## II. EXECUTIVE SUMMARY

The preparation, physical and chemical properties, and CO hydrogenation activity/selectivity behavior of cobalt and iron metal borides were investigated. The accomplishments are best summarized according to Task:

Task 1. Catalyst Preparation and Characterization. Over 30 catalysts were prepared and characterized. Cobalt and iron metal borides were prepared by three different techniques: (1) gas phase reduction of cobalt and iron salts at 200-350°C with 1% diborane/hydrogen, (2) ethanolic, diglyme or aqueous phase sodium borohydride reduction of cobalt or iron salts, or (3) reduction of anhydrous acetates of cobalt and iron with diborane/THF. Unsupported and supported cobalt and iron catalysts and sodium-promoted cobalt and iron catalysts were prepared by simple impregnation/drying/hydrogen reduction methods using nitrate salts of cobalt and iron.

Catalysts were characterized by hydrogen and carbon monoxide adsorption uptakes, BET surface area measurements, x-ray diffraction (XRD), and temperature-programmed desorption (TPD) of CO.

Although hydrogen adsorption was found to be activated, it was necessary to conduct measurements at room temperature, since bulk metal boron hydrides were found to form at elevated temperatures. Cobalt and iron metal borides prepared by the three different techniques were found to have BET surface areas ranging from 4 to 200 square meters per gram. Percent metal areas estimated from the comparison of hydrogen and BET adsorption data ranged from 4-100%, depending upon preparation. Phases identified by XRD in metal boride catalysts varied considerably with preparation. In borides prepared by gas phase diborane (DB) reduction the major phases were cobalt and iron metals. Both metal and stoichiometric metal borides were observed in samples prepared by sodium borohydride or diborane/THF reduction. TPD spectra of CO desorption from cobalt catalysts indicate that CO adsorption states are shifted to higher temperatures and binding energies in boron and boron/sodium-containing samples relative to cobalt-only samples.

Task 2. Activity/Selectivity Measurements. CO hydrogenation activity/selectivity measurements were conducted at 175-300°C, 1-20 atm, and low conversion (5-10%). Turnover frequencies (TOFs) for sodium-free cobalt borides prepared from diborane/THF are a factor of 10 higher than for unsupported cobalt; the order of decreasing specific activity based on TOFs for cobalt catalysts is CoB(DB/THF) > CoB ($DB/H_2$) = CoB/Na ($NaBH_4$) = Co > Co/Na. A similar order is observed for alumina supported cobalt catalysts. The order of decreasing specific activity for iron catalysts is Fe > FeB/Na > FeB(commercial) > FeB(DB/THF). The products produced over CoB catalysts contain lighter hydrocarbons than those produced over CoB/Na and Co catalysts. Products produced during synthesis over FeB catalysts are similar to those produced by unsupported Fe.

Task 3. Moessbauer Spectroscopy Studies. A comprehensive Moessbauer spectroscopic (MS) investigation of iron borides was conducted at 77-298K to determine (1) the phases present in catalysts prepared by different techniques and (2) the phases present following FT synthesis. A commercial FeB catalyst was found by MS to contain 97% FeB and 3% $Fe_2B$. The MS spectrum of the iron

boride prepared by gas phase DB/hydrogen reduction showed primarily iron metal to be present, while those for the iron borides prepared by reduction with either DB/THF or $NaBH_4$ indicated mainly FeB and small amounts of $Fe_2B$ and Fe to be present.

Technical Communications and Miscellaneous Accomplishments. In connection with this contract 5 papers were published, submitted or in preparation while 7 papers were presented at national and regional meetings and 11 seminars were presented at universities and companies. The PI visited 26 laboratories and received 34 visitors during the contract period. Seven students were involved in studies associated with the contract; three theses and one dissertation resulted from this work.

## 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 in Tables 3-7. Ten metal boride catalysts were prepared during the first year of study. (Table 3) Eight of these catalyst preparations involved the reduction of the metal precursor with $NaBH_4$ or $KBH_4$ (22-26). Preparation of an iron boride catalyst using $NH_3BH_3$ in ethanol was unsuccessful (24). Two catalysts were prepared during the fourth quarter. A Na-promoted cobalt catalyst was prepared by simple impregnation of a silica support with a methanol solution of cobalt and sodium nitrates. The catalyst was dried and bulk reduced in $H_2$ at 250°C for 15 hours following procedures described earlier (22-24). A silica-supported, sodium-free metal boride, FeBS-106, was prepared by reduction with tetrabuty ammonium borohydride in methanol.

Two problems were encountered in the preparation involving $NaBH_4$ as a reducing agent: (i) it was not possible to completely remove Na impurities by washing in methanol or ethanol (see results in Table 3) and (ii) washing in water caused oxidation, and loss of boron (see large M/B ratios in Table 3 for Fe-B-101).

Since previous efforts to remove sodium impurities from $NaBH_4$-reduced catalysts had met with only limited success (22-24), boron-containing reducing agents other than $NaBH_4$ were investigated, including organic complexes of borane or the borohydride ion. Unfortunately these preparations were unsuccessful, either involving slow, incomplete reductions or leading to inactive catalytic materials.

Three boron-promoted catalysts (CoB-104, 105 and 106) were prepared during the second year by methods described in detail in the fifth quarterly report (24). This method involved mainly the coaddition of cobalt nitrate and $NaBH_4$ solution into water or ethanol. The resulting fine precipitate was washed in ethanol to remove the impurities i.e. Na. Water and methanol are not suitable as washing agents since they tend to oxidize the catalysts. Moreover, it was not possible to completely remove Na impurities by washing in ethanol. The chemical compositions for these catalysts are listed in Table 4.

Four cobalt boride catalysts free of alkali impurities (CoB-107 to CoB-110A) were prepared by exposure of the reduced, unsupported cobalt catalyst to 1% $B_2H_6/H_2$ at 350°C following procedures described in the sixth quarterly report (25 and Table 4). However, in the course of preparation (after a few hours exposure to 1% $B_2H_6/H_2$) a brown dirt-like material was formed on top of the catalyst bed. The brown deposit on top of the catalyst bed consisted of mainly boron and 5% cobalt. Also, the inside wall of the Pyrex cell used for boriding was covered with a layer of glassy, black deposit. Both compounds were probably formed by the reaction of $B_2H_6$ at high temperature to produce some polymeric boron material. Both materials were highly resistent to removal by conventional solvents and acids. It was observed that below 200°C, no glassy, black deposited on the cell.

