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Borided Metal Catalysts in Methanation of Carbon Monoxide

I. Initial Activity and Conversion-Temperature Behavior of Unsupported Catalysts

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Unsupported metal borides were prepared by reduction at 273–300 K of Ni^{II} and Co^{II} by sodium borohydride in aqueous and ethanolic solvents in the presence and absence of noble metal promoters. These materials were further activated by H_2 reduction at 675–725 K which resulted generally in borided metals having higher metal : boron ratios than commonly encountered in the chemically reduced materials. Chemical, physical, and catalytic properties were determined by chemical analysis, BET surface area measurements, H_2 adsorption measurements, and reactor studies of methanation activity/selectivity properties at 1 atm and 475–675 K. Though generally slightly less active and selective than commercial Raney nickel, borided nickel catalysts are nevertheless very effective methanation catalysts compared to pure nickel. Borided cobalt is apparently as active as Raney nickel on a site basis but less selective for CH_4 production. Ruthenium- and rhodium-promoted nickel borides are slightly more active and about as selective for methane production as unsupported nickel.

INTRODUCTION

During recent years many different catalysts have been investigated for methanation of carbon monoxide (*1*). Alumina-supported nickel and Raney nickel catalysts are currently the leading commercial candidates because of their high activity and selectivity for methane production. However, because conventional nickel methanation catalysts suffer rapid, substantial loss of activity in the presence of sulfur poisons at ppm levels, there is considerable interest and motivation in the development of more sulfur-tolerant catalysts. Metal borides, finely divided catalysts resulting from reduction of Ni and Co salts by sodium borohydride, are of interest because of their potentially high activity and sulfur tolerance for methanation (*2*).

Borohydride reduced catalysts were first investigated by Schlesinger *et al.* (*3*). Subsequent workers explored the realm of reaction conditions for preparation of metal borides (*4*), their stoichiometries (*5–8*), and their applications to various reaction systems (*4*). The resultant materials known as either metal boron hydrides or metal borides have proven to be catalytically active for many reactions, but are especially well suited to low-temperature, liquid-phase hydrogenation reactions (*4*) for which application they are competitive with Raney nickel (*9, 10*). Upon heating above 400–500 K in H_2, metal boron hydrides lose hydrogen and boron to form a mixture of metal borides and metal (*4*) which will be referred to hereafter as borided metals. The activity of borided metals in high-temperature, gas-phase hydrogenation reactions has received relatively little investigation (*4*).

The use of borided nickel supported on silica gel in hydrogenation of CO was first reported by Kurita and Tsutsumi (*11*). Recently, Russell (*12*) obtained conversion-temperature data for supported borided nickel, while Mitchell and co-workers (*8*) reported conversion-temperature characteristics of unsupported Rh-promoted Ni and Co borides for methanation. Finally, Hammer and Hakim (*13*) worked with an unsupported metal boride composite:

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$Ni_2B/Ni(OH)_2/Mg(OH)_2$, which proved to be an effective methanation catalyst.

None of these previous studies, however, were performed under well-defined, chemical-reaction-controlled conditions using well-characterized catalysts. Thus specific activities, based on metal surface areas, could not be determined nor quantitatively compared with those for Ni or Raney Ni. Moreover, conversion-temperature data for different catalysts were obtained at different space velocities, rendering valid comparison of their high-temperature, high-conversion performance questionable.

The purpose of this investigation was to measure specific, intrinsic activities and conversion-temperature characteristics of well-characterized borided nickel and cobalt catalysts and to compare their performance with those of Ni and Raney Ni in methanation of CO.

EXPERIMENTAL METHODS

Materials

Eight unsupported metal boride catalysts were prepared for this study. $Ni(NO_3)_2 \cdot 6H_2O$ and $Co(NO_3)_2 \cdot 6H_2O$, which had been partially dried to reduce water of hydration to approximately 1.5 moles/mole of metal, were used in all preparations. Unless otherwise noted, all metal reductions were conducted in absolute ethanol with ice bath cooling using 4 moles of sodium borohydride per mole of metal salt. Evolution of NH_3 was detected by its characteristic scent during this step (*14*). Most of the resultant precipitates were too fine to be adequately washed by filtration; thus, impurities were removed by absolute methanol using settling and decanting over several weeks. Drying was conducted slowly to allow passivation of metal particles.

Ni-B-102 was prepared by adding sodium borohydride slurried in ethanol very slowly to the metal salt dissolved in ethanol. When all bubbling ceased, the precipitate was washed with methanol. The use of the methanol rather than ethanol wash was found to be necessary in order to remove all impurities. Co-B-101 and Ni-Co-B-101 were prepared similarly, with equimolar amounts of Ni^{II} and Co^{II} in the case of the latter sample. In preparation of Ni-B-104 the Ni^{II} reduction was conducted in a glove box containing N_2 using deaerated ethanol as the reaction medium. However, after drying, it was exposed to air. An exception to the above-described technique occurred in preparation of Ni-B-101, conducted in aqueous phase according to Ref. (*15*), Method A, using $Ni(C_2H_3O_2)_2$ as the metal precursor.

