Hydrogenation Activity and Selectivity of Cobalt Boride and Cobalt Nickel Binary Boride Catalysts

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Co–B catalyst has higher selectivity than Ni–B catalyst for the formation of α,β-unsaturated alcohols from α,β-unsaturated aldehydes and lower selectivity for the formation of olefins from acetylenes. The differences between the two catalysts can be ascribed to the differences in the adsorption strength of reactants on Co and Ni metals. The hydrogenation activities of the Co–Ni–B catalysts vary through a maximum, but the selectivities vary monotonously with nickel content. These features are explained in terms of the surface composition measured by XPS and of the surface area of the catalysts. The enrichment of nickel on the surface and the increase of the surface area are observed for the Co–Ni–B catalysts. Co–B catalysts modified by a small amount of metal salts (Fe, Cr, Cu, *etc.*) are more effective for the selective hydrogenation of α,β-unsaturated aldehydes than co-precipitated binary boride catalysts.

Paul *et al.* reported in 1951[1)] that cobalt boride (Co–B) prepared by the liquid-phase reduction of cobalt salt with sodium tetrahydroborate has catalytic activity for the hydrogenation of safrole. Since then, the Co–B catalyst has been used in several reactions, such as in selective hydrogenation of nitriles to primary amines,[2)] in the reduction of nitro compounds[3)] and carbon monoxide,[4)] and in hydrogenolysis of hydrogen peroxide.[5)] With regards to the hydrogenation of olefins, aldehydes and ketones on Co–B catalyst, however, there have been only a few reports, probably because the activity of the Co–B catalysts is much lower than that of the Ni–B catalyst.

On the other hand, there have been some reports showing the difference between nickel and cobalt catalysts in the activity and selectivity for hydrogenations of various compounds.[6)] We have reported the surface state of Ni–B catalyst and its catalytic activity and selectivity for hydrogenation reactions in comparison to other nickel catalysts.[7)] In this work, we studied the selective hydrogenation of α,β-unsaturated aldehydes to unsaturated alcohols and that of acetylenes to olefins on the Co–B catalyst, which might exhibit higher selectivity than the Ni–B catalyst.

Furthermore, although a small amount of a metal such as Mo, W, Cr, or Rh, added to the Co–B or Ni–B catalyst is known to promote the catalytic activity,[1,5,8)] there has been no detailed report on the catalytic activity and selectivity of binary boride catalysts with various compositions. In the present work, a series of co-precipitated cobalt nickel boride (Co–Ni–B) catalysts was examined in order to elucidate the relation between the catalytic activity or selectivity and the surface state of the binary boride catalysts. The effects of metal salt additives to the Co–B and Ni–B catalysts on their selectivities were also studied in order to reveal the influence of preparation methods of binary boride catalysts and to find a more effective catalyst for the selective hydrogenation of α,β-unsaturated aldehydes to unsaturated alcohols.

Experimental

Catalysts. Co–B catalyst was prepared by reducing cobalt(II) acetate with sodium tetrahydroborate in water at 30 °C according to the method described previoursly.[7e)] Co–Ni–B catalysts were prepared in a similar way from mixtures of measured amounts of cobalt acetate and nickel acetate. The total weight of reduced metal was held constant. A freshly prepared catalyst was used for each experiment, immediately after washing with water and ethanol. The modification of Co–B or Ni–B catalyst by metal salts was carried out by stirring the washed catalyst with a measured amount of metal acetate or chloride in 20 cm^3 of ethanol for 20 min under a hydrogen atmosphere prior to the hydrogenation reaction.

BET surface areas of the catalysts were measured by N_2 adsorption at 77 K after they were washed with acetone and after evacuation by a diffusion pump for 4 h at ambient temperature. The surface areas of several catalysts were also measured after heating at 300 °C for 2 h *in vacuo*.

