

Fig. 39 Mössbauer analysis after high pressure CO hydrogenation on (a) FeB2 (b) FeB5.

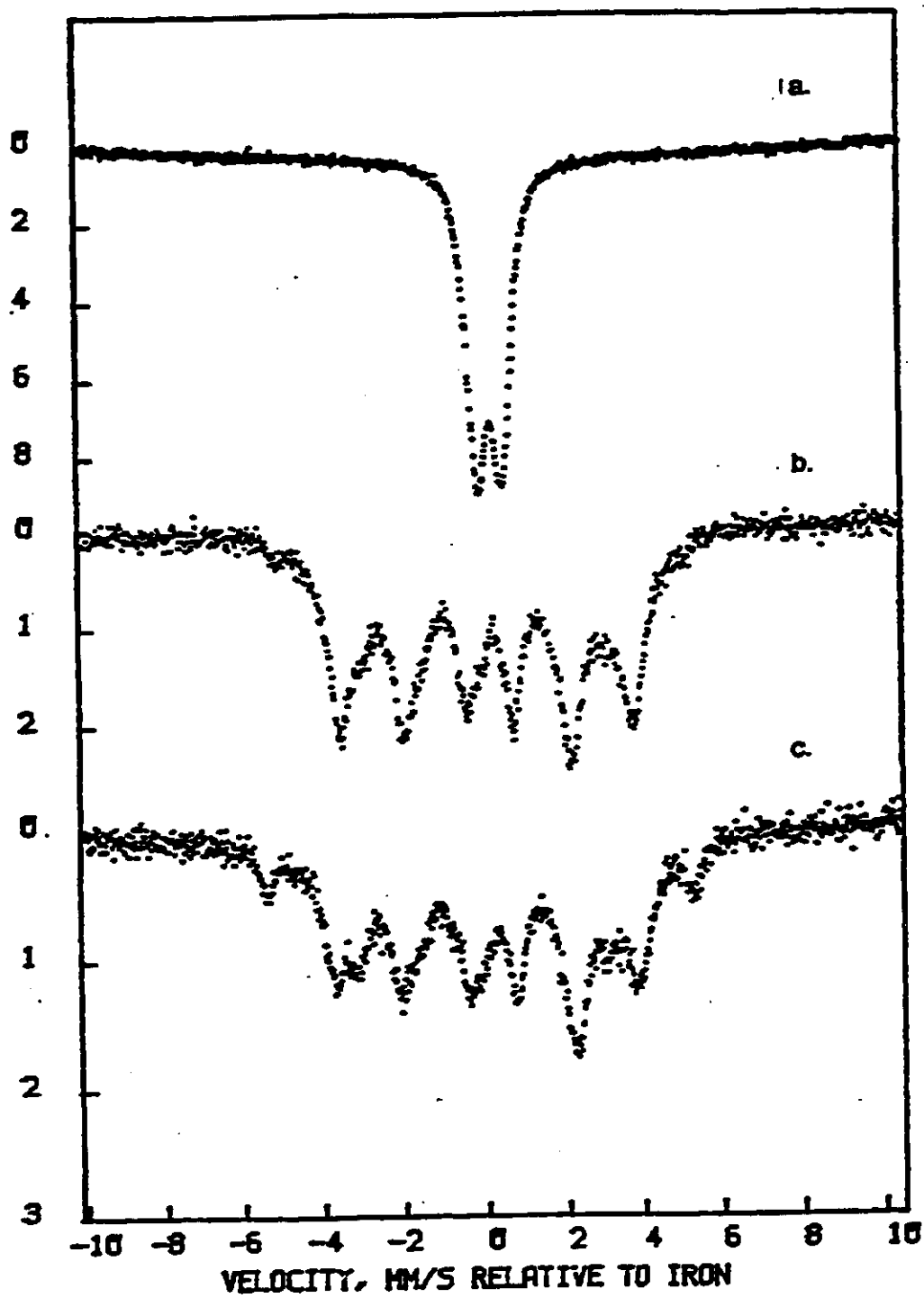


Fig. 40 Mössbauer spectra of sodium contained iron boride catalyst: (a) before (b) after washing with MeOH, and (c) after CO hydrogenation runs.

approximate agreement with the company claim that the product is 99% FeB. Surprisingly, the small amount of Fe₂B almost vanished after CO hydrogenation (Fig. 31b). No change was observed otherwise.