Two Ni boride catalysts were promoted with 5 mole% (with respect to the total metal) Ru and one with 5% Rh. Ni-Ru-B-101 was prepared by reducing a solution of $Ni(NO_3)_2$ and 5 mole% hydrated $RuCl_3$ dissolved in ethanol with sodium borohydride slurried in ethanol. Borohydride addition to dissolved Ru ion prevents formation of potentially explosive compounds (*16, 17*). Ni-Rh-B-103 was prepared in analogous fashion using 5 mole% hydrated $RhCl_3$. Finally, Ni-Ru-B-102 followed the same recipe as Ni-Ru-B-101 except that the liquid-phase reduction was carried out in a N_2 atmosphere using deaerated ethanol.

The Raney Ni used in this study was ground from Alfa Product's activated (previously reduced and passivated) Raney Ni pellets. The unsupported Ni was a high-purity powder, designated INCO Type 287, produced by International Nickel Company. Absence of impurities on the surface of this powder was confirmed by ESCA and reported in an earlier paper (*18*).

Apparatus and Procedure

The catalysts were characterized by BET surface area and H_2 uptake measurements in all cases before and in selected cases after activity tests. Total surface areas were measured by argon BET assuming an argon surface area of 0.169 nm^2/atom. Metal surface areas were determined by means of H_2

chemisorption at 295 K (except for ruthenium-promoted catalysts for which data were collected at 398 K) using a conventional Pyrex-glass constant-volume system capable of 10^{-7} kPa evacuated by means of oil diffusion and mechanical pumps isolated from the adsorption system by means of a liquid-nitrogen-cooled trap. System pressure was monitored with Varian thermocouple and ionization gauges, while adsorption pressures were measured with a Texas Instruments quartz spiral Bourdon gauge with a 0–500 Torr (1 Torr = 133.3 N m^{-2}) range. H_2 adsorption uptakes were determined as a function of pressure, and the isotherm was extrapolated to obtain the adsorption at zero pressure. A one-to-one correspondence between adsorbed H and surface metal atoms (*18–23*) was assumed, and site densities were calculated based on the three lowest index planes of each metal (6.77×10^{-2} nm/atom in the case of Ni).

Selected catalysts were analyzed by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (ESCA), optical emission spectroscopy (OES), and wet chemical techniques. Analyses were performed on borohydride reduced samples (0.5–1.0 g) which had been either air-dried only or air-dried and reduced further in flowing H_2 at 675 K.

During surface area measurements and activity tests catalyst samples were housed in a sealed Pyrex flow-through reactor (*24*) which could be isolated or evacuated by appropriate manipulation of attached stopcocks; the sample was held in place by plugs of glass wool. Pretreatment for surface area measurements included reduction in flowing H_2 (minimum space velocity of 2000 h^{-1}) at 675 K for at least 2 hr, followed by evacuation to 1.3×10^{-6} kPa while at 675 K. The rate of temperature rise during the initial reduction was less than 3 K/min with at least a 1-hr hold at 475 K. H_2 purity was ensured by passing it through an Air Products and Chemicals deoxygenation catalyst and then drying it by means of a molecular sieve trap at 190 K.

Reduced catalysts were activity tested immediately following the initial surface area measurements. These tests included specific activity and conversion-temperature measurements utilizing a previously described (*24*) laboratory reactor system. Gases were analyzed by means of a Hewlett–Packard 5834 gas chromatograph using a thermal conductivity detector.

Specific activity measurements were conducted at high space velocities (about 100,000 h^{-1}) and low conversions using a dilute reactant mixture (1% CO, 4% H_2, 95% N_2) to minimize influences of pore diffusion and heat and mass transfer. Samples were pretreated by reduction in pure H_2 at 675 K for 2 hr. Because low product concentrations resulting from the differential test were difficult to measure accurately, five or six chromatographic samples of the product gas were obtained at each temperature of interest (500, 525, and 550 K).

Conversion-temperature characteristics were measured at a space velocity of approximately 30,000 h^{-1}, using the same reactant mixture. The reactor temperature was increased slowly in 20 K increments from 475 to 675 K allowing time at each increment for chromatographic sampling.

RESULTS

Results of Catalyst Characterization

Chemical analyses of borohydride-reduced, air-dried samples of Ni-B-101 and Ni-B-102 revealed significant differences resulting from their preparations in aqueous and ethanolic solution, respectively. Ni-B-101 had a Ni/B ratio of 2/1 and a single-point BET area of 19.3 m^2/g. It also contained approximately 0.5% sodium. Ni-B-102 had an unexpectedly low Ni/B ratio of approximately 1/1.9, indicating a stoichiometry of NiB_2, and an unusually large single-point BET area of 334 m^2/g. These results indicate a significant chemical difference as well as a much higher dispersion for catalysts produced by M^{II}-borohydride reduction in alcohol compared to water.

Five representative borided metal samples were also analyzed by XRD, OES, and wet chemical techniques after reduction in flowing H_2 at 675 K. These results are summarized in Table 1. The analyses for metals and boron account for about 90% by weight of all elements in each of the five samples. The portion not accounted for in these samples is logically oxygen since the samples were passivated in air following the high-temperature reduction and since pH measurements and chemical analysis indicate only traces of water-soluble alkaline impurities from the initial chemical reduction to be present within the samples.