The preparation and composition of cobalt and iron boride catalysts prepared during the third and fourth years by reduction of the anhydrous

Table 3. Summary of Catalysts Prepared During the First Contract Year and their Chemical Compositions

| Catalyst Code | Preparation Method | Chemical Analysis (Wt.%) | | | | M/B[a] |
|---|---|---|---|---|---|---|
| | | Co | Fe | B | Na | |
| CoB-102 | $NaBH_4$ redn[b] | 47.5 | -- | 2.49 | 0.16 | 3.5 |
| | $H_2$ redn, 400°C[c] | 83.3 | -- | 3.03 | 3.07 | 5.0 |
| CoB-S-101 | $NaBH_4$ redn[b] | 11.8 | -- | 0.73 | 1.52 | 3.0 |
| | $H_2$ redn, 400°C[c] | 12.2 | -- | 0.79 | 1.76 | 2.9 |
| FeB-101 | $NaBH_4$ redn[d] | -- | 67.5 | 1.2 | 0.009 | 10.9 |
| | $H_2$ redn, 400°C[e] | -- | 76.0 | 1.6 | 0.19 | 9.0 |
| FeB-103 | $NaBH_4$ redn[d] | -- | 60.5 | 2.30 | 0.035 | 5.1 |
| FeB-104 | $NaBH_4$ redn[d,f] | -- | | | | |
| FeB-105 | $NaBH_4$ redn[g] | -- | 9.51 | 10.3 | 15.4 | -- |
| FeB-106 | $KBH_4$ redn | | | | | |
| FeB-107 | $NH_3BH_3$ redn[h] | | | | | |
| FeB-108 | $NaBH_4$ redn[i] | | | | | |
| FeB-S-106 | $NH_4B(Bu)_4$ redn[j] | | | | | |

[a]Metal/boron ratio in atomic %.

[b]Reduced in ethanolic solution; washed in methanol.

[c]After washing in methanol and 400°C reduction in $H_2$.

[d]Reduced in ethanolic solution; washed in water.

[e]After washing in water and 400°C reduction in $H_2$.

[f]Exposed to air during preparation.

[g]Chemically reduced; not washed.

[h]Chemical reduction of ferric citrate in ethanolic solution didn't work.

[i]Aqueous phase reduction of ferric citrate.

[j]Reduction by tetrabutylammonium borohydride in methanol.

Table 4: Chemical Compositions, BET Surface Areas, and $H_2$ Adsorption Uptakes of Cobalt Boride Catalysts. (Prepared during 2nd Year of Contract)

| Catalyst Code | Chemical Analysis (wt%) | | | Co/B atomic ratio | $H_2$ Uptakes ($\mu$ mole/g) | BET S.A. ($m^2/g$) |
|---|---|---|---|---|---|---|
| | Co | B | Na | | | |
| Co-103 | 100 | | | | 26.8 | |
| CoB-104[a] | 47.5 | 8.91 | 1.78 | 0.98 | | |
| CoB-105[b] | 83.3 | 10.23 | 1.92 | 1.49 | 33.3[d] | 186 |
| | | | | | 41.0[e] | 172 |
| CoB-106[c] | 73.9 | 11.10 | 0.92 | 1.22 | | |
| CoB-107[f] | 90.1 | 9.83 | | 1.68 | | |
| CoB-108[f] | 85.7 | 9.79 | | 1.61 | | |
| CoB-109[f] | 87.7 | 11.9 | | 1.35 | 11.5 | |
| CoB-109R[g] | 88.9 | 10.1 | | 1.61 | 13.6 | 16.2 |
| CoB-110A[h] | 95.2 | 4.6 | | 3.8 | | |
| Deposit/CoB-110A[i] | 5.2 | 94.5 | | | | |
| CoB-A-102 | 13.6 | 17.8 | | 0.14 | 73 | |

[a]Made in ethanol medium, with Co/B ratio of 1:4 in the raw material
[b]Made in $H_2O$ medium, with Co/B ratio of 1:4 in the raw material
[c]Made in $H_2O$ medium, with Co/B ratio of 1:8 in the raw material
[d]Reduction at 250°C for 15 hrs; $H_2$ adsorption at room temp
[e]$H_2$ chemisorption was performed by cooling in $H_2$ from 250°C to 25°C
[f]Prepared by gas phase boriding at 350°C for 48 hours
[g]Catalyst after CO hydrogenation reactor run
[h]Prepared by gas phase boriding at 350°C for 22 hours
[i]Brown material formed on top of CoB-110A

acetate with diborane in THF or by reduction with $NaBH_4$ of the cobalt acetate are detailed in Tables 5-7. Unsupported cobalt and sodium-promoted cobalt catalysts prepared for comparison purposes are also described in Table 5, while iron boride catalysts prepared by gas phase reduction in 1% $B_2H_6/H_2$ are described in Table 7. The solvent phase reduction of iron and cobalt acetates by diborane in THF was found to be most successful for preparing cobalt and iron borides free of impurities.

The preparation of sodium-free cobalt and iron boride catalysts in $B_2H_6$/THF solution was adapted from a new preparation procedure for nickel boride catalysts, proposed by Rei et al. [28]. The procedure is summarized as follows:

1. A 10% $B_2H_6/H_2$ gas mixture was bubbled slowly at room temperature through THF to prepare a saturated $B_2H_6$/THF solution. A saturated solution contains 0.25 M $B_2H_6$ at room temperature.