Figure 32 contains the Moessbauer spectrum for the gas phase reduced catalyst FeB-107-G. The presence of a 6-line spectrum having a hyperfine field of about 330 kOe shows that the bulk phase of the catalyst is essentially ferromagnetic Fe⁰. Apparently the small amount of boron present in this sample (less than 1%) is localized (probably at the metal surface) and does not affect the electronic, chemical or magnetic structure of the majority of iron atoms.

Serial spectra were taken at various stages of preparation when B₂H₆/THF was used as the reducing agent (Fig. 33). The first spectrum (33a) indicates that 3 % of the iron in anhydrous iron acetate was oxidized to Fe³⁺ and the rest remained as Fe²⁺. Spectrum 33b of a partially reduced iron acetate indicates that 43% of the iron acetate remains unreacted while spectrum 33c shows the totally reacted sample. Although the sharp doublet peak at the central part could be interpreted as either fine particles of iron oxide or iron boride, we conclude it is iron boride species because we have minimized the chances of oxidation by either water or oxygen during the preparation. Indeed, when the sample was reduced in H₂ at 400°C for about 2 hours, the resulting spectrum (Fig. 34a) indicates that the particle size grew and the doublet split into a six-peak pattern characteristic of FeB. Indeed, the magnetic hyperfine field (103 kOe) and isomer shift (0.24) are close to the values of the metallurgically prepared FeB sample (118 kOe and 0.25 respectively) reported in the literature [34-36] (Table 32). When treated with H₂ at 460°C for 18 hours, the six-line spectrum for FeB, located from -1.3 mm/sec to 2.0 mm/sec, is even more pronounced (Fig. 34b). At the same time, part of the iron is reduced to a zero valence state (about 7%), and about 12% of the sample transforms to Fe₂B (outer peaks at about 4 and -4 mm/sec).

Since the FeB2 sample had been used up in various characterization and activity/selectivity experiments, another batch of the catalyst prepared in the same manner (FeB5) was used for Moessbauer experiments. A series of spectra taken in an *in situ* Moessbauer cell at room temperature were obtained (Figs. 35 and 36). Fig. 35a is a spectrum taken right after the fresh sample was mounted prior to any treatment. Spectra 35b and 35c were taken after H₂ and 2:1 H₂/CO treatments respectively at 250°C for 18 hours. It appears that the 250°C reduction does not change the state of the sample while the CO/H₂ treatment broke down about 5% of the sample to a Fe²⁺ state (outer doublet of low intensity). However, the Fe²⁺ doublet disappears (Fig. 36a) when the catalyst is treated again with H₂ at 350°C. The Fe⁰ species also begins to appear at this temperature. After 400°C and 500°C reduction, more sample is reduced to the zero valence state and the Fe₂B species is also observed (Fig. 36b, 36c). Again it is thought that the inner doublet in Figures 35 and 36 corresponds to small superparamagnetic particles of FeB and Fe₂B.