Based on boron and nickel assays (Table 1) the stoichiometry of Ni-B-102 corresponds to Ni_3B, a composition characteristic of a typical stoichiometric Ni boride. The value of $M/B = 5$ for Ni-Ru-B-101 indicates that a near-stoichiometric Ni boride was formed. The other three samples, however, exhibited much higher metal : boron ratios consistent with stoichiometries of $Ni_{14}B$, $Co_{15}B$, and $(Ni\text{-}Co)_{20}B$ for Ni-B-104, Co-B-101, and Ni-Co-B-101, respectively. The fact that the Ni-B-102 composition changed from NiB_2 to Ni_3B after H_2 reduction at 675 K indicates that the high-temperature reduction caused a significant boron loss.

BET (total) surface area and H_2 chemisorption uptake data are summarized in Tables 2 and 3 for all high-temperature-reduced catalysts investigated in this study. Based on these measurements the borided metals have generally lower, but in most cases not very much lower, total surface areas and H_2 adsorption uptakes relative to Raney Ni. Another important result illustrated in Table 2 is that all the Ni-containing catalysts prepared in ethanol have greater BET surface areas than Ni-B-101 prepared in aqueous solution. This shows again that chemical reduction in alcohol produces a more highly dispersed catalyst. It should be noted that Ni-Ru-B-101 and -102 prepared in almost identical fashion display nearly identical adsorption properties.

From a comparison of the BET and metal surface areas for each catalyst in Table 2 it is possible to estimate the fraction of the surface composed of reduced metal atoms. Values of percentage metal area (relative to BET area) suggest that the surface of most borided metal catalysts contains about 30% metal atoms, with the exception of Ni-B-101 prepared in aqueous solution (and containing a 0.5% Na impurity) and Ni-B-104 prepared in the absence of O_2. Apparently in these later two catalysts, the surface is predominantly elemental Ni. In Raney Ni,

TABLE 1

Analytical Results for Five Metal Boride Catalysts[a]

Analytical method	Ni-B-102	Ni-B-104	Co-B-101	Ni-Co-B-101	Ni-Ru-B-101
X-Ray diffraction	Ni metal	Ni metal	Cobalt metal	Ni metal; no Co detected	Ni metal; no Ru detected
Metal assay[b] by 0.1 *M* titration with EDTA	78.8% Ni	89.5% Ni	88.3% Co	42.8% Ni, 42.9% Co	75.0% Ni
Metal assay[b] by OES[c,d]					1.6% Ru
Boron assay[b] by OES	4.5%	1.1% B	1.1% B	0.8% B	3.1% B
Atom% metal/atom% boron	3.2	13.6	14.8	19.7	4.6
Approximate pH when placed on moist pH Hydrion paper	7.5[e]	10	7.5	9	7.5

[a] Data obtained by Dr. L. Guibault and co-workers of the Ventron Corporation.

[b] Percentage by weight.

[c] OES optical emission spectroscopy.

[d] All samples were ferromagnetic.

[e] Infrared spectrographic analysis indicated only a trace of OH on Ni-B-102.

TABLE 2

Argon BET and Hydrogen Adsorption Data for Unsupported Metal Boride and Ni Catalysts Reduced in H_2 at High Temperatures

Sample	BET area[a] (m^2 g^{-1})	H_2 adsorption[b] (μmoles g^{-1})	Metal area[c] (m^2 g^{-1})	Percentage metal area[d]
Raney Ni[e]	64.0	267	21.9	34
INCO Ni	0.4	5.0	0.41	100
Ni-B-101	9.8	161	13.2	134
Ni-B-102[e]	24.6	103	8.5	34
Ni-B-104[e]	13.4	154	12.6	94
Co-B-101	27.4	14.7	1.2	4
Ni-Co-B-101	29.4	126	10.4	35
Ni-Ru-B-101	56.4	188	15.4	27
Ni-Ru-B-102	47.7	182	14.9	31
Ni-Ru-B-103	57.8	185	15.1	26

[a] Argon adsorption at 78 K after reduction at 675 or 725 K assuming 0.169 nm^2/argon atom.

[b] Total H_2 adsorption at 295 K after reduction at 675 or 725 K and evacuation at 675 K.

[c] Calculated assuming an area of 0.0677 nm^2/Ni atom.

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

[e] Reduced at 725 K, all others reduced at 675 K.

the surface likewise consists of about 34% metal.

Additional data regarding surface composition and chemistry were obtained from ESCA measurements (*25*). The ESCA spectrum for a representative borided Ni prepared and reduced at 675 K in the absence of air indicated the presence of both B_2O_3 and elemental B in Ni at the surface in proportions of roughly 2 : 1. If, however, the sample was exposed to air and reduced *in situ* at 675 K, only surface B_2O_3 was observed. Two borided catalysts from this study (Ni-B-102 and -104) previously reduced in flowing H_2 at 675 K and passivated in air were ESCA analyzed before and after *in situ* rereduction in flowing H_2 at 675 K. A sample spectrum is shown in Fig. 1 and results are summarized in Table 4. Two significant findings are noticeable. First, surface boron in both passivated and *in situ* reduced samples exists principally as boron oxide. In other words, the surface boron oxide cannot be reduced even at 675 K in flowing H_2! Second, the borided Ni precipitated under an inert gas blanket (Ni-B-104), subsequently reduced at 675 K and passivated, shows evidence of less surface oxygen after passivation. Moreover, according to the ESCA results a larger fraction of the surface of Ni-B-104 consisted of Ni metal compared to Ni-B-102 after *in situ* H_2 reduction, consistent with the surface area measurements in Table 2.

