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METAL BORIDE CATALYSTS FOR INDIRECT LIQUEFACTION: FINAL TECHNICAL PROGRESS REPORT, FOR PERIOD SEPTEMBER 1, 1982 TO SEPTEMBER 30, 1986

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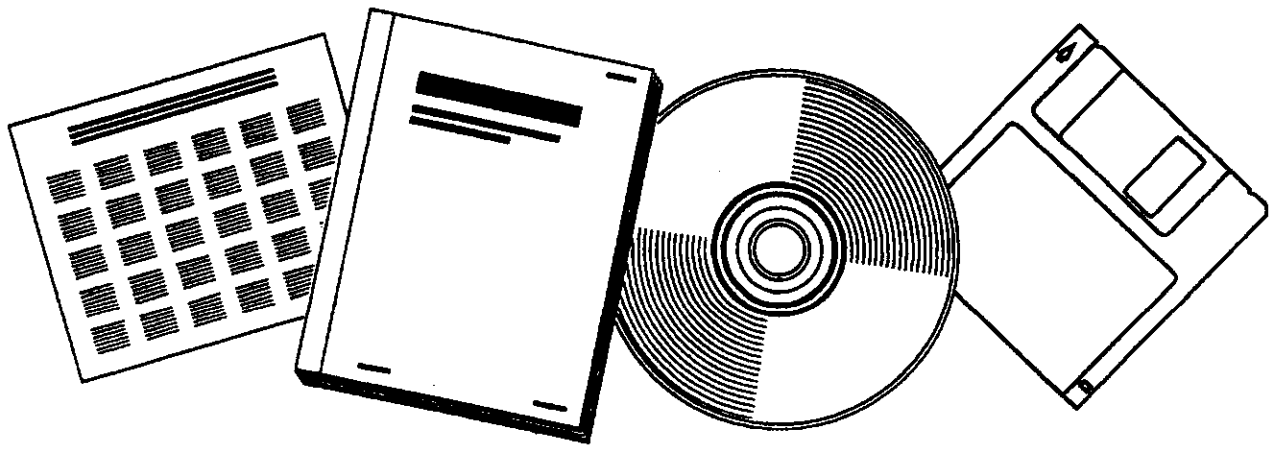

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METAL BORIDE CATALYSTS FOR INDIRECT LIQUEFACTION

Final Technical Progress Report
For Period Sept. 1, 1982 to Sept. 30, 1986

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DISCLAIMER

FOREWORD

This report summarizes technical progress during a four-year (Sept. 1, 1982 to Sept. 30, 1986) 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.

Duane Davis, Jay Wang and Chang Wang, graduate students, and Dean Gessel and Brian Armstrong, undergraduate students, in Chemical Engineering, contributed to the technical accomplishments and to his report. Jay Wang and Dr. Bartholomew were the principal authors. Cindy Poulsen provided typing services.

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ABSTRACT

The preparation, physical and chemical properties, and CO hydrogenation activity/selectivity behavior of cobalt and iron metal borides were investigated. Over 30 metal boride catalysts were prepared by three different techniques and were characterized by hydrogen and CO adsorptions, x-ray diffraction, temperature-programmed desorption (TPD) of CO, and Moessbauer spectroscopy. Cobalt and iron metal borides were found to have BET surface areas ranging from 4-200 m^2/g and percent metal areas ranging from 4-100% depending upon preparation. Phases in metal boride catalysts identified by XRD and Moessbauer varied with preparation. In borides prepared by gas phase diborane (DB) reduction, the major phases were cobalt and iron metals; apparently the boron was concentrated at the surface. Borides prepared by $NaBH_4$ or DB/THF reduction consisted mainly of stoichiometric MB and M_2B borides with small amounts of metal present. From CO hydrogenation activity measurements at 175-300°C, 1-20 atm, the order of decreasing specific activity based on turnover frequencies for cobalt catalysts is CoB(DB/THF) > CoB (DB/H_2) = CoB/Na ($NaBH_4$) = Co > Co/Na. The order of decreasing specific activity for iron catalysts is Fe > FeB/Na > FeB (commercial) > FeB(DB/THF). The products observed during synthesis over CoB catalysts contain lighter hydrocarbons than those produced over CoB/Na and Co catalysts; those observed over FeB catalysts are similar to those produced by unsupported Fe. These and other significant 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 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 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 was divided into three areas of study:

1. Preparation and characterization of unsupported and supported cobalt and iron borides. Supports included SiO_2 and Al_2O_3.