In order to see the hyperfine split pattern of these small particles in FeB5, low temperature (-196°C) Moessbauer analyses were carried out (Figs. 37, 38). Figure 37a and 37b represent the spectra taken after reduction at 250°C and treatment in a H₂/CO mixture respectively, while Figures 38a, 38b and 38c represent the spectra taken after 350°C, 400°C and 500°C reduction in

series. Fig. 37a shows a broad envelope located between -1.5 mm/sec and $+2$ mm/sec suggesting the existence of FeB species in addition to the central doublet peak. Curve fitting and integration indicate about 37% of the sample to be present as ferromagnetic FeB. Interestingly, the envelope disappears after the H_2/CO treatment, while the Fe^{2+} species appears (shoulder at right). When the sample is reduced at $350^\circ C$, the envelope comes back (Fig. 38c) and a portion of the metal boride is reduced to iron metal as indicated by the appearance of 3 of the 6 lines for ferromagnetic iron. The spectra obtained at liquid nitrogen temperature (Fig. 38b, 38c) and room temperature (Fig 36b, 36c) for catalysts reduced at 400 and $500^\circ C$ are almost identical, which could be due to a larger average particle size after these treatments at elevated temperature. From these series of experiments, it appears that FeB is stable at lower reduction temperatures ($<350^\circ C$) but unstable at reduction temperatures above $400^\circ C$. Both Fe^0 and Fe_2B content increase with increasing reduction temperature (Fig. 38 and Table 33). It should be pointed out that despite these observed changes in the chemical states of the sample, the boron element is not lost during the reduction process (Table 7).

After high pressure runs during CO hydrogenation for about a week, the FeB2 and FeB5 catalysts were subjected to Moesbauer analysis. Figure 39a and 39b contain the spectra for FeB2 and FeB5 respectively. Both spectra contain a six line pattern of Fe^0 , as well as a sharp doublet peak representing the Fe^{2+} species. Apparently, after a long exposure to the CO/H_2 mixture at temperature $250^\circ C$ to $300^\circ C$, the iron boride phase is gone. The Fe^{2+} species could be due to the oxidation of the sample by the water produced from the FT reaction.

Figure 40 shows the Moesbauer spectra of the sodium-containing catalyst, FeB/Na, before washing with methanol, after washing with methanol as well as after $220-250^\circ C$ reactor tests. Without washing by methanol the spectrum is identical to that of the sodium-free catalyst even though 56% of the sample consists of undesirable impurities (see chemical analysis results in Table 7). However, after washing with MeOH the catalyst is of high purity (97% iron plus boron phases) and its spectrum contains a well-defined six line pattern which has the same parameters as that reported for Fe_2B [34-36, Table 32, Fig. 40]. After reactor testing for more than a week, the spectrum of the catalyst shows the appearance of Fe^0 and Fe^{2+} species as minor phase, (Fig 40c). However, unlike the sodium-free catalysts, most of Fe_2B structure still remains.

D. Technical Communications and Miscellaneous Accomplishments

Technical communications were an important part of this contract work. Table 34 summarizes publications in connection with this contract. Altogether 5 papers were published, submitted or are in preparation. Seven papers were presented at national and regional meetings while 11 seminars were presented at universities and companies (see Table 35). The principal investigator visited 26 laboratories and received 34 visitors (see Tables 36 and 37).

Probably the most important aspect of this contract work was the education and training of undergraduate and graduate chemical engineering students. Table 38 lists the students supported by this contract, while dissertations completed as part of this contract are listed in Table 34.

Table 34 Publications in Connection
With This Contract

Journal Publications

1. C.H. Bartholomew and R.M. Bowman, "Sulfur Poisoning of Cobalt and Iron Fischer-Tropsch Catalysts," *Appl. Catal.* 7, 179 (1983).
2. J.L. Rankin and C.H. Bartholomew, "Effects of Calcination on the CO Hydrogenation Activity/Selectivity Properties of Potassium-Promoted Iron/Silica," *J. Catal.*, 100, 526 (1986).
3. J.L. Rankin and C.H. Bartholomew, "Effects of Potassium and Calcination Pretreatment on the Adsorption and Chemical/Physical Properties of Iron/Silica," *J. Catal.*, 100, 533 (1986).
4. C. Wang and C.H. Bartholomew, "Physical Chemical and Activity/Selectivity Properties of Cobalt Boride Fischer-Tropsch Catalysts," Paper in preparation, 1986.
5. J. Wang and C.H. Bartholomew, "Physical Chemical and Activity/Selectivity Properties of Cobalt Boride Fischer-Tropsch Catalysts," Paper in preparation, 1986.