TABLE 3

The Effect of Hydrogen Reduction Temperature on BET Surface Area and Hydrogen Chemisorption Uptake for Two Unsupported Boride Catalysts

Sample	Reduction temperature (K)	BET surface (m^2 g^{-1})	H_2 uptake (μmoles H_2 g^{-1})
Ni-B-101	675	9.8	161
	725	7.5	89
Ni-Rh-B-103	675	58	194
	725	3.6	95

Thermal degradation of unsupported catalysts can be a serious problem. It was observed that some of the borided metal catalysts exhibited significant losses of total surface area and H_2 adsorption uptake when reduced at 725 K. For example, data in Table 3 for Ni-B-101 and Ni-Rh-B-103 show that surface areas are significantly higher for samples reduced at 675 K com-

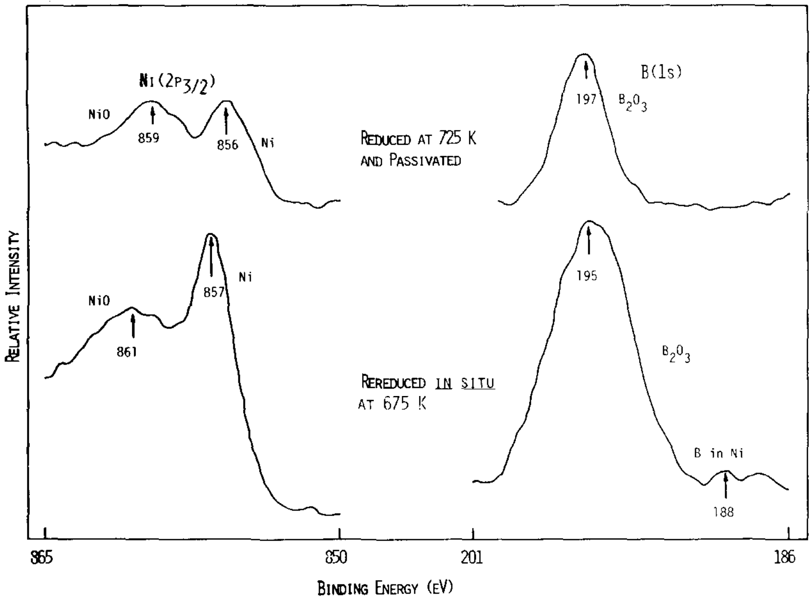

FIG. 1. ESCA spectra of Ni-B-102 after high-temperature reduction and passivation in air followed by rereduction *in situ* at 675 K.

pared to 725 K. In the case of Ni-Rh-B-103, the BET surface area was reduced 20-fold whereas H_2 uptake was lowered by only a factor of 2. Therefore, heat treatments in excess of 675 K were avoided in subsequent experiments.

Intrinsic Activity/Selectivity Data

Initial specific rates expressed as turnover numbers at 525 K, product yields, and activation energies are listed in Table 5 for borided metals, Raney Ni, and INCO Type 287 Ni powder. Turnover numbers are defined as rates of CH_4 production or CO conversion in molecules per catalytic site (measured by H_2 chemisorption) per second; yield is defined as the fraction of converted CO appearing as a specified

TABLE 4

Summary of ESCA Results for Two Metal Boride Catalysts[a]

Sequence with respect to *in situ* reduction at 675 K	Surface constituent analyzed	Results of analysis	
		Ni-B-102[b]	Ni-B-104[b]
Before	Nickel	NiO and elemental Ni in approximately equal amounts	Mostly elemental Ni, some NiO
Before	Boron	Boron oxide	Boron oxide
After	Nickel	Mostly elemental Ni, some NiO	All elemental Ni
After	Boron	Boron oxide	Mostly boron oxide with 5–10% reduced boron

[a] Data obtained by Schreifels *et al.* at the University of South Florida (see Ref. (*25*)).

[b] Samples previously reduced in H_2 at 675 K and passivated in air prior to ESCA analysis.

TABLE 5

Initial Specific Rates of Carbon Monoxide Hydrogenation and Methane Formation and Product Yields for Nickel and Metal Boride Catalysts

Catalyst	Turnover number[a] at 525 K × 10^3 (s^{-1})		Percentage Yield[b] at 525 K			E_{act}[c] (kJ/mole)	
	CO	CH_4	CH_4	C_{2+}	CO_2	CO	CH_4
Raney Ni	29[d]	25[d]	85	5	10	117	134
INCO Ni	2.8	2.4	84	11	5	117	113
Ni-B-101	0.03	0.002	7	91	2	71	113
Ni-B-102	0.9	0.6	64	29	7	71	126
Ni-B-104	1.8	1.5	86	4	10	79	121
Co-B-101	38	27	70	24	6	63	92
Ni-Co-B-101	9.7	7.0	73	21	6	84	88
Ni-Ru-B-101	4.2	3.4	81	18	1	84	92
Ni-Ru-B-102	4.2	3.4	80	20	0	79	100
Ni-Rh-B-103	2.7	2.6	98	0	2	75	88

[a] Rate of methane production of carbon monoxide conversion in molecules per catalytic site per second in 1% CO, 4% H_2, 95% N_2 at 130 kPa and at conversions generally less than 10%.