Apparatus, Procedure, and Materials. The hydrogenation reactions of acetone (2 cm^3), crotonaldehyde, cinnamaldehyde, and acetylenes (0.5 cm^3 for each) were carried out at 30 °C in 20 cm^3 of 99% ethanol under atmospheric pressure of hydrogen by using an apparatus similar to that described previously.[9)] A sufficient amount of hydrogen was adsorbed on each catalyst prior to the hydrogenation reactions. The amount of catalyst used was 0.2 g of metal for the hydrogenation of crotonaldehyde and acetylenes, and 0.5 g for that of acetone and cinnamaldehyde. The reaction rates were found not to be controlled by diffusion under these reaction conditions.

The initial hydrogenation rates were measured manometrically by the uptake of hydrogen in the initial stage of the reaction. The decomposition rate of hydrogen peroxide was also measured for comparison from the volume of oxygen evolved on 0.2 g of catalyst at 0 °C in 20 cm^3 of ethanol.

The selectivity of a catalyst for the hydrogenation of α,β-unsaturated aldehydes (S_1) was determined as the ratio of the yield of unsaturated alcohols to the total yield of the products based on GLC analysis at about 50% conversion. With the hydrogenation of acetylenes, the olefin selectivity (S_2) of a catalyst was defined as the molar ratio of olefin in olefin plus paraffin.

All reactants and solvent used for the hydrogenation reactions were dried and distilled before use. Metal salts and $NaBH_4$ were commercially obtained guaranteed or extra pure grade reagents (Nakarai Chemicals) and were used without further purification.

Analysis. Analysis of the reaction products was carried out by GLC using a Shimadzu 4APT gas chromatograph with a 2 m column of 20% PEG 20 M on Celite 545,

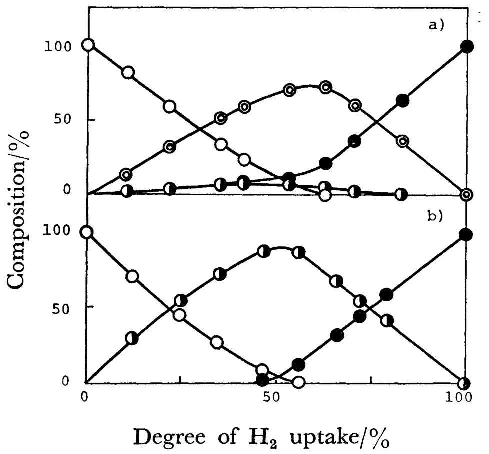

Fig. 1. Hydrogenation of cinnamaldehyde on (a) Co–B and (b) Ni–B catalysts.
○: Cinnamaldehyde, ◑: 3-phenylpropionaldehyde, ◎: cinnamyl alcohol, ●: 3-phenyl-1-propanol.

X-Ray photoelectron spectra(XPS) of some of the Co–Ni–B catalysts were measured to estimate the surface composition of the catalysts by using a Hitachi 507 photoelectron spectrometer. The detailed procedures were reported elsewhere.[7e)] The surface concentration of nickel in a Co–Ni–B catalyst was estimated from the relative peak area intensities of Ni $2p_{3/2}$ and Co $2p_{3/2}$ and from the relative atomic sensitivities obtained by measuring the X-ray induced spectra of $NiSO_4$ and $CoSO_4$.

Results

Co–B Catalyst. The Co–B catalyst prepared from cobalt(II) acetate is a fine, nonpyrophoric, and nonferromagnetic precipitate, and appears amorphous from the X-ray diffraction pattern. These properties of Co–B catalyst are similar to those of the Ni–B catalyst reported previously.[1,7)] The Co–B catalyst prepared from cobalt(II) chloride is, however, ferromagnetic and has a little lower activity for hydrogenation reactions than the one prepared from cobalt(II) acetate. Although the BET surface area of the Co–B catalyst is 38 m^2/g, twice as large as that of the Ni–B catalyst, the catalytic activity of the Co–B catalyst for hydrogenation reactions is considerably lower than that of the Ni–B catalyst. For example, the relative specific hydrogenation rates over the Co–B catalyst to that over the Ni–B catalyst are 1/3 for acetone, 1/15 for cinnamaldehyde, and 1/35 for crotonaldehyde. The low hydrogenation activity and the low resistivity to fatigue of cobalt catalyst may be partly attributed to the strong affinity of cobalt metal for oxygen,[10)] as is expected from the following result of the decomposition reaction of hydrogen peroxide.

