Surface Characterisation of Nickel Boride and Nickel Phosphide Catalysts by X-ray Photoelectron Spectroscopy

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The surface characterisation of nickel boride (NiB) and nickel phosphide (NiP) catalysts has been undertaken with X.p.s. Boron combined with nickel metal in NiB catalysts was found to donate electrons to the nickel metal, resulting in electron rich metal, whereas phosphorus bonded to nickel metal in NiP catalysts accepted electrons from the nickel metal, causing electron deficient metal. Preparation methods (different solvent, precursor salt and temperature) affected the surface concentrations of boron and phosphorus bonded to the nickel metal, surface areas and specific hydrogenation activities of the catalysts. The specific activities for hydrogenation reactions increased with increasing surface boron content in NiB catalysts, whereas they decreased with increasing surface phosphorus content in NiP catalysts. These positive and negative promoting effects of boron and phosphorus are explained in terms of the electron density of the nickel metal. Co-, Fe-, Pd- and PtB catalysts were also investigated for comparison.

Various nickel catalysts, such as Raney nickel, nickel boride, nickel phosphide and Urushibara nickel, are widely used in hydrogenation reactions and are well known to exhibit peculiar properties of selectivity and activity for the reactions. However, there has been no systematic interpretation of these features. In order to reveal the peculiarities of such nickel catalysts, it is fruitful to characterize the surface states of the catalysts, that is, the chemical states of additives or promoters (*e.g.*, Al in Raney nickel, B in nickel boride, P in nickel phosphide and Zn in Urushibara nickel), the interactions between the promoters and nickel metal and the surface concentrations of the promoters. Furthermore, the catalytic activities and selectivities of these catalysts should be compared with the surface states of the catalysts to shed light on the dominating factors. X-ray photoelectron spectroscopy (X.p.s.) is a valuable technique for such investigations, since it reveals both the chemical state and composition of the surface layer of a solid and therefore provides a probe for defining the catalyst surface.

In the present study, nickel boride (NiB) and nickel phosphide (NiP) catalysts were examined systematically. NiB catalyst exhibits high resistivity to sintering [1] and poisoning [2, 3] and shows high activities and selectivities for certain hydrogenation reactions.[4-9] These features are explained on the basis of the increased electron density of the nickel metal induced by boron,[2, 3, 8] although no decisive evidence has been presented. With regard to NiP catalyst, it shows specific hydrogenation selectivity for the formation of n-alcohol from 1,2-epoxides [10] and for the selective production of 2-butene from butadiene,[11] although the catalytic activity of NiP catalyst is low compared with other nickel catalysts.[7, 8, 12]

With cobalt boride catalyst, Maybery *et al.* using X.p.s.[13] have suggested contamination of the catalyst by sodium chloride. However, no precise description of the surface state has been presented. For transition metal boride compounds, Mavel *et al.*[14] have pointed out the importance of surface oxidation. Their studies, however, are not highly relevant because nickel boride is not included and metal boride catalysts are usually amorphous,[7, 15, 16] unlike the crystalline metal borides studied by them.

In this paper, NiB and NiP catalysts, prepared under various conditions, were studied with X.p.s. in order to characterize the surface states of the catalysts and to investigate the role played by the additives or promoters in hydrogenation reactions. Co-, Fe-, Pd- and Pt-B catalysts were also studied for comparison.

EXPERIMENTAL

CATALYSTS

Metal boride catalysts were prepared by reducing metal salts with $NaBH_4$ in water (P-1 method) or in 95 % ethyl alcohol (P-2) following Brown's method.[17,19] NiP catalysts were prepared following a method described by Sada.[12]

Ni-, Co- AND Fe-B CATALYSTS

Twenty cm^3 of a 1.28 mol dm^{-3} $NaBH_4$ aqueous solution was added dropwise to a 50 cm^3 aqueous solution containing 8.52 mmol of a metal salt listed in table 1 under vigorous stirring at 30°C. After 10 min, the precipitated catalyst was washed 3 times with distilled water and subsequently 3 times with 99 % ethyl alcohol. This preparation method is designated (P-1), according to Brown.[17-19] 95 % ethyl alcohol was used instead of water with the (P-2) preparation method.