[b] Percentage of converted CO appearing as a given product.

[c] Determined over the temperature range of 500–525 K.

[d] Extrapolated from 475 and 500 K.

product. Activation energies were determined from an Arrhenius plot of turnover numbers at 500 and 525 K. Of the Ni catalysts, Raney Ni is clearly the most active, exceeding the activity of Ni by a factor of 10. The Ni-B-101, prepared in aqueous solution and containing 0.5% Na, is 3 orders of magnitude less active than Ni, while Ni-B-102 and 104, prepared in ethanolic solution, are factors of 4 and 2 less active than Ni. The Ru-promoted catalysts are 50% more active than Ni while Ni-Rh-B has the same activity as Ni. Of particular interest is the surprisingly high CH_4 turnover number for Co-B-101, which is the same as for Raney Ni within experimental accuracy (estimated to be ± 25%). Apparently, Ni-Co-B-101 has a specific activity intermediate between that of Co and Ni borides.

In terms of product yields from Table 5, Raney Ni and Ni-B-104 (the boron-deficient catalyst with a surface composed predominantly of Ni metal) exhibit behavior very similar to that of pure Ni. Ni-B-102, the borided catalyst having an overall stoichiometry of Ni_3B, produces less CH_4 and a threefold higher yield of C_{2+} hydrocarbons than Ni. The Na-promoted Ni-B-101, however, behaves as a promoted Fischer–Tropsch catalyst producing primarily C_{2+} hydrocarbons. Cobalt-containing borides produce somewhat less CH_4 whereas Ni-Ru-B catalysts less (almost no) CO_2 and both catalyst types twofold greater yield of C_{2+} hydrocarbons than Ni, behavior consistent with Co and Ru catalysts. The Rh-promoted Ni boride produces primarily CH_4, a selectivity behavior characteristic of Pt and Rh.

Conversion-Temperature Data

Conversion of CO and production of CH_4 and CO_2 are plotted against temperature in Fig. 2 for Raney Ni and Ni-Ru-B-102. CH_4 or CO_2 production is defined as the fraction

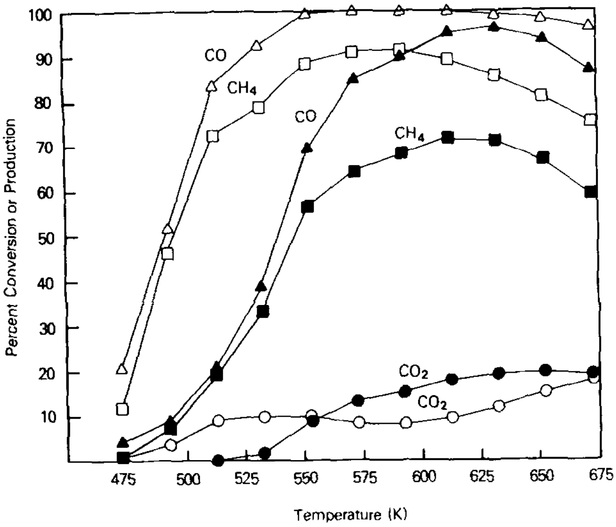

FIG. 2. Conversion vs temperature characteristics at 130 kPa comparing Raney nickel (open symbols) with nickel ruthenium boride 102 (closed symbols) at a space velocity of 30,000 h^{-1}; (△, ▲) CO conversion, (□, ■) CH$_4$ production (○, ●) CO$_2$ production.

of reactant CO converted to either CH$_4$ or CO$_2$ respectively. Conversion of CO for Raney Ni rises sharply with temperature above 475 K and is essentially complete above 555 K. CH$_4$ production passes through a maximum of 90% at about 590 K whereas CO$_2$ production is generally low (10% or less). The Ni-Ru-B-102 typifies unsupported borided metal catalysts in that any given percentage conversion of CO occurs at a higher temperature than for Raney Ni and its percentage production of CH$_4$ is less while its percentage production of CO$_2$ is generally higher.

Conversion-temperature data for all catalysts investigated in this study are summarized in Table 6. This table lists temperatures for 50 and 95% CO conversion, product yields, and reaction rates on both a catalyst mass and a catalyst volume basis at 600 K, obtained at a space velocity of about 30,000 h^{-1} (±15%) unless otherwise noted. In terms of conversion-temperature and selectivity characteristics, Raney Ni is superior to the other catalysts, obtaining higher CO conversions at lower temperatures and a higher CH$_4$ yield at 600 K. Since the catalysts were tested at slightly different space velocities near 30,000 h^{-1}, rates of CH$_4$ production are approximate. Nevertheless, the data show CH$_4$ production rates on a volume basis for Ni-Ru-B-101 and -102 are about the same as for Raney Ni, while rates per volume for Ni-B-104 and Ni-Co-B-101 are only 30% less. Some of the rates based on mass for the borided metals are larger than for Raney Ni because these catalysts have significantly lower densities.