The hydrogenation profiles of cinnamaldehyde on the Co–B and Ni–B catalysts are shown in Fig. 1. A considerable amount of unsaturated alcohol, *i.e.*, cinnamyl alcohol, was produced together with much smaller amounts of saturated aldehyde and saturated alcohol from the initial to the middle of the reaction stage on the Co–B catalyst, whereas no unsaturated alcohol was detected at all for the reaction on the Ni–B catalyst. In the case of crotonaldehyde, we also obtained crotyl alcohol with 21% of selectivity on the Co–B catalyst as well as on the platinum boride catalyst modified by copper(II) salt or iron(II) salt, as reported in our previous paper.[11)]

Table 1. Hydrogenation of acetylenes on cobalt and nickel catalysts

Reactant	Catalyst	Hydrogenation rate r/H_2-ccSTP $min^{-1}\cdot g^{-1}$	Olefin selectivity $S_2/\%$
Phenylacetylene	Co–B	46.1	79.0
	R-Co	0.4	76.6
	Ni–B	117.0	90.0
1-Heptyne	Co–B	35.5	68.5
	R-Co	8.9	61.0
	Ni–B	57.0	72.5
2-Heptyne	Co–B	17.7	97.3
	R-Co	0.7	93.4
	Ni–B	63.7	95.3

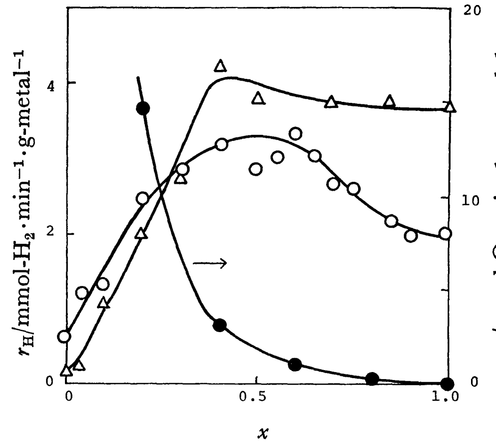

Fig. 2. Initial reaction rates as a function of nickel content *x*.
Substrate: ○, acetone(×10); △, crotonaldehyde; ●, hydrogen peroxide.

On the other hand, the selectivities to olefins(S_2) in the hydrogenation of acetylenes on the Co–B catalyst were somewhat lower than those on the Ni–B catalyst, while somewhat higher than those on Raney cobalt(R-Co) catalyst (Table 1). With regards to the hydrogenation rate of acetylenes, the Co–B catalyst showed considerably high activity, while the R-Co catalyst showed very low activity.

Co–Ni–B Catalysts. Figure 2 shows the initial hydrogenation rates (r_H) of acetone and crotonaldehyde and the initial decomposition rate(r_D) of hydrogen peroxide on the Co–Ni–B catalysts against nickel content (x=Ni/Co+Ni) in the catalyst. A maximum activity for hydrogenation reactions was obtained with a catalyst containing nickel in a concentration around $x=0.5$; however the shape of maximum was not sharp. X-Ray diffraction analysis showed that no crystalline phase existed in any of the Co–Ni–B catalysts used.