2. In the case of the cobalt catalyst the $B_2H_6$/THF solution was added directly to anhydrous cobalt acetate (pink color) (it was not dissolved in a solvent such as water, methanol or ethanol since these are potential oxidizing agents for CoB catalysts). Anhydrous cobalt acetate was selected, since it contains no crystal water to react with $B_2H_6$ to form the undersirable byproduct boric acid. Moreover, since cobalt acetate is only very slightly soluble in THF, it would be much easier to separate the catalyst and unreacted cobalt acetate from the solution. The reaction of cobalt acetate with $B_2H_6$ to produce the CoB catalyst (black color) was allowed to proceed over a period of ten hours. In the case of the iron catalyst, anhydrous iron acetate was added directly into the $B_2H_6$/THF solution and stirred with a magnetic bar. The solution turned black and began bubbling right after adding the powder. However, a slow reaction continued over a period more than 24 hours. When the reaction reached near completion (indicated by very little bubbling), the solution was decanted. Another portion of saturated diborane/THF solution was then added with the black precipitate, the same process was repeated 3-4 times before the reaction was completed (no bubbling observed). Then the excess solution was decanted and the precipitate was dried at about 100 °C under $N_2$ flow. A metallic, highly ferromagnetic and relatively coarse powder was obtained.

3. The solvent was evaporated and the black compound was dried. All the procedures were carried out in the dry box under $N_2$ purified by passing through a Molecular Sieve Trap to remove $H_2O$. During the evaporation, the solvent was swept out of the dry box by $N_2$. The possibility of oxidizing the prepared catalyst or introducing $H_2O$ in the process of making catalyst was minimized in this way. The chemically-reduced, dry-powdered catalyst was black and magnetic.

An unsupported cobalt catalyst was also prepared by thermal decomposition of cobalt nitrate in air at 200°C for 16 hours followed by reduction of thus-formed cobalt oxide in $H_2$ at 400°C for 16 hours.

Sodium containing iron catalysts were prepared in a similar way as described above except using $NaBH_4$ dissolved in diglyme (diethylene glycol dimethyl ether) as the reducing solution. The reduction reaction required about 3 days before its completion and resulted in a muddy black precipitate

Table 5

Cobalt Catalysts Prepared During Contract Years 3 and 4

| Catalyst | Reducing Agent/ Reaction Medium | Preparation Techniques |
|---|---|---|
| Co-104 | $H_2$ | Calcined cobalt nitrate at 200 °C; reduced in $H_2$ at 350 °C |
| Co/Na-100 | $H_2$ | Calcined Co/Na nitrate at 200 °C; reduced in $H_2$ at 350 °C |
| CoB-250[a,b] | $B_2H_6$/ THF | Solvent phase reduction of cobalt acetate in $B_2H_6$/THF; reduce in $H_2$ at 250 °C |
| CoB/Na-250[b] | $NaBH_4$/ diglyme | Solvent phase reduction of cobalt acetate in $NaBH_4$/diglyme; reduce in $H_2$ at 250 °C |
| CoB-109G | $B_2H_6/H_2$ | Gas-Phase Boriding the reduced cobalt in $B_2H_6/H_2$ at 350 °C |
| CoB/$Al_2O_3$-250[c] $Co(Ac)_2/Al_2O_3$ | $B_2H_6$/ THF | Solvent phase reduction of in $B_2H_6$/THF; reduce in $H_2$ at 250 °C |
| CoB/Na/$Al_2O_3$-250[c] | $NaBH_4$/ diglyme | Solvent phase reduction of $Co(Ac)_2/Al_2O_3$ in $NaBH_4$/diglyme; reduce in $H_2$ at 250°C |

[a] Stoichiometric cobalt borides obtained by fusion of the elements at temperature over 1000 °C have the formulas of CoB, $Co_2B$, and $Co_3B$. CoB is used here for convenience. The stoichiometries of catalysts have to be identified.

[b] Chemical reduction by adding the reducing solvent to anhydrous cobalt acetate followed by washing in THF or methanol, drying under vacuum at 100 °C, and reduction in $H_2$ at 250 °C, all in the absence of air.

[c] Chemical reduction by adding the reducing solvent to dried $Co(Ac)_2/Al_2O_3$ followed by washing in THF, drying under vacuum at 100 °C, and reduction in $H_2$ at 250 °C, all in the absence of air.

Table 6

Chemical Analysis of Borided Cobalt Catalysts

| Catalyst Code | Co wt% | B wt% | Na wt% | Atom% Boron / Atom% Cobalt |
|---|---|---|---|---|
| CoB-109G [a] | 87.7 | 11.9 | -- | 0.74 |
| | (88.9) [d] | (10.1) | -- | (0.62) |
| CoB-250 [b] | 64.6 | 13.8 | -- | 1.16 |
| | (54.3) | (5.9) | -- | (0.59) |
| CoB/Na-250 [c] | 80.3 | 15.2 | 1.96 | 1.03 |
| | (79.6) | (15.1) | (2.11) | (1.03) |
| CoB/$Al_2O_3$-250 [b] | 3.72 | 1.95 | -- | 2.86 |
| CoB/Na/$Al_2O_3$-250 [c] | 3.67 | 0.95 | 2.32 | 1.41 |

[a] Prepared from boriding reduced cobalt with $B_2H_6/H_2$ gas at 350 °C.

[b] Prepared from boriding cobalt acetate with $B_2H_6$/THF solution in THF at 25 °C and further reduced in $H_2$ at 250 °C.

[c] Prepared from boriding cobalt acetate with $NaBH_4$/Diglyme solution in THF at 25 °C and further reduced in $H_2$ at 250 °C.

[d] Values in parenthesis ( ) denote the catalyst composition after reactor run.