Ni-B-101 (containing 0.5% Na) was the least active catalyst studied, demonstrating the poorest conversion-temperature methanation characteristics and lowest rates of CH$_4$ production. Nevertheless, its negligible CO$_2$ yield and high yield of C$_{2+}$ hydrocarbons with relatively high conversions of CO at temperatures above 600 K indicate a behavior typical of a Fischer–Tropsch catalyst.

DISCUSSION

Chemical Properties of Borided Metals

Previous literature (*4*) has established that metal boron hydrides (produced by low-temperature borohydride reduction of metal salts) decompose when heated at high

TABLE 6

Results of Conversion-Temperature Measurements[a] at 130 kPa and a Space Velocity of 30,000 h^{-1}

Catalyst	Temp. (K) for CO conversion of:		Temp. (K) of maximum CH_4 production	At 600 K					
	50%	95%		Percentage CO conversion	Percentage yield[b]			Rate of CH_4 production × 10^7	
					CH_4	CO_2	C_{2+}	moles g^{-1} sec^{-1}	moles cm^{-3} sec^{-1}
Raney Ni	492	540	590	100	91	9	0	23	36
INCO Ni[c]	579	605	610	93	71	23	6	5	7
Ni-B-101[d]	633	660	670	26	25	0	75	0.5	0.8
Ni-B-102	658(45%)[e]		640	40	81	7	12	5	8
Ni-B-104	527	582	610	98	77	20	3	14	25
Co-B-101	552	633(73%)[e]	630	68	58	28	14	17	15
Ni-Co-B-101	516	574	630	98	70	23	7	26	24
Ni-Ru-B-101	528	633	610	91	77	14	9	50	40
Ni-Ru-B-102	540	612	610	92	76	18	6	51	34
Ni-Rh-B-103	558	634(86%)[e]	630	77	81	15	4	31	20

[a] In a reaction mixture containing 1% CO, 4% H_2, 95% N_2.

[b] Yield is the fraction of converted CO appearing as specified product.

[c] Space velocity 9100 h^{-1}.

[d] Space velocity 4200 h^{-1}.

[e] 50 or 95% conversion was not obtained; number in parentheses is the maximum CO conversion.

temperatures, liberating H_2 and possibly boron. Chemical analyses performed as part of this study document that boron is indeed lost when Ni and Co boron hydrides are heated to 675 K in H_2. Generally, the resulting materials have stoichiometries of M_xB, where $x = 14–20$, although values as low as 3 and 5 were observed in preparations of Ni-B-102 and Ni-B-Ru-101. Apparently the chemical reduction in air in the case of Ni-B-102 or the presence of a noble metal promoter in the Ni-B-Ru catalysts served to enhance the thermal stability of the materials. Ni-B-102 with a Ni/B ratio of 3 could be a stoichiometric Ni_3B or a mixture of Ni_2B and nickel metal (*4*). The boron-deficient materials could be a mixture of stoichiometric borides such as M_2B and M_3B and reduced metal (*4*).

Despite the less than stoichiometric boron content in the bulk, the percentage metal area data in Table 2 establish that surfaces of borided metals generally consist one-third of metal atoms and two-thirds of boron and oxygen atoms. Moreover, in terms of percentage metal present at the surface, borided nickels are very similar to Raney Ni, the surface of which has been reported to contain 20–50% Ni (*26–28*). Thus our data showing 30% Ni metal at the surface of Raney Ni are in good quantitative agreement with previous literature. The fact that 100% metal was observed at the surface of the INCO Ni confirms the high purity of this material. The percentage metal area for Ni-B-104 was unexpectedly high, but it nevertheless confirmed qualitatively by ESCA data in Table 4 showing the surface to be rich in Ni metal.

To our knowledge, these chemisorption and ESCA data (Tables 2 and 4) provide the first quantitative estimates of surface composition for borided metal catalysts. This information is useful in understanding the activity/selectivity properties of the catalysts discussed below. For example, Ni-B-102 having a surface composition of approximately $NiBO_2$ should have different activity/selectivity properties than Ni-B-104 with surface properties more characteristic of pure Ni. Indeed, this is confirmed by the data in Table 5.

In addition to surface composition, the ESCA data in Table 4 and Fig. 1 plus additional data from Schreifels *et al.* (*25*) provide important information regarding the chemical states of surface atoms. Apparently borided nickel catalysts prepared in the absence of air and reduced in H_2 at high temperature contain principally Ni metal atoms, boron oxide, and some reduced boron in combination with Ni at the surface. Once exposed to air, however, a stable surface boron oxide is formed which cannot be reduced by H_2 at 673 K, even though the surface Ni is quantitatively reduced again to the metal. The stability of surface boron oxide is not altogether unexpected as Cusumano *et al.* (*29*) have shown formation of boron oxide to be thermodynamically favorable. However, the presence of boron oxide at the surface of the reduced metal boride catalyst has at least two important implications: (i) activity/selectivity properties may be influenced differently than if reduced boron were present at the surface and (ii) leaching of boron by formation of H_3BO_3 may be facilitated in the presence of water.