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 catalyst preparation plans are listed in Table 1 along with details of the proposed preparation techniques.

Unsupported cobalt and iron borides were prepared using borohydride and diborane 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) were also attempted. Gas phase reductions were conducted by exposing prereduced cobalt and iron catalysts to 1% B_2H_6/H_2 at 200-300°C. Two solvent phase preparations involved (i) adding a nitrate salt of either cobalt or iron to an ethanolic solution of a boron-containing reducing agent such as $NaBH_4$ at 0-25°C followed by washing of the metal-boride precipitate in either methanol or water or (ii) chemically reducing anhydrous acetate salts of cobalt or iron with B_2H_6/THF at 25°C. Three different reducing agents, $NaBH_4$, KBH_4 and NH_3BH_3 were investigated, to determine how alkali metal impurities affect the catalytic properties. The dry reduction involved 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.

Supported catalysts were prepared in similar fashion. However, the solvent phase reduction involved 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. Nitrate or chloride salts and catalyst supports of highest available purity were used, e.g. Cab-O-Sil SiO_2 and Conoco Dispal Al_2O_3.

Chemically reduced samples were generally washed with methanol, ethanol, and/or water to remove alkali salt impurities, dried in H_2 at 25-50°C and reduced in flowing hydrogen at 250-400°C all in the absence of air.

Table 1. Catalyst Preparation Plans (Task 1)

Catalyst/Support	Reducing Agent	Preparation Technique
FeB	$NaBH_4$	Ethanolic or diglyme reduction[a]
	KBH_4	" "
	NH_3BH_3	" "
FeB	$NaBH_4$	Dry reduction[b]
	NH_3BH_3	"
FeB	B_2H_6/H_2	Gas phase reduction at 200-300°C
FeB	B_2H_6/THF	Reduction at 25°C of anhydrous iron acetate in THF solvent
CoB	$NaBH_4$	Ethanolic or diglyme reduction[a]
	NH_3BH_3	" "
CoB	$NaBH_4$ or NH_3BH_3	Dry reduction[b]
CoB	B_2H_6/H_2	Gas phase reduction at 200-300°C
CoB	B_2H_6/THF	Reduction at 25°C of anhydrous cobalt acetate in THF solvent
CoB/SiO_2	" "	Solvent phase[c] or dry[d] reduction
CoB/Al_2O_3	" "	of impregnated support

[a]Chemical reduction in ethanolic or diglyme solution (normally nitrate salt of Co or Fe is added to solution of boride salt) followed by washing in methanol or water, drying in H_2 at 25-50°C, and reduction at 250-300°C, all in the absence of air.

[b]Dry mixture of Co or Fe chloride and boride salt is heated in H_2 to 300-400°C followed by washing in methanol or water, drying in H_2 at 80-100°C, and reduction at 250-300°C, all in the absence of air.

[c]Chemical 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).

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

[e]Time 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 were characterized by a number of different techniques including H_2 chemisorption, x-ray diffraction, electron microscopy, temperature programmed desorption (TPD) and chemical analysis. Metal dispersions were measured for all fresh and used catalysts by hydrogen and CO adsorptions at 298 K (9,10,13) and were checked in selected cases using x-ray line broadening and transmission electron microscopy (see Table 2). In addition, BET measurement were conducted on the unsupported materials. X-ray diffraction scans and Moessbauer spectroscopy were 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 were determined by temperature programmed reduction (14) and Moessbauer spectroscopy (10,11,15-17). All samples were chemically analyzed to determine transition metal and boron contents.

Task 2: Activity/Selectivity Measurements. The experimental plan in Table 2 summarizes the catalysts tested and the purpose of their study. Conditions used for a general comparison of activity/selectivity properties were 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) were 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 was adjusted in each test so that the CO conversion was in the range of 5-10% in order that intrinsic activities in the absence of diffusional influences could be obtained. 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 relatively high space velocities minimized thermal gradients in the catalyst bed. Samples were reduced in situ for 2 hours and then conditioned under the reaction conditions for a period of 20-30 hours during which time chromatograph samples were 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 were able to check this experimentally.