TABLE 1.—SURFACE CHARACTERIZATION OF METAL–BORIDE CATALYST

catalyst	preparation method	precursor salt	surface area/m^2 g^{-1}	metal [a] /%	B/M [b] ratio	B-I /%	B-II /%	B-H /%	B-I /metal [c]
NiB	P-1	$Ni(CH_3COO)_2$	21.8	61	0.54	51	49		0.45
	P-1	$NiSO_4$	22.7	86	0.55	58	42		0.37
	P-1	$NiCl_2$	23.3	83	0.47	56	44		0.32
	P-1	$NiBr_2$	26.3	77	0.38	56	44		0.27
	P-1	$Ni(HCOO)_2$	2.96	≈15					
	P-1	$Ni(NO_3)_2$		≈0					
	P-2	$Ni(CH_3COO)_2$	38.2	72	0.40	37	63		0.21
	P-2	$NiCl_2$		77	0.51	33	67		0.21
CoB	P-1	$CoSO_4$	25.1	83	0.37	56	44		0.25
	P-1	$CoCl_2$	26.1	83	0.38	51	49		0.24
	P-1	$Co(HCOO)_2$	20.9	81	0.39	48	52		0.23
	P-1	$CoBr_2$	29.7	85	0.25	53	47		0.17
	P-1	$Co(CH_3COO)_2$	33.5	≈10					
FeB	P-1	$FeCl_2$		81	0.29	22	78		0.08
PdB		$PdCl_2$	22	94	0.020	67	13	20	0.014
PtB		H_2PtCl_6	12.8	83	0.011	27	13	60	0.004
DNi		$Ni(HCOO)_2$	44	88					

[a] Fraction of metal in total surface metal; [b] total boron/total metal in surface; atomic ratio; [c] concentration of boron bonded to metal; atomic ratio.

PtB CATALYST

Five cm^3 of a $NaBH_4$ solution (a mixture of 3.8 g of $NaBH_4$ in 95 cm^3 of 99 % ethyl alcohol and 5 cm^3 of a 2 mol dm^{-3} NaOH aqueous solution) was added quickly to a mixture of 1 cm^3 of H_2PtCl_6 aqueous solution (0.17 mol dm^{-3}) and 40 cm^3 of 99 % ethyl alcohol under vigorous stirring at 30°C. Four cm^3 of a 4 mol dm^{-3} HCl aqueous solution was added after 1 min. The precipitated catalyst was rinsed 3 times with water and subsequently 3 times with 99 % ethyl alcohol.

PdB CATALYST

One cm^3 of an aqueous solution of $PdCl_2$ (0.28 mol dm^{-3}) was added to 40 cm^3 of 99 % ethyl alcohol. Five cm^3 of a $NaBH_4$ solution in ethyl alcohol (1.0 mol dm^{-3}) was added dropwise to the above solution under vigorous stirring at 30°C, followed by the addition of 4 cm^3 of a 6 mol dm^{-3} HCl aqueous solution. The precipitated PdB catalyst was washed as described above.

NiP CATALYST

An aqueous NaOH solution was added to an aqueous $NiCl_2$ solution and the nickel hydroxide thus obtained was reduced at 72°C using NaH_2PO_2 in water with vigorous stirring. The precipitated catalyst was washed as in the case of the NiB catalyst. The catalyst is denoted NiP-1 here. NiP-2 catalyst was also prepared by using 50 % ethyl alcohol instead of water for NiP-1 catalyst, when nickel hydroxide was reduced with NaH_2PO_2, with the intention of varying the phosphorous content in NiP catalyst.

DNi CATALYST

Decomposed nickel catalyst (DNi) was prepared by decomposing nickel formate at 300°C for 3 h in vacuum,[8] followed by washing similarly to metal boride catalysts in order to remove sodium ion which was detected by X.p.s.

CATALYTIC ACTIVITY MEASUREMENTS

The hydrogenation activities of the catalysts for styrene, cyclohexene and cyclo-octene were measured at 30°C in 99 % ethyl alcohol under atmospheric pressure of hydrogen using a similar apparatus to that reported previously.[20]

B.E.T. surface areas of the catalysts (N_2 adsorption at 77 K) were measured after washing the catalysts with acetone instead of 99 % ethyl alcohol and evacuating the acetone at 100°C for several h. The reproducibility of the surface area measurements was within ±5 %.