Does the surface oxidation state of boron make a difference catalytically? In some reactions it may. Brown and Ahuja (*30*) reported that avoiding exposure of borohydride-reduced Ni to air during preparation yields a more active hydrogenation catalyst. Recently Swartz and co-workers (*31*) obtained data suggesting that the surface boron/boron oxide ratio significantly influences selectivity in the ethanolic-phase hydrogenation of ethylene nitrile to ethane nitrile and 3-ethoxy propionitrile.

However, recent data obtained in this laboratory for supported metal borides (*32*) reveal that neither activity nor selectivity in CO methanation is affected by an exposure to air following chemical reduction in the absence of air. Moreover, since oxygen is a likely surface intermediate in methanation and present at the surface in H_2O and CO_2, it is unlikely that boron would remain in the reduced state during prolonged reaction. Thus precautions to exclude air after chemical reduction are probably not necessary in the preparation of methanation catalysts. Chemical reduction in an inert or reducing environment may be advisable (*33*) depending upon the catalyst properties (i.e., boron content) desired. However, addition of noble metal promoters may obviate the need for excluding air during catalyst preparation since they are known to enhance reduction of supported Ni to the metal (*34*). Indeed, the chemical, physical, and activity/selectivity properties of Ru-promoted Ni borides prepared in the presence (Ni-B-Ru-101) and absence (Ni-B-Ru-102) of air are identical within experimental error (see Tables 2 and 5). Moreover, evidence to be presented in a later paper (*32*) indicates that alumina-supported Ni borides are stable with respect to boron loss when reduced in H_2 at high temperature regardless of whether they are exposed to air either during or after chemical reduction.

Physical Properties of Borided Metals

Wade *et al.* (*4*) reported that BET surface areas for typical Ni and Co boron hydrides prepared at low temperatures range between 5 and 60 m^2/g. The metal boron hydrides prepared in this study by chemical reduction in ethanolic solution were of extremely high surface area (200–400 m^2/g) as evidenced by (i) extremely long settling times in solution (several hours to several days) and (ii) very large BET areas, e.g., 334 m^2/g for Ni-B-102. Compared to catalysts prepared in ethanolic solution, the BET area for Ni-B-101 prepared in aqueous solution was 2–5 times lower. Moreover, during aqueous-phase washing of Ni-B-101, catalyst particles settled in a matter of hours, compared with several days for catalysts precipitated and washed with alcohols. This indicates metal borides prepared in water have larger particles than those prepared in ethanol. Other workers have also observed better reaction rates and dispersions for catalysts prepared in ethanol, typically describing them as colloidal as opposed to granular for water-prepared catalysts (*30*, *35–37*).

We propose that the rate of chemical reduction controls particle size: the slower the rate, the smaller the particles formed. Since the rate of reduction depends positively on reactant concentrations, the solubility of reactants in the solvent becomes an important factor in controlling the rate. Accordingly, ethanol is expected to produce a more highly dispersed catalyst than water because sodium borohydride is less soluble in ethanol (4 g/100 g solvent at 293 K) than in water (approx 33 g/100 g solvent at 293 K).

Upon reduction in H_2 at high temperatures, the surface areas of metal borides were substantially reduced, e.g., more than a factor of 10 for Ni-B-102 to 25 m^2/g. Nevertheless, the BET or total surface areas reported for borided metals in Table 2 after high-temperature reduction ranging from 10 to 58 m^2/g compare very favorably with those previously reported for catalysts prepared at low temperature. The BET surface area obtained for Raney Ni falls well between previously reported values of 50 and 120 m^2/g (*5*, *38–40*). Thus, it appears that the Ni boron hydrides produced by chemical reduction in this study have significantly larger surface areas than Raney Ni. After high-temperature reduction, the borided metals prepared in this study are lower but still comparable with Raney Ni. Raney Ni and borided metals also compare very well in terms of metal surface area (Table 2).

Mitchell *et al* (*8*) reported that Rh-promoted Ni and Co boron hydrides were thermally stable, i.e., showed no loss of hydrogenation activity at temperatures up to 773 K. However, the data in Table 3 showing that a very similar Rh-promoted Ni boron hydride loses more than a factor of 20 total surface area and a factor of 2 metal surface area when heated from 675 to

725 K suggest that this catalyst is not thermally stable above 675 K and apparently no more stable than an unpromoted Ni boride above this temperature. Nevertheless, data to be published in a companion paper (*32*) reveal that very high metal boride surface areas can be maintained up to 725 K if the catalysts are supported on Al_2O_3.

Activity and Selectivity Properties of Borided Metals

Among the most interesting results obtained in this study are the significantly higher specific rates of CO hydrogenation and CH_4 formation determined for Raney Ni and Co-B-101 relative to nickel (Table 5). Apparently the Raney Ni tested in this study is more active than that studied by Dalla Betta *et al* (*20*) by a factor of four, if turnover number data are corrected to the same conditions using the kinetic expression of Vannice (*41*) for Ni/Al_2O_3 and the activation energy determined by Dalla Betta *et al.* of 130 kJ/mole (or 134 kJ/mole from this study). Differences in catalyst composition and pretreatment could be responsible for this. Dalla Betta and coworkers' Raney Ni was a laboratory specimen from which only 60% aluminum was leached while the Raney Ni of this study was a commercial sample (Alfa Products No. 88001) which is reported as $Ni/Al/Al_2O_3$ having 82% Ni (*42*).