With respect to the decomposition reaction of hydrogen peroxide, however, the Co–B catalyst has the maximum activity, while a catalyst containing more nickel shows much lower activity. This feature cannot

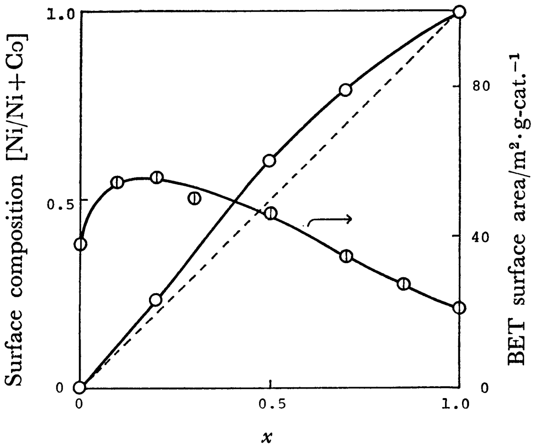

Fig. 3. Surface composition and BET surface area of Co–Ni–B catalyst as a function of nickel content x.

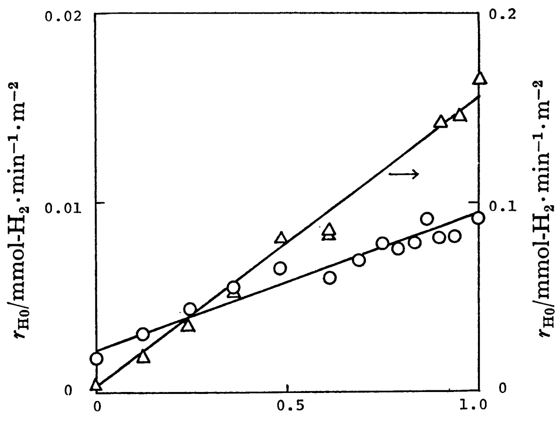

Fig. 4. Intrinsic hydrogenation activity r_{H0} of Co–Ni–B catalyst for acetone(○) and crotonaldehyde(△) as a function of surface composition.

be explained only by the increase of surface area of Co–Ni–B catalysts. It can be seen from Fig. 2 that the degree of variation in activity with nickel content is larger for the catalysts containing less nickel.

In Fig. 3, surface compositions of some Co–Ni–B catalysts obtained by XPS measurement are plotted, together with the BET surface areas of the catalysts, against nickel content in the bulk. The nickel content on the catalyst surface was found to be larger than that in the bulk.

Since the catalytic activities should be compared with the surface states of the catalysts, the intrinsic hydrogenation activities(r_{H0}) of Co–Ni–B catalysts per unit surface area were calculated based on the data in Fig. 2 and Fig. 3, and are plotted against the nickel content on the surface of the catalyst (Fig. 4).

The catalytic selectivities of the Co–Ni–B catalysts for the hydrogenations of α,β-unsaturated aldehydes(S_1) and phenylacetylene(S_2) are also plotted against nickel content(x) in Fig. 5. Both selectivities (S_1 and S_2) vary monotonously with nickel content in the catalysts. Each selectivity, S_1 or S_2, of the Co–Ni–B catalysts is lower than that of the Co–B or the Ni–B catalyst. The degree of variation in these selectivities with nickel content is also larger for the catalysts containing less nickel.

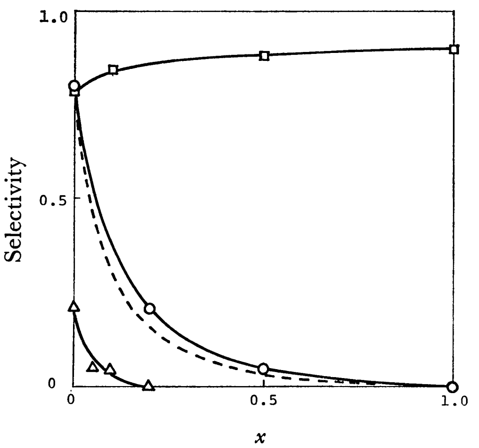

Fig. 5. Selectivity of Co–Ni–B catalyst as a function of nickel content x.
○: Selectivity to cinnamyl alcohol from cinnamaldehyde(S_1), △: selectivity to crotyl alcohol from crotonaldehyde(S_1), □: selectivity to styrene from phenylacetylene(S_2).