Table 7. Chemical analyses, surface areas and $H_2$, CO uptakes of Iron Boride Catalysts Prepared during Contract years 3 & 4

| Catalyst | Chem. Anal. Fe | B | wt% Na | Total wt % | B/Na/Fe Ratio | Uptake ($\mu$mol/g)[a] $H_2$ | CO | BET ($m^2/g$) | % D[b] |
|---|---|---|---|---|---|---|---|---|---|
| FeB-105-G[c] | 88.2 | 11.6 | — | 99.8 | 0.68/-/1 | 132* | — | — | — |
| FeB-107-G[d] | 98.6 | 0.51 | — | 99.1 | 0.027/-/1 | ND** | ND | ND | -- |
| FeB-COM-250[e] | 67.5 | 16.1 | — | 83.6 | 1.23/-/1 | 0.9 | ND | 0.7 | .015 |
| FeB-COM-350[e] | 67.5 | 16.1 | — | 83.6 | 1.23/-/1 | 1.0 | ND | -- | .016 |
| FeB2-250[f] | 76.8 | 24.4 | — | 101.2 | 1.64/-/1 | 81.7 | 75.3 | 4.1 | 1.2 |
| FeB2-350[f] | 62.1 | 20 | — | 82.1 | 1.49/-/1 | 7.7 | 0.6 | ND | .14 |
| FeB5-250[g] | 73.5 | 25.3 | — | 98.8 | 1.79/-/1 | 121 | 102 | 6.3 | 1.8 |
| FeB5-500[g] | 53.4 | 16.7 | — | 70.1 | 1.61/-/1 | — | — | — | — |
| FeB5-RXN[h] | 40.5 | 13.0 | — | 53.5 | 1.64/-/1 | | — | — | — |
| Fe/B/Na-2[i] | 21.7 | 4.2 | 5.5 | 31.4 | 1.01/0.63/1 | ND | ND | — | — |
| Fe/B/Na-3[j] | 39.2 | 10.5 | 4.5 | 54.2 | 1.39/0.28/1 | ND | — | — | — |
| Fe/B/Na-NW[k] | 21.8 | 7.8 | 14.4 | 44.0 | 1.82/1.58/1 | — | — | — | — |
| Fe/B/Na[l]-250 | 74.1 | 21.2 | 1.8 | 97.1 | 1.47/0.06/1 | 7.8 | 1.5 | 9.2 | .12 |
| Fe/B/Na[m]-RXN | 52.8 | 9.8 | 1.5 | 64.1 | 2.33/0.16/1 | — | — | — | — |

* gas uptake at elevated temperature( 250-25 °C ).
** ND represents " not detectable ".

a. $H_2$ and CO uptakes were measured at room temperature after 8-10 hours equilibrium period.
b. Percentage dispersion is defined as the percentage of surface metal atoms to the total metal atoms calculated by equation: %D = 0.02 (X) (Mw)/(%w) (f) (see Appendix A).
c. Prepared by passing 1% $B_2H_6$ in $H_2$ mixture over prereduced Fe(reduced at 450 °C) at 250 °C for 18 hours.
d. Same precursor as in a. but reduced at 250 °C for 1.5 hour.
e. Commercial iron boride catalyst, 99% purity of FeB, -35 mesh, purchased from Alfa Products. 250 °C or 350 °C reduction by $H_2$ prior to the measurement.
f. Prepared by chemical reduction of anhydrous iron acetate with $B_2H_6$/THF solution thoroughly; 250 °C or 350 °C reduction before measurement.
g. Catalysts prepared in the same method as d. in different batch, and reduced at 250 or 500 °C.
h. FeB5 which has been test for CO hydrogenation reaction.
i. Same preparation method as previous report (34) : $NaBH_4$/ethanol was used to reduce iron nitrate followed by washing with MeOH 3-4 times.
j. Catalyst in f. was washed again with MeOH twice.
k. NaBH4/diglyme reduced catalyst without washing.
l. NaBH4/diglyme reduced catalyst washed with methanol.
m. Fe/B/Na catalyst after synthesis reaction.

at the bottom of the flask. The wet precipitate was then washed several times with THF to remove the excess diglyme and dried at about 140 °C for at least 6 hours under $N_2$ flow. After drying and cooling to room temperature, the powder was washed with MeOH and filtered several times in an hour to remove the impurities and excess sodium salt. The catalyst was dried at 140 °C for several hours before storage and was called Fe/B/Na.

For comparison purposes, commercial iron boride (99% purity of FeB, -35 mesh) purchased from Alfa Products and named FeB-COMM here. This sample was prepared metallergically at temperature above 1200 °C.

2. Catalyst Characterization. Metal surface areas of reduced catalysts were measured following $H_2$ reduction by $H_2$ and/or CO chemisorption(s) and nitrogen BET adsorption (See Tables 4, 7-10). Procedures for measuring $H_2$ and CO uptakes and BET surface areas were described previously (22-26). During the first two years of study it was determined that $H_2$ adsorption on cobalt and iron borides was activated; accordingly it was concluded that monolayer uptakes would be best measured by evacuating at a few °C below the reduction temperature followed by cooling in $H_2$ from the evacuation temperature to room temperature. Most of the adsorption data in Tables 4 and 8 were determined by this method. Unfortunately it was determined during the third year of study that exposures of metal borides to hydrogen at elevated temperatures caused formation of metal boron hydrides leading to unrealistically large hydrogen uptakes. Accordingly, during the third and fourth years, hydrogen uptakes were measured after several hours of equilibration at room temperature (see Tables 7, 9 and 10).

Data in Tables 4 and 8 indicate that the sodium-containing cobalt boride catalysts prepared by $NaBH_4$ reduction in either ethanol or water adsorb large quantities of hydrogen (25-364 micromoles/g) and have relatively high BET surface areas (90-210) $m^2/g$). The hydrogen uptakes and surface areas of the corresponding sodium-containing iron borides prepared by $NaBH_4$ reduction (Tables 7 and 8) are significantly smaller ($H_2$ uptakes of 5-26 and BET areas of 9-82 $m^2/g$). Hydrogen uptakes and surface areas of cobalt and iron boride catalysts prepared from high temperature diborane/hydrogen reduction or room temperature diborane/THF reduction were generally significantly lower than those prepared by $NaBH_4$ reduction (see Tables 4, 7, 9 and 10). For example the hydrogen uptakes for CoB (gas), CoB (THF), and CoB/Na (see Table 10) are 11.5, 17.6 and 121 micromoles respectively, while BET areas were 2.7, 46.4, and 14.9 respectively. Percent metal areas obtained by comparing hydrogen uptakes with BET areas (Table 10) were 46, 4, and 87% respectively for CoB(gas), coB(THF) and CoB/Na; in other words, the surface of the catalyst prepared from diborane/THF consists of only 4% cobalt metal atoms and presumably 96% boron atoms, while that prepared from $NaBH_4$ is 87% cobalt metal atoms.

