectivities of Cobalt Catalysts

Catalyst		Reaction Temperature (°C)	Reaction Time (hr.)	% CO Conversion	$N_{CO}^a \times 10^3$ Molecule/Site Sec.	Product Selectivity (wt.%)						Propagation Probability α	E_{act} (kJ/mole)
I.D. Code	Run No.					CH ₄	C ₂ -C ₄	C ₅ -C ₁₁	C ₁₂ +	Alcohols	CO ₂		
Co-103	1	195	55.0	15.64	1.4	12.6	19.4	46.2	18.3	--	3.6	0.82	72
		210	21.0	14.38	3.0	20.0	25.9	39.2	11.0	--	4.0	0.72	
		225	26.0	16.44	4.6	31.0	30.0	26.9	6.1	--	6.0	0.62	
		240	20.0	19.00	7.2	35.4	30.8	20.3	5.1	--	8.4	0.54	
Co3-109		212	28	1.94	1.1	35.4	31.9	28.5	--	--	4.2	2.58	118
		225	22	4.76	2.7	40.2	34.1	21.5	--	--	4.2	0.52	
		240	22	10.59	5.5	54.8	30.5	11.2	--	--	3.5	0.44	
Co/Na-S-100	1	195	43.5	0.76	0.07	12.9	23.2	25.7	5.4	--	32.9	0.72	102
		210	22.5	1.64	0.16	12.8	22.5	21.4	3.4	--	39.8	0.67	
		225	10.5	3.95	0.39	12.8	20.6	16.1	4.0	4.3	42.1	0.70	
		240	12.0	7.34	0.72	12.3	18.1	13.3	3.4	3.0	50.0	0.71	
Cc8-102	10	195	49.0	8.12	2.1	10.7	18.0	48.9	18.0	0.7	3.6	0.79	68
		210	19.0	10.05	6.7	18.0	24.9	42.7	8.9	0.9	4.6	0.70	
		225	40.0	7.72	7.4	19.7	26.2	36.1	9.6	0.5	7.9	0.68	
		240	14.5	9.86	11.0	27.9	28.4	25.8	5.6	0.3	12.0	0.64	

^aCO turnover frequency CO molecules converted per catalytic site per second.

C. Task 3: Moessbauer Spectroscopy Studies

No runs were made during this period. A new 64 K Radio Shack Color Computer with disk drives was added to the spectrometer. The old 6800 computer used a tape recorder for inputing and outputing data.

D. Technical Communication and Miscellaneous Accomplishments

Professor Bartholomew was invited January 9 to address the Chicago Catalysis Club on the topic of "Oxygen Adsorption on Molybdenum Sulfides and Correlations with Catalytic Activity." On January 10 he visited Amoco Oil Company with Mike Baird as host. Several members of our catalysis group attended the Emmett Lectures presented at the University of Utah by Professor Albert Vannice of Penn State during the week of January 9-13. Professor Bartholomew and several students attended the Ninth Symposium of the Rocky Mountain Fuel Society held February 22-24 in Salt Lake City at which Mr. Jeffery L. Rankin presented a paper on the "Effects of Support and Promoters on the Activity and Selectivity of Iron FT Catalysts."

IV. CONCLUSIONS

1. It is possible to prepare cobalt borides, free of alkali impurities, by exposure of reduced cobalt catalysts to 1% B_2H_6/H_2 at 350°C.
2. The surface of CoB prepared by this technique consists of 10% metallic cobalt and 90% boron.
3. The addition of sodium to cobalt increases its binding energy with H_2 and its activation energy for H_2 adsorption.
4. Boron does not affect the specific activity of cobalt; sodium reduces its specific activity by a factor of 10.
5. CoB produces lighter hydrocarbons compared to cobalt; sodium-promoted cobalt produces heavy hydrocarbons, more CO_2 , and more alcohols than Co.
6. The product distribution of CoB/Na is very sensitive to reduction temperature and time.

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