Most of the activity/selectivity tests were carried out in a tubular, differential reactor system similar to that described earlier (9,10) a schematic of which is shown in Fig. 1. 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 used for testing of powdered samples at low and high pressure is shown in Fig. 2. The analysis of gaseous phase hydrocarbons from 1 atm runs was conducted using a capillary column as previously described (10,11,22). Liquid and aqueous phase samples collected in high pressure runs were also analyzed using a mass spec./GC available in the BYU Chemistry department.

Task 3: In Situ Moessbauer Spectroscopy Characterization. Catalysts investigated using Moessbauer spectroscopy and the purposes for study are summarized in Table 2. All of the iron boride catalysts were 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, 2-3 selected catalysts were analyzed as a function of time during reaction in controlled atmosphere cells to determine the chemical stability of iron boride

Table 2. Experimental Plan

Task	Experiment and Purpose of Study	Catalysts
1. Catalyst Characterization	a. H_2 and CO 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.	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. *In situ* 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

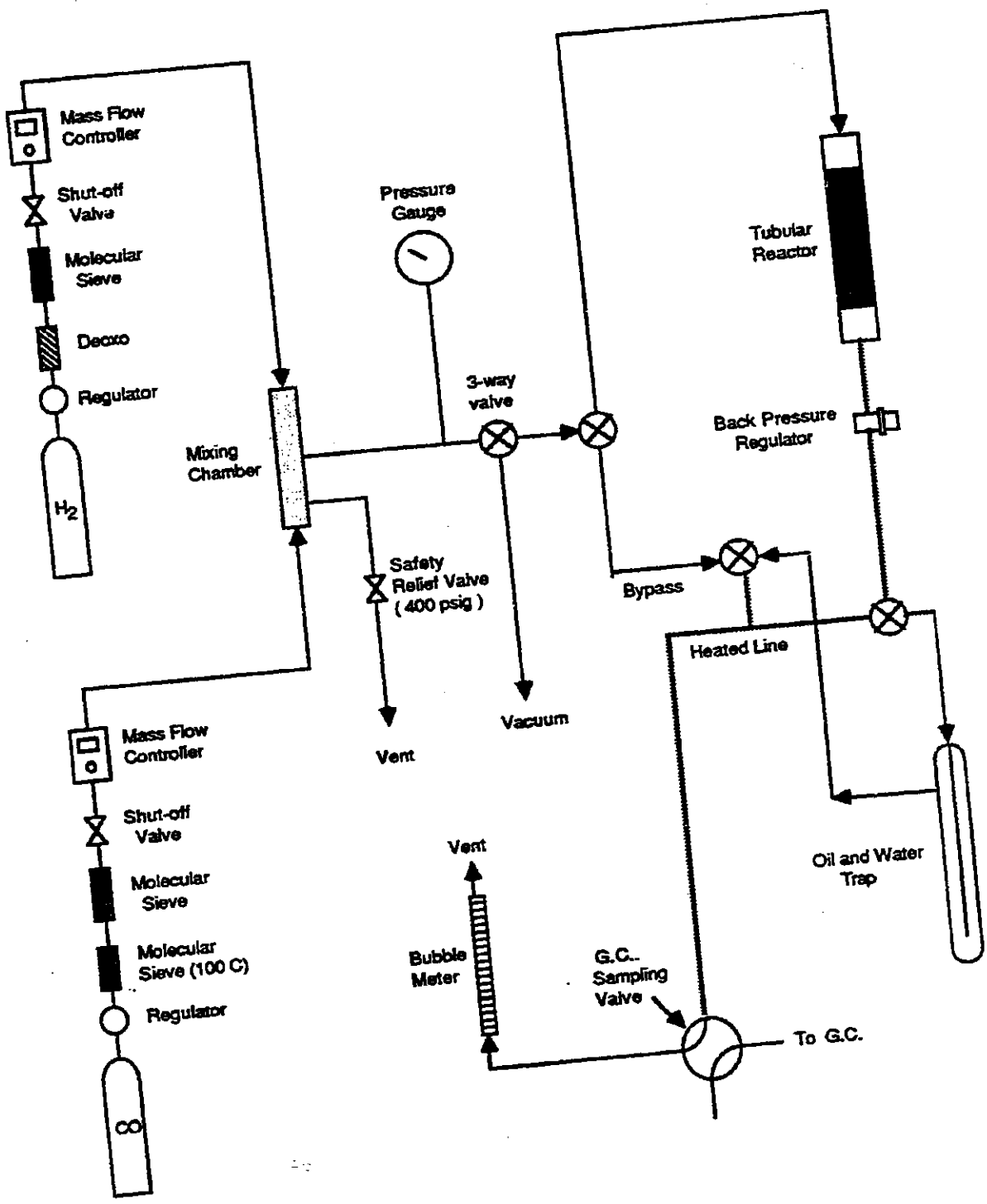

Fig. 1. Flow Diagram of High Pressure Reactor System

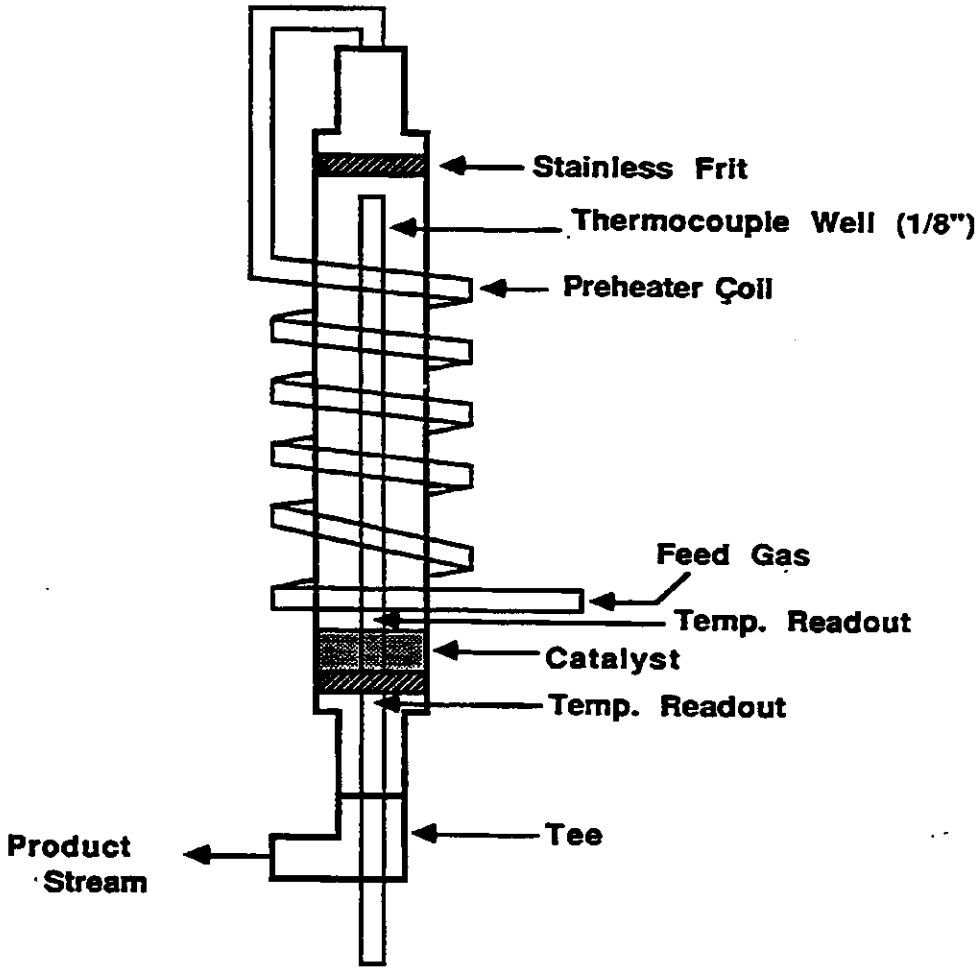

Figure 2. Stainless Steel Reactor

phases towards carbide formation.

As a technique to facilitate the unambiguous identification of important catalytic phases in each catalyst, the proposed Moessbauer experiments included the determination of spectra for model compounds i.e. unsupported FeB and Fe_2B. These spectra and any available literature data were compared with the spectra for the working catalyst to enable the latter spectra to be more easily decomposed. Since there were no previously reported investigations of iron boride catalysts using Moessbauer spectroscopy, the proposed investigation provided new data on the structures of the bulk catalytic phases.