Table 11 lists the crystallite diameters calculated from hydrogen adsorption, x-ray diffraction and TEM data. From comparison of the surface mean diameters calculated from TEM with those calculated from hydrogen chemisorption it is evident that the estimates based on $H_2$ adsorption are generally larger (very much larger in the case of FeB). This result is probably due to presence of Na impurities, B phases, and unreduced oxide phases at the surface which do not absorb $H_2$. Volume mean diameters from TEM were in fair agreement with those calculated from XRD data for the iron

Table 8. Hydrogen Chemisorption and BET Surface Area Measurements for Unsupported Iron and Cobalt Boride Catalysts

| Catalyst Code | Reduction Temperature (°C) | $H_2$ Uptake[a] (μ moles/g) | BET ($m^2$/g) |
|---|---|---|---|
| CoB-102 | 250 (2 hours) | 205±15 | 200 |
| CoB-102 | 250 | -- | 176 |
| CoB-102 | 250 (15 hours) | 364 | 210 |
| CoB-102[b] | 400 | 260±20 | 90.2 |
| CoB-S-101 | 250 (2 hours) | 26.3 | -- |
| CoB-S-101 | 250 (15 hours) | 33.4± | -- |
| CoB-S-101[c] | 400 | 21.3 | -- |
| CoB-S-101[b] | 400 | 20.8 | -- |
| CoB-S-101 | 400 | 42.4 | -- |
| FeB-101[c] | 400 | 5.71 | 60.9 |
| FeB-103 | 300 | 9.98 | 82.3 |
| FeB-108 | 300 | 26.2 | 28.1 |
| FeB-108[e] | 300 | -- | 20.6 |
| FeB-108 | 25 | 0 | -- |
| FeB-108[d] | 25 | 14.3 | -- |

[a] $H_2$ chemisorption performed by evacuating at 5°C below the reduction temperature then introducing $H_2$ at that temperature and allowing the catalyst to cool in $H_2$ to room temperature. This procedure was followed unless otherwise specified.

[b] Chemisorption at 100°C.

[c] Chemisorption at 25°C.

[d] Evacuated at 300°C then the chemisorption was performed by cooling in $H_2$ from 300°C to 25°C.

[e] After reactor testing in $CO/H_2$.

Table 9
Chemisorption Data[a] for Borided Cobalt Catalysts

| Catalyst Code | Total $H_2$ Uptake [a] | Total CO Uptake | Irreversible CO Uptake | Total CO / Total H | Irreversible CO / Total H |
|---|---|---|---|---|---|
| Unsupported | | | | | |
| CoB [b] | 17.6 | 29.2 | 7.2 | 0.83 | 0.20 |
| CoB/Na [b] | 121.0 | 102.4 | 85.6 | 0.42 | 0.35 |
| Co [c] | 32.3 | 40.2 | 28.3 | 0.62 | 0.44 |
| $CoB_{(gas)}$ [b] | 11.5 | 20.2 | 13.5 | 0.88 | 0.59 |
| Co/Na [c] | 16.5 | 6.4 | 4.0 | 0.19 | 0.12 |
| Alumina-Supported | | | | | |
| $CoB/Al_2O_3$ [b] | 6.8 | 16.7 | 8.5 | 1.01 | 0.625 |
| $CoB-Na/Al_2O_3$ [b] | 31.0 | 49.3 | 36.7 | 0.75 | 0.59 |
| $Co/Al_2O_3$ [d] | 5.6 | 40.0 | 12.0 | 3.57 | 1.07 |

[a] Chemisorption uptake in unit of μmoles per gram of catalyst.
[b] $H_2$ or CO adsorbed at 25 °C and equilibrate for 16 hours at 25 °C.
[c] $H_2$ adsorbed at 350 °C and CO adsorbed at 25 °C and equilibrate for 45 minutes at 25 °C.
[d] 3% $Co/Al_2O_3$, data from Reuel[24].

Table 10

BET and $H_2$ Adsorption Data for Unsupported Cobalt Catalysts

| Catalyst Code | BET area [a] ( $m^2/g$ ) | $H_2$ Uptake [b] ( mmoles/g ) | Metal area [c] ( $m^2/g$ ) | Percentage [d] metal area |
|---|---|---|---|---|
| CoB | 46.4 | 17.6 | 1.9 | 0.04 |
| CoB/Na | 14.9 | 121.0 | 13.0 | 0.87 |
| Co | 3.36 | 32.3 | 3.48 | 1.03 |
| $CoB_{(gas)}$ | 2.70 | 11.5 | 1.24 | 0.46 |
| Co/Na | 1.02 | 16.5 | 1.78 | 1.74 |

[a] Nitrogen adsorbed at -196 °C assuming 0.162 $nm^2$/nitrogen molecule after reduction in $H_2$ at 250 °C for solution-phase prepared CoB and CoB/Na or at 350 °C for Co, $CoB_{(gas)}$ and Co/Na.

[b] Isotherm measurement at 25 °C .

[c] Calculated assuming an area of 0.0894 $nm^2$/cobalt atom.

[d] Metal area divided by BET area times 100.

Table 11. Average Crystallite Diameters of Iron Boride and Cobalt Boride Catalysts

| Catalyst Code | Method of Calculation | | | |
|---|---|---|---|---|
| | $H_2$ Adsorption | TEM | | XRD |
| | $\bar{d}_s$(nm) | $\bar{d}_s$(nm) | $\bar{d}_v$(nm) | $\bar{d}_v$(nm) |
| FeB-101 | 464 | 18 | 23 | 53 |
| FeB-S-105 | 82 | 16 | 19 | 28 |
| CoB-102 | 22 | 16 | 18 | 20 |
| CoB-S-101 | 19 | 7.1 | 8.9 | -- |

catalysts. However, in the case of CoB, average crystallite diameters determined by different techniques were in excellent agreement.

X-ray diffraction data were also obtained for FeB-108 during the first year. The x-ray powder spectrum included peaks at positions characteristic of FeB and $Fe_2B$ (and perhaps iron metal).