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. C. Wang, "Physical, Chemical, and Activity/Selectivity Properties of Iron Boride Fischer-Tropsch Catalysts," M.S. Thesis, Brigham Young University, Dec. 1986.
4. J. Wang, "Physical, Chemical, and Activity/Selectivity Properties of Cobalt Boride Fischer-Tropsch Catalysts," Ph.D. Dissertation, Brigham Young University, April, 1987.

Table 35

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

Technical Meeting Papers

1. 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.
2. 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.
3. C.H. Bartholomew, "Metal Boride Catalysts for Indirect Liquifaction," University Coal Research Contractors Conference, Pittsburgh, PA, October 18-20, 1983.
4. 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.
5. C.H. Bartholomew and J.L. Rankin, "Effects of Pretreatment of Support on the Activity and Selectivity of Potassium-Promoted Iron," 1984 Annual Meeting of the AIChE, San Francisco, Nov. 25-30, 1984.
6. C.H. Bartholomew and J.L. Rankin, "Effects of Calcination on the CO Hydrogenation Activity/Selectivity Properties of Potassium-Promoted Iron/Silica Catalysts," Ninth North American Catalysis Society Meeting, Houston, March 18-21, 1985.
7. C.H. Bartholomew, "Deactivation of Syngas Conversion Catalysts," Tenth Canadian Symposium on Catalysis, Kingston Ontario, June 15-18, 1986.

Presentations at Universities and Companies

1. C.H. Bartholomew, "Cobalt Support Interactions," Department of Chemical Engineering, University of Texas, Austin Texas, September 18, 1984.
2. C.H. Bartholomew, "Structure Sensitivity of Cobalt in CO Hydrogenation," Symposium in Honor of Wolfgang Sachtler, Monsanto Co., St. Louis, Mo., September 21, 1984.
3. C.H. Bartholomew, "Effects of Precalcination on the Adsorption and Catalytic Properties of Fe/K/Silica Catalysts, Department of Chemical Engineering, Washington State University, Pullman, Washington, March 4,

1985.

4. C.H. Bartholomew, "The Magic Of Catalysts," College Lecture Series, College of Engineering and Technology, BYU, March 7, 1985.
5. C.H. Bartholomew, "Structure Sensitivity of Cobalt in CO Hydrogenation," Department of Chemical Engineering, Univ. of Southern Calif., April 9, 1985.
6. C.H. Bartholomew, "Structure Sensitivity of Cobalt in CO Hydrogenation," Physics Division, Sandia Laboratories, Albuquerque, NM, May 3, 1985.
7. C.H. Bartholomew, "Effects of Calcination on the CO Hydrogenation Activity/Selectivity Properties of Potassium-Promoted Fe/Silica," Eastman Kodak, Kingsport, Tennessee, September 16, 1985.
8. C.H. Bartholomew, "The Morbidity and Mortality of Catalysts," Hercules, Wilmington, Del., September 18, 1985.
9. C.H. Bartholomew, "The Mortality and Immortality of Catalysts," Univ. of Utah, Dept. of Chem. Eng., November 5, 1985.
10. C.H. Bartholomew, "Mortality of Catalysts," Union Carbide, Charleston, WV, February 19, 1986.
11. C.H. Bartholomew, "Cobalt in Fischer-Tropsch Synthesis," Union Carbide, Tarrytown, N.Y., February 20, 1986.