The higher specific activity of Raney Ni relative to pure Ni in this study suggests that aluminum metal (or Al_2O_3 at the surface) is a chemical promoter for methanation of CO, presumably as a result of an electronic interaction in the Ni-Al alloy. Addition of boron to Ni and the presence of B_2O_3 at the surface do not appear to have the same promotional effect, as turnover numbers for borided Ni are slightly less than for pure Ni (Table 5). Since Co catalysts span a wide range of activities and can be either more or less active than Ni catalysts (*43–45*), the high activity of Co-B-101 relative to Ni can mean one of two things: Either boron is an effective promoter for Co or Co itself is simply more active than Ni. Thus, further research is needed to resolve this question.

Since unsupported Ni was a standard for comparison in this study, it should be emphasized that our CH_4 turnover numbers and activation energy of 113 kJ/mole for the INCO catalyst are in very good agreement with turnover numbers and activation energies of 103–130 kJ/mole reported by other workers (*41*, *46*, *47*) for unsupported Ni. Activation energy data for CH_4 production over Ni borides (Table 5) also fall comfortably within the range of 105–138 kJ/mole reported (*41*, *46*, *47*) for unsupported Ni, suggesting that a similar mechanism operates for borided Ni. However, methanation activation energies for borided Co, Ni-Co, and noble-metal-promoted Ni are significantly lower than corresponding values for similar nonboron-containing metallic or bimetallic catalysts (*43–45*).

In addition to having the highest specific activity for CH_4 production under chemical-reaction-controlled conditions, Raney Ni proved to be the most active and selective for methanation under any condition of comparison, obtaining maximum CH_4 production and high CO conversion at lower temperatures than any borided metal. Also, it had the highest CH_4 yield and, except for Ni-B-101, the lowest CO_2 production. Nevertheless, the rate data in Table 6 show that under specified conditions (600 K, 130 kPa, and 30,000 h^{-1}) rates of CH_4 production for promoted metal boride catalysts are very nearly the same for Raney Ni on a catalyst volume basis.

Comparison of conversion-temperature data for unsupported borided metals with available literature data is difficult because of significant differences in experimental conditions. Mitchell *et al.* (*8*) reported their $(Ni_2B)_{10}RhH_{15}$ catalyst to achieve a 60% conversion of CO to CH_4 at 760 K and an estimated space velocity of about 8000 h^{-1}. In comparison, the Rh-promoted Ni boride in this study achieved 86% conversion of

CO to CH_4 at 634 K and a space velocity of 30,000 h^{-1}; in other words the catalyst in this study produced methane at a substantially higher rate and lower temperature. The significantly better performance of our catalyst suggests their catalyst was either contaminated with inorganic impurities from the initial metal precipitation step or suffered loss of activity due to carbon deposition or sintering at higher temperatures. Despite its favorable performance in methanation, the Rh-promoted Ni boride is clearly less active than Raney Ni, a conclusion contrary to a previous and somewhat preliminary report of Mitchell *et al.* (*4*). Other workers have reported maximum CH_4 production temperatures for silica-supported Ni borides of 550 K (*11*) and 580–620 K (*12*) and for Co borides prepared on silica gel of 610 K (*11*) and 590 K (*12*), respectively. These values for supported materials are only slightly lower than temperatures in Table 6 for the corresponding unsupported materials. The slightly more efficient performance of the supported materials could be due to metal–support interactions (*32*) and differences in experimental conditions, the latter of which probably dominate.

CONCLUSIONS

1. Reduction of metal salts dissolved in absolute ethanol by sodium borohydride produces more highly dispersed metal boron hydride catalysts than similar reductions in aqueous solution. The attainment of higher catalyst dispersions in ethanol is believed to relate to the lower solubility of $NaBH_4$ and hence lower rates of reaction in this nonpolar solvent compared to water.

2. High-temperature reduction of metal boron hydrides in H_2 atmosphere generally removes oxygen, a portion of bulk and surface boron, and presumably bound hydrogen. Thus it produces boron-deficient catalysts (borided metals) with metal: boron ratios generally higher and in some cases considerably higher than the commonly reported ratios of 2 or 3. Exposure to air during chemical reduction and use of noble metal promoters appear to prevent loss of boron.

3. The surface of a typical borided Ni or promoted Ni consists about one-third of metal atoms and two-thirds of boron or boron oxide. Once O_2 is allowed to contact surface boron, either during preparation or during passivation, it forms boron oxide which cannot be reduced to zero-valent boron even in flowing H_2 at 675 K.

4. Although borided metals are active methanation catalysts, they are generally not as active or selective for production of CH_4 as Raney Ni. Nevertheless, noble-metal-promoted Ni borides are almost as active at 600 K as Raney Ni on a mass or volume basis. Borided Ni and Rh- or Ru-promoted Ni borides are about as active as Ni on a turnover number basis; however, borided Co is as active as Raney Ni and a factor of 10 more active than Ni when compared on a site basis. Using different preparations and promoters it is possible to substantially modify product selectivity of borided metals over a wide range, i.e., from 90% C_{2+} hydrocarbons to 98% CH_4 and to obtain a range of activities extending over three orders of magnitude.

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