Extensive x-ray studies of cobalt and iron borides were performed during the third and fourth contract years. The phases identified by x-ray varied considerably with preparation. For example, in the case of borides prepared by gas phase borohydride reduction the major phases were cobalt and iron metals in the cobalt and iron catalysts respectively. This is illustrated for the iron boride catalyst in Figure 3 where the x-ray powder diffraction spectrum of FeB-107-G is nearly identical to that for metallic iron. Thus, the boron is apparently concentrated on the outer atomic layers of the iron crystallites in these catalysts. The x-ray patterns for iron boride catalysts prepared from $NaBH_4$ or diborane/THF were consistent with a mixture of iron metal and stoichiometric FeB and $Fe_2B$ (see Figures 4 and 5 and Table 12). Indeed, from the spectrum of commercial iron boride (mainly FeB) and standard parameters of FeB and $Fe_2B$ from ASTM data, the most intensive peaks for FeB should locate at 41, 45, 48, 77, and 82 degree and for $Fe_2B$ should locate at 45 degree. The spectra in Figs. 4 and 5 do contain some of these peaks, especially in the case of the FeB2-460 catalyst, but the intensities are quite weak compared to other signals. After reactor testing of FeB (Fig. 4a) or 460 °C reduction (Fig. 4b) of those sodium free catalysts the peaks for the $\alpha$-iron phase are quite evident. The intense peak at 27 degree for FeB2-460 and Fe/B/Na samples could be assigned to the (110) orientation of FeB.

The x-ray diffraction patterns for unsupported borided cobalt catalysts prepared from diborane/THF and $NaBH_4$, i.e. CoB-250 and CoB/Na-250, are amorphous when freshly prepared and vacuum dried at 100°C. The CoB-250 catalyst remained amorphous even after thermal treatment in $H_2$ at 250°C, as shown in Figure 6b. After thermal treatment in $H_2$ up to 350°C, both CoB-250 and CoB/Na-250 were sintered to crystalline cobalt (h.c.p) metal as compared with the pure cobalt catalysts depicted in Figure 6a. These results indicate that borided cobalt catalysts prepared in solution phase are structurally different from the cobalt boride metallurgically prepared from direct fusion of boron and cobalt at over 1000°C, i.e. the boron may be concentrated in the surface layers.

As displayed in Figure 7b, the x-ray spectrum of CoB-109G prepared from boriding reduced cobalt with diborane/$H_2$ at 350°C is also indicative of the h.c.p. cobalt phase only. It is interesting to observe that the order of the intensity of peak changes in the presence of 2 wt% of Na in the cobalt catalyst. The most intense peak shifts from $2\theta = 44.8°$ for pure cobalt to 47.6 ° for the Co/Na catalyst. Furthermore, the bulk phase of the Co/Na catalyst, after being tested for CO hydrogenation activity at 260-300 °C, is partially carbided to cobalt carbide species as indicated in Figure 7d by the peaks appeared at $2\theta = 37.4°$ ($Co_3C$), 42.8° ($Co_2C$), and 45.7° ($Co_2C$ or $Co_3C$). These cobalt carbides formed during reaction are probably not active phases for hydrogenation of CO since the Co/Na catalyst possessed very low activity relative to the pure cobalt catalyst.