Table 36

Laboratories Visited by the Principal Investigator
During Contract Period

	<u>Comp./Location</u>	<u>Host(s)</u>	<u>Date</u>
1.	Dept. Chem. Eng. University of Colorado	John Falconer	April 21, 1983
2.	Dept. of Chemistry Colorado School of Mines	Scott Cowley	April 22, 1983
3.	Dept. Fuels Engineering University of Utah	Frank Hansen Frank Massoth Joseph Shabtai	May 19, 1983
4.	Dept. Chem. Eng. Montana State University	John Sears Warren Scarrah Doug Smith Daniel Shaffer	Nov. 17, 1983
5.	Amoco Oil Company	Mike Baird John Peri	Jan. 10, 1984
6.	Topsoe Catalyst Co.	Henrik Topsoe Rostrup-Nielsen	June 28-29, 1984
7.	Institute of Solid State and Radiochemistry	Frigyés Solymosi	July 12, 1984
8.	Institute of Isotopes Budapest	Zoltan Poal	July 13, 1984
9.	Dept. Chem. Eng. Univ. of Texas (Austin)	John Eckerdt	Sept. 18, 1984
10.	Monsanto Co.	Barry Haymore Bob Friedeman	Sept. 21, 1984
11.	Dept. Chem. Eng. Washington St. Univ.	James Lee	March 4, 1985
12.	Dept. Chem. Eng. Univ. So. Calif.	Theo Tsotsis	April 9, 1985
13.	Sandia National Labs Surface Science Div.	Wayne Goodman	May 2, 1985
14.	Dept. Chem. Eng. Queens Univ.	Bohdan Wojciechowski	Aug. 1, 1985

15.	Eastman Kodak Kingsport, Tenn.	Bruce Gustafson	Sept. 16, 1985
16.	Air Products Allentown, PA	Eamon Carroll	Sept. 17, 1985
17.	Hercules Wilmington, Del	Steve Hardwick	Sept. 18, 1985
18.	Dept. Chem. Eng. Arizona State Univ.	Tim Cole	Sept. 26, 1985
19.	Physical Chemistry Dept. General Motors Res. Labs	Bob McCabe	Nov. 21, 1985
20.	Dept. Chem. Eng. U. Michigan, Ann Arbor	Johannes Schwank	Nov. 22, 1985
21.	Dept. Chem. Eng. Rice Univ.	Joe Hightower	Jan. 23, 1986
22.	Mobil Oil Paulsboro, NJ	Jim Katzer	Feb. 18, 1986
23.	Union Carbide So. Charlestown, WV	Wayne Nauman	Feb. 19, 1986
24.	Union Carbide Tarrytown, N.Y.	Jule Rabo	Feb. 20, 1986
25.	Shell Develop Catalysis Dept.	Woody Shiftlett	April 24, 1986
26.	Surface Science Group	Wayne Goodman	May 19- Aug. 1, 1986
27.	Univ. New Mexico	Frank Williams	July 8, 1986

Table 37

Visitors and Speakers, BYU Catalysis Laboratory
During Contract Period

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 Hurcules 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 Karlsruhe 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
Dr. Fritz Dauzenberg	Catalytica Associates	Jan. 24, 1985
Dr. Jimmy Williams	Corning Glass Works	February 11-22, 1985
Dr. Fritz Solymosi	Hungarian Acad. Sciences	March 25, 1985
Prof. Robert Merrill	Cornell Univ.	April 3-4, 1985
Prof. Robert L. Kabel	Penn. State	May 13, 1985
Mr. Yoshi Tanda	Idemitsu Kosan Co.	June 5, 1985
Prof. Gustavo Fuentes	Univ. Autonoma Metropolitana	June 18, 1985
Prof. Jaques Oudar	Ecole National Superieure de Chimie de Paris	Aug. 12, 1985
Dr. Ruud Shel	CSIR, So. Africa	Sept. 4, 1985
Prof. Joe Hightower	Rice Univ.	Oct. 31, 1985
Dr. Robert McCabe	General Motors Res.	Feb. 27, 1986
Prof. Theo Tsostis	Univ. So. Calif	April 1, 1986
Dr. Ed. Sughrue	Phillips Pet.	Aug. 19, 1986
Prof. James Goodwin	Univ. Pittsburgh	Sept. 11, 1986