In addition, the resistivity against sintering of the Co–Ni–B catalysts was studied by measuring the BET surface areas of the catalysts heated at 300 °C for 2 h *in vacuo.* The resistivity to the fatigue due to oxidation of the catalyst surface was also evaluated by measuring the decomposition rate of hydrogen peroxide repeatedly on once-used catalyst. Both resistivities increased rapidly with the increase of nickel content.

Co–B Catalyst Modified with Metal Salt. Table 2 lists the products distribution for the hydrogenation of crotonaldehyde and cinnamaldehyde on Co–B catalysts modified by various metal salts (0.17 mmol/g-Co). The addition of certain metal salts was found to increase the yield of unsaturated alcohols(UA) on the Co–B catalyst, as reported on R-Co catalyst,[12] while it was not effective at all in the case of the Ni–B catalyst. The effectiveness of metal salts added to the Co–B catalyst decreased in the order: Fe≃Cr>Cu>Cd>Zn>Ru>Co.

When the amount of the metal salts added was more than 0.17 mmol/g-Co (1 mol% of the amount of the Co–B catalyst), it was less effective. In the case that metal salts were added to the aqueous solution of cobalt acetate prior to the reduction with NaBH$_4$, the resulting coprecipitated binary boride catalysts, even Co–Ni–B or Co–Cr–B catalyst, were not so selective as the modified cobalt boride catalyst.

Discussion

From the fact that the plots in Fig. 4 give a straight line, the variation of the specific activity of the Co–Ni–B catalysts with nickel content shown in Fig. 2 is evidently explained in terms of the surface area and the surface composition of the catalysts. In other words, the maximum hydrogenation activity of the Co–Ni–B catalyst containing nickel in concentrations around x=0.5 is due not only to the increase of the

TABLE 2. THE MODIFYING EFFECT OF METAL SALT ADDED TO Co-B CATALYST ON THE SELECTIVITY FOR THE HYDROGENATION OF α,β-UNSATURATED ALDEHYDES

Run[a)]	Modifier	Reaction time/min	Conversion/%	Product yield/%		
				SD	UA	SA[c)]
1)	None	73	50	60	21	19
2)	$CuCl_2 \cdot 2H_2O$	220	48	50	37	13
3)	$FeCl_2 \cdot nH_2O$	254	26	36	47	17
4)	$CrCl_3 \cdot 6H_2O$	220	52	42	44	14
5)	$Cd(CH_3COO)_2 \cdot 2H_2O$[b)]	120	20	60	28	12
6)	$Zn(CH_3COO)_2 \cdot 2H_2O$	150	40	60	26	14
7)	$RuCl_3 \cdot H_2O$	45	55	71	22	7
8)	$Co(CH_3COO)_2 \cdot 4H_2O$	155	55	61	22	17
9)	None	120	39	15	78	7
10)	$FeCl_2 \cdot nH_2O$	360	19	6	87	6
11)	$CrCl_3 \cdot 6H_2O$	147	65	6	90	4

a) Reactants are crotonaldehyde(6 mmol) for run 1 to run 8 and cinnamaldehyde(4 mmol) for run 9 to run 11. b) The amount of cadmium salt added is 0.085 mmol/g-Co instead of 0.17 mmol/g-Co. c) SD: saturated aldehyde, UA: unsaturated alcohol, SA: saturated alcohol.

surface area but also to the enrichment of nickel on the surface of the catalyst.

The features of the dependence of the selectivities (S_1 and S_2) on nickel content mentioned before (Fig. 5) are also explicable by the enrichment of nickel on the catalyst surface and by the higher hydrogenation activity of Ni metal than that of Co metal in the catalyst. The dashed line in Fig. 5 represents the variation of the calculated selectivity with nickel content for the hydrogenation of cinnamaldehyde, based on the surface composition of the catalysts and the values of selectivities and activities of Co–B and Ni–B catalysts.

The rapid increase in the resistivities against sintering or the fatigue with the increase of nickel content in Co–Ni–B catalysts can also be understood as a result of the enrichment of nickel on the surface of the catalysts, because the Ni–B catalyst is well known to have high resistivities against sintering or fatigue.