Not unexpectedly, the x-ray diffraction measurements in Figure 8

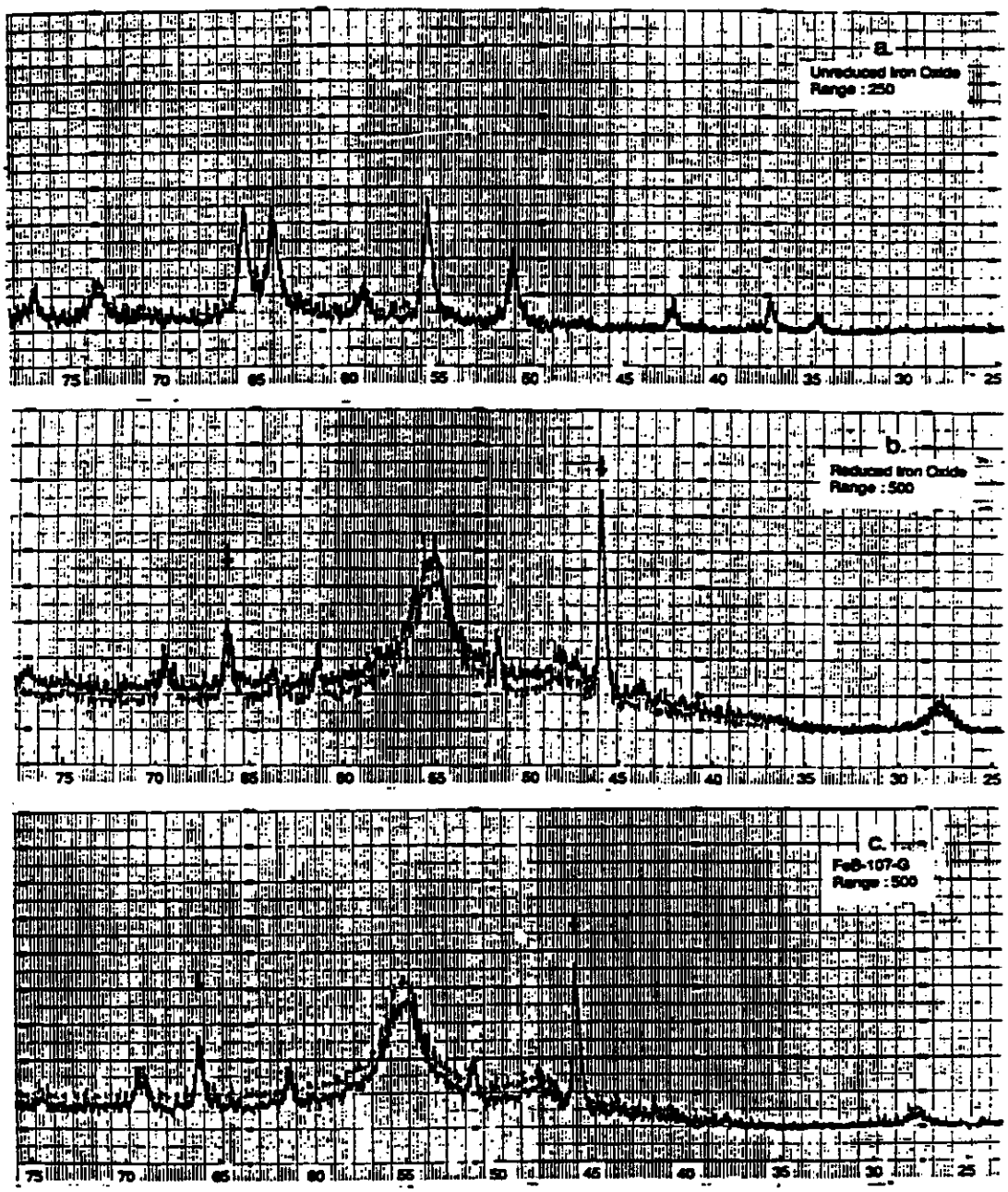



Fig. 3. X-ray diffraction spectra of (a) unreduced iron oxide (b) 250 °C reduced iron oxide, and (c) FeB-107-G.

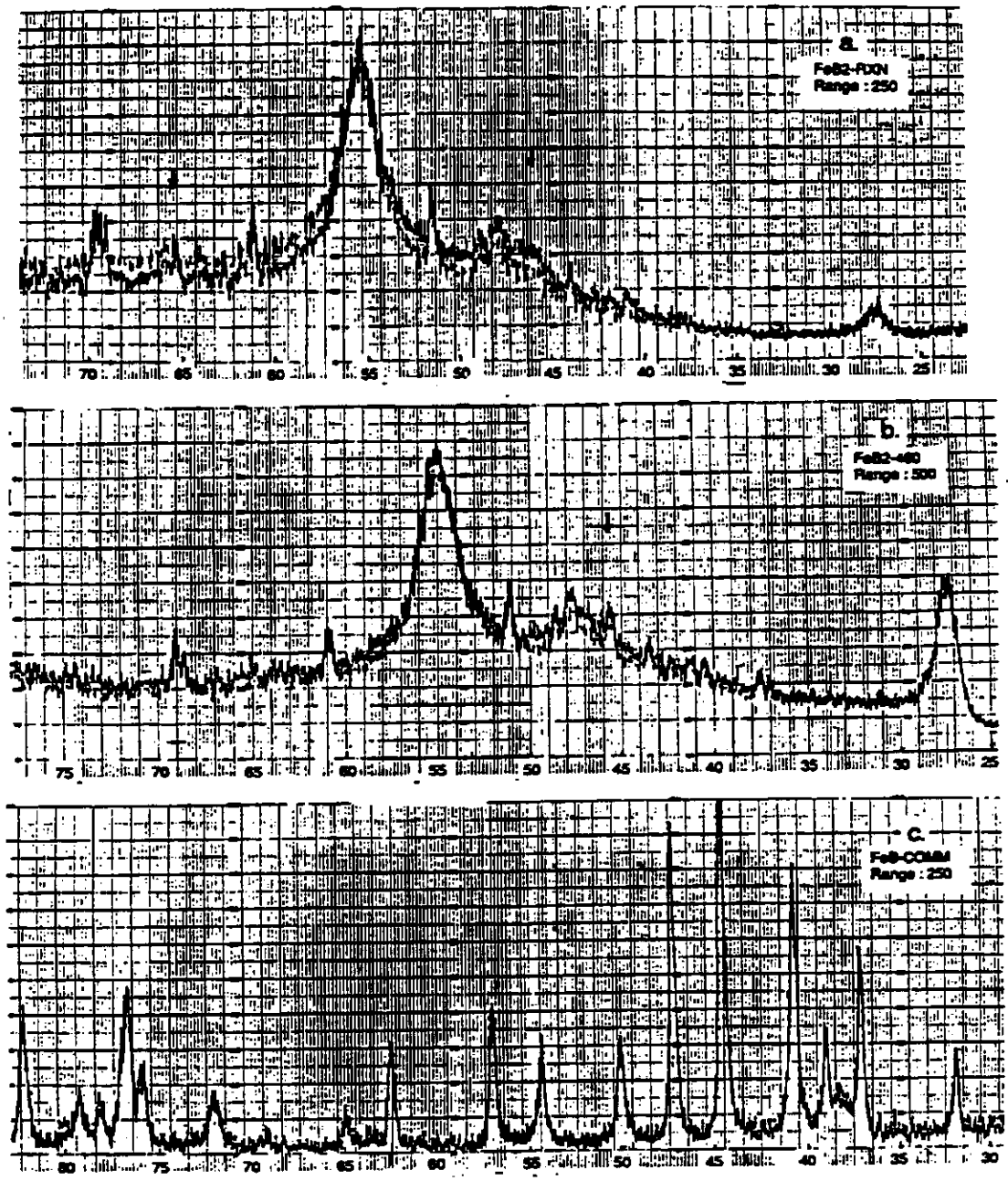



Fig. 4. X-ray diffraction spectra of (a) after $CO/H_2$ reaction on FeB-RXN (b) 460 $^{o}C$ reduced catalyst, FeB2-460 and (c) commercial iron boride catalyst.