Table 38
Students Supported by DOE/PETC Contract

Jueh Wang	Ph.D.	Finished in Winter 1987
Richard M. Bowman	M.S.	Finished M.S. in Spring 1983, accepted position with Exxon
Chang Wang	M.S.	Finished M.S. Fall 1986
Duane M. Davis	M.S.	Finished M.S. in Fall 1983, accepted position with National Semiconductor
Brian Armstrong	B.S.	Graduated with B.S. in 1984 Accepted employment with an observatory in Sunspot, New Mexico
Dean Gessel	B.S.	Graduated with B.S. in 1984
Evan Witt	B.S.	Accepted position with Amoco

IV. CONCLUSIONS

1. Of the three preparation methods investigated, only the chemical reduction of anhydrous acetates by diborane (DB) in THF results in alkali-free metal borides. The higher temperature gas phase reduction in 1% DB/hydrogen produces metal particles, the surfaces of which are apparently boron-rich, while the reduction of metal nitrates in nonaqueous phase with NaBH_4 results in metal borides containing 0.5-2 wt.% sodium.

2. BET surface areas of metal borides range from 5 to 200 square meters/gram depending upon preparation methods. Sodium-containing cobalt borides prepared by NaBH_4 reduction have the highest surface areas (50-200 square meters per gram).

3. Percent metal areas (percentages of the surface containing metal atoms) range from 4 to 100% in cobalt and iron borides and depend greatly on preparation.

4. The kinetics and energetics of hydrogen and carbon monoxide adsorptions on iron and cobalt are significantly changed by the presence of boron additives. Hydrogen adsorption on metal borides is highly activated in the range of 25-200°C and is thus a slow process at room temperature. Moreover, the adsorption of hydrogen is complicated by metal boron hydride formation above room temperature (i.e. 100-400°C). Carbon monoxide adsorption states on cobalt are shifted to higher temperature and high binding energies by the addition of boron. Moreover, CO adsorption at room temperature is more reversible on metal borides relative to cobalt and iron metals.

5. Specific activities of cobalt and iron borides for CO hydrogenation vary with preparation and sodium impurity level. The order of decreasing specific activity (site-based) for cobalt catalysts is $\text{CoB}(\text{DB}/\text{THF}) > \text{CoB}(\text{DB}/\text{H}_2) = \text{CoB}/\text{Na}(\text{NaBH}_4) = \text{Co} > \text{Co}/\text{Na}$. A similar order is observed for alumina-supported cobalt catalysts. The order of decreasing specific activity for iron catalysts is $\text{Fe} > \text{FeB}/\text{Na} > \text{FeB}(\text{commercial}) > \text{FeB}(\text{DB}/\text{THF})$.

6. Products formed during CO hydrogenation on CoB catalysts contain lighter hydrocarbons than those produced over CoB/Na and Co catalysts. Products obtained during synthesis over FeB catalysts are similar to those produced by unsupported Fe.

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	14. 9/1/82 to 9/30/86		
15. Supplementary Notes			
16. Abstracts <p>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 m²/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 NaBH₄ or DB/THF reduction consisted mainly of stoichiometric MB and M₂B 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/H₂) = CoB/Na (NaBH₄) = Co > Co/Na. The order of decreasing specific activity for iron catalysts is Fe > FeB/Na > FeB (commercial) > FeB(DB/THF). The hydrocarbons than those produced over CoB catalysts contain lighter 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.</p>			
17. Key Words and Document Analysis. 17a. Descriptors <p>Boron-promoted cobalt and iron catalyst Cobalt and iron Fischer-Tropsch catalysts Fischer-Tropsch synthesis Indirect liquefaction</p>			
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