An advantage of the coprecipitated binary boride catalyst, Co–Ni–B, is the increase of hydrogenation activity. As for the catalytic selectivity, these binary boride catalysts were found to be ineffective. On the other hand, another type of binary boride catalysts, prepared by the modification of the Co–B catalyst with a small amount of metal salt, has an increased selectivity for the hydrogenation of α,β-unsaturated aldehydes. In this case, since the added metal cations interact with cobalt metal only on the surface of the catalyst, the addition of only small amounts of metal salt was more effective, compared to the case of the coprecipitated binary boride catalyst. It can be concluded, therefore, that the coprecipitated binary boride catalysts are effective for the increase of hydrogenation activity but that the modified binary boride catalysts are effective for the increase of the catalytic selectivity.

As can be seen from Fig. 5, the variations of the catalytic selectivities, S_1 and S_2, with nickel content of the catalysts are quite different; S_1 is the largest for the Co–B catalyst, whereas S_2 is the largest for the Ni–B catalyst. In the competitive hydrogenation of acetophenones over Ni and Co catalysts, Kajitani *et al.* reported that the characteristic difference in the susceptibility to the effects of substituent groups and solvents between R-Ni and R-Co catalysts can be mainly attributed to the differences between nickel and cobalt metals.[6c)] In the previous work, we reported that the hydrogenation activities and selectivities over various nickel catalysts, as well as the high resistivity of the Ni–B catalyst to poisoning,[7f)] are explained in terms of the surface *d*-electron density of the catalyst.[7g)] The characteristic differences in the hydrogenation activities and selectivities between the Co–B and Ni–B catalysts may, therefore, be due to the difference in the surface *d*-electron density of the two metals; the surface *d*-electron density of Co is smaller than that of Ni. That is to say, the reactants are adsorbed more strongly on the Co–B catalyst than on the Ni–B catalyst, resulting in lower hydrogenation rates on the Co–B catalyst than on the Ni–B catalyst. This is consistent with the results reported previously.[7g)] Blyholder and Shihabi pointed out in their study of IR spectra that a metal-oxygen bond rather than a metal-carbon bond is responsible for the bonding between acetone and the metal surface of silica-supported nickel and cobalt.[13)] Moreover, cobalt has stronger affinity for oxygen than nickel, as mentioned earlier. Therefore, the carbonyl group of α,β-unsaturated aldehydes will be adsorbed as strongly as the carbon-carbon double bond on the Co–B catalyst. This will relatively favor the hydrogenation of the carbonyl group on the Co–B catalyst, since the stronger adsorbate has an advantage in competitive hydrogenations. Especially for the hydrogenation of cinnamaldehyde, which has a large steric hindrance around the carbon-carbon double bond, the carbonyl group will be hydrogenated much more easily than the carbon-carbon double bond. On the Ni–B catalyst, however, the carbonyl group is adsorbed too weakly to be hydrogenated prior to the hydrogenation of the carbon-carbon double bond.

With regard to the hydrogenation of acetylenes, since a carbon-carbon triple bond is adsorbed on metal much more strongly than the double bond, the hydrogenation of an acetylenic bond will be much more difficult than that of an olefinic bond on the Co–B catalyst, as compared with those on the Ni–B catalyst. Moreover, the olefinic bond is also adsorbed too strongly on the Co–B catalyst to desorb before being hydrogenated to the single bond. This will favor the hydrogenation of an olefinic bond formed by the hydrogenation of an acetylenic bond, resulting in the lower olefin selectivity(S_2) on the Co–B catalyst than on the Ni–B catalyst. This idea is supported by the fact that the olefin selectivities(S_2) for the hydrogenation of 1-heptyne, which is comfirmed to be adsorbed on catalysts more strongly than 2-heptyne by the result of competitive hydrogenation of 1-heptyne and 2-heptyne, are lower than those for the hydrogenation of 2-heptyne, as shown in Table 1.

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