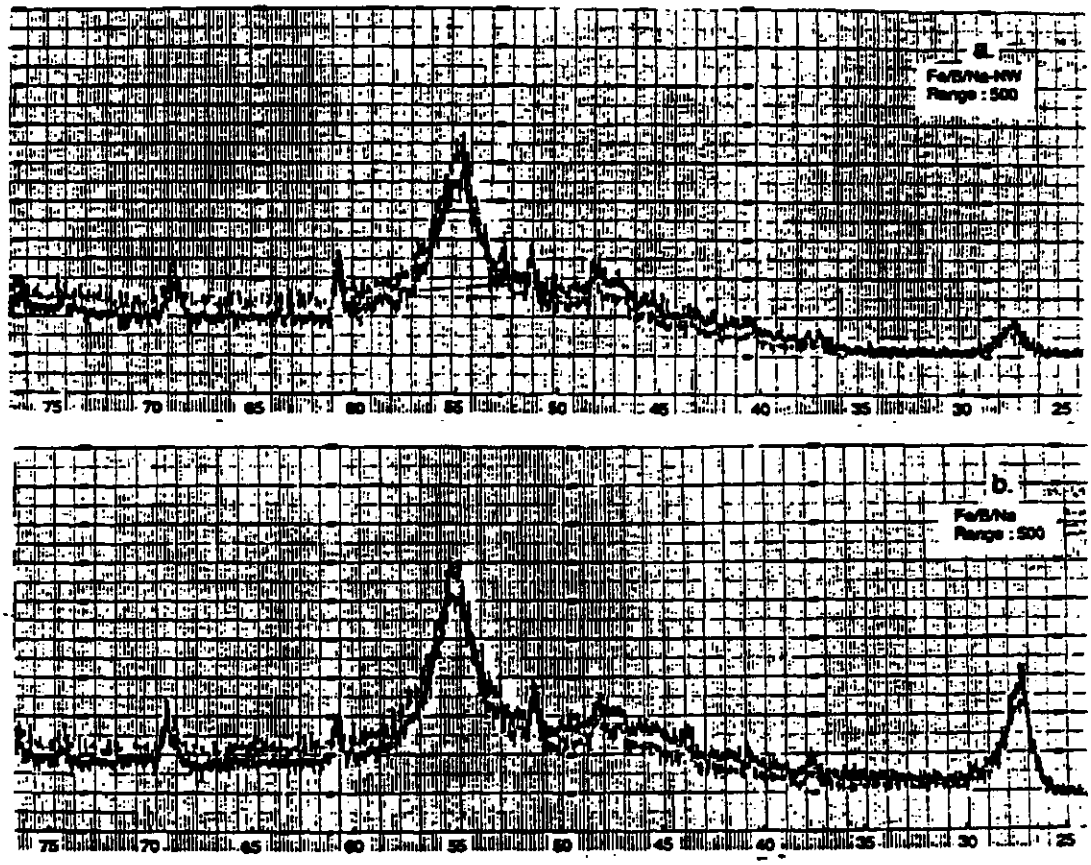


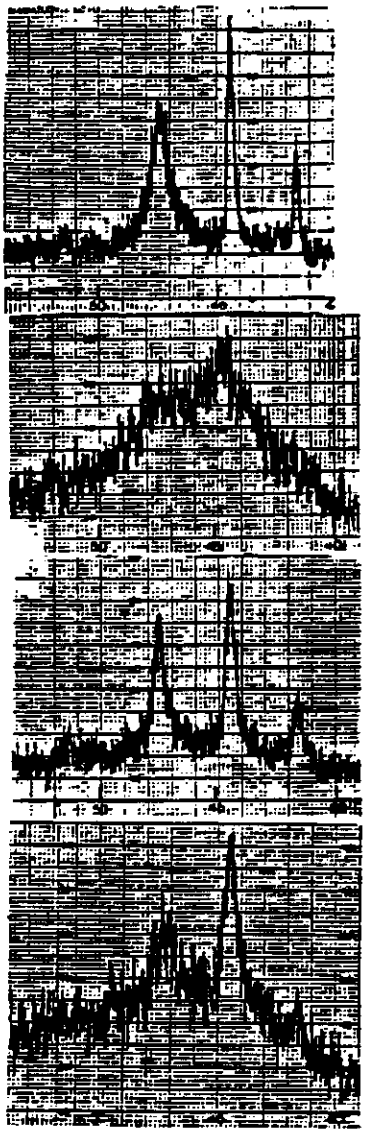

**Fig. 5. X-ray diffraction spectra of (a) Fe/B/Na-NW (b) Fe/B/Na.**

Table 12. Standard parameters of FeB and $Fe_2B$ from ASTM diffraction data card.

| Species | FeB* | | | $Fe_2B$** | | | |
|---|---|---|---|---|---|---|---|
| | dA° | 2θ | $I/I_1$ | hkl | dA° | 2θ | $I/I_1$ | hkl |
| | 3.26 | 27.3 | 60 | 110 | 3.61 | 24.6 | 7 | 110 |
| | 2.74 | 32.7 | 80 | 020 | 2.56 | 35.0 | 15 | 200 |
| | 2.38 | 37.8 | 80 | 101 | 2.12 | 42.6 | 25 | 002 |
| | 2.28 | 39.5 | 80 | 120 | 2.01 | 45.1 | 100 | 121 |
| | 2.19 | 41.2 | 100 | 111 | 1.83 | 49.8 | 6 | 112; 220 |
| | 2.01 | 45.1 | 100 | 021 | 1.63 | 56.4 | 18 | 202; 130 |
| | 1.90 | 47.8 | 100 | 210 | 1.29 | 73.3 | 6 | 132; 400 |
| | 1.81 | 50.4 | 80 | 121 | 1.20 | 79.9 | 13 | 123; 330 |
| | 1.67 | 54.9 | 80 | 130 | 1.19 | 80.7 | 10 | 141 |
| | 1.60 | 57.6 | 80 | 211 | 1.05 | 94.4 | 6 | 332 |
| | 1.48 | 62.7 | 60 | 002 | | | | |
| | 1.30 | 72.7 | 60 | 140 | | | | |
| | 1.25 | 76.1 | 60 | 041 | | | | |
| | 1.24 | 76.8 | 100 | 122; 231 | | | | |
| | 1.20 | 79.9 | 60 | 311 | | | | |
| | 1.17 | 82.3 | 100 | 212 | | | | |
| | 1.12 | 86.9 | 60 | 321 | | | | |
| | 1.11 | 87.9 | 80 | 132 | | | | |

* Relative intensity $I/I_1$ lower than 60% are omitted.

** Relative intensity $I/I_1$ lower than 6% are omitted.



a. **Unsupported Cobalt**
( Reduced in $H_2$ at 350 °C )

b. **Unsupported CoB-250**
( Reduced in $H_2$ at 250 °C )

c. **Unsupported CoB-250**
( Reduced in $H_2$ at 350 °C )

d. **Unsupported CoB/Na-250**
( Reduced in $H_2$ at 350 °C )

**Figure 6.** **X-Ray diffraction patterns for unsupported Co (a), CoB-250 (b, c), and CoB/Na-250 (d) catalysts.**