X.P.S. MEASUREMENTS

X-ray photoelectron spectra were recorded on a Hitachi 507 photoelectron spectrometer equipped with a cylindrical mirror analyser and a pretreatment chamber using Al $K\alpha_{1,2}$ radiation (10 kV, 50 mA). The spectrometer was linked to a multichannel analyser (Hitachi 505) in the multiscaler mode to improve the signal-to-noise ratios of the spectra. The spectrometer was calibrated using the Fermi level (0.0 eV) and Pd $3d_{5/2}$ (335.5 eV) for Pd metal.[21] The instrumental resolution expressed by the half width of Au $4f_{7/2}$ was 2.1 eV.

A catalyst sample was mounted quickly onto a grid attached to a sample holder made of stainless steel in the pretreatment chamber, keeping the catalyst soaked in 99 % ethyl alcohol to prevent the oxidation of the catalyst by air. The ethyl alcohol was evacuated at room temperature until the pressure in the pretreatment chamber reached 1×10^{-5} Torr (1 Torr = 133.3 N m^{-2}). Then the catalyst was transferred to the X.p.s. analyser chamber. The pressure of the analyser chamber was $\approx 1 \times 10^{-7}$ Torr during measurements.

All binding energy values were referenced to the contaminant carbon (C $1s$ = 285.0 eV) in order to facilitate the comparisons of the values among the catalysts and standard compounds. The extents of surface charging of the catalysts thus measured were within a few tenths eV. The accuracy of the binding energy values for the catalysts examined here was ±0.3 eV, judged by the reproducibility of the binding energies for several samples prepared separately. In the cases of standard compounds, the reproducibility of the binding energies was within ±0.2 eV.

Peak area intensities were used for (semi-) quantitative purposes: they were measured by planimetry of graphic displays of the spectra, assuming linear base lines as described by

Honda and Hirokawa.[22] With the Ni $2p_{3/2}$, Fe $2p_{3/2}$ and Co $2p_{3/2}$ levels, the shake-up satellite peaks associated with oxides or hydroxides were included. The typical peak height intensities of the Ni $2p_{3/2}$ level for the nickel catalysts were 3000-4000 counts per second. The peak area intensity ratios of the C $1s$ level (due to contaminant carbon) to the Ni $2p_{3/2}$ level were almost invariant (C $1s$/Ni $2p_{3/2} = 3 \pm 1 \times 10^{-3}$) for NiB and NiP catalysts studied in this paper, except for unwashed NiB catalyst [2×10^{-2} for (P-1) and 9×10^{-2} for (P-2) catalysts]. Therefore, the effects of contaminant carbon on the B/Ni and P/Ni ratios were neglected. The differences in escape depths of photoelectrons would cause errors in the determination of the surface composition of the catalysts, particularly when samples are extensively contaminated or are heterogeneous in the direction of depth. Accordingly, the boron and phosphorous contents given here are semi-quantitative rather than absolute. However, the relative values are believed to be correct.

Deconvolutions of the metal spectra into metal and oxide peaks was carried out graphically and checked partly by using a Du Pont 310 curve resolver, taking into account the spectra for bulk metal and oxide or hydroxide including satellite peaks associated with them. The reproducibility of the deconvolution process was ±5 %.

RESULTS AND DISCUSSION

SURFACE CHARACTERISATION

NiB CATALYST

The X-ray photoelectron spectra of Ni $2p_{\frac{3}{2}}$ and B $1s$ levels for the NiB (P-1) catalyst prepared by reducing nickel acetate are shown in fig. 1. Before washing the catalyst, surface segregation of large amounts of contaminant compounds was observed; Na^+, CH_3COO^- (C $1s$ = 288.3 eV, which value coincides with that for nickel acetate) and boron having a B $1s$ binding energy of 192.0 eV. After rinsing the catalyst 3 times with water and subsequently 3 times with 99 % ethyl alcohol, these contaminants were removed nearly completely except for a small amount of CH_3COO^-. However, a new peak appeared, unexpectedly, around the binding energy of 199 eV. This signal can be attributed to adsorbed chlorine as an impurity, on the basis of the binding energy. With the NiB (P-2) catalyst prepared from nickel acetate as a precursor in 95 % ethyl alcohol, the contamination on the catalyst surface was much more intense before washing than that on the (P-1) catalyst. This is due to the lower solubilities of the contaminant salts in ethyl alcohol than in water. A trace amount of Na^+ was detected on the (P-2) catalyst surface even after washing. Brown *et al.*[4, 5] have reported considerable differences in selectivities for hydrogenation reactions over unwashed NiB (P-1) and (P-2) catalysts. These differences are to be ascribed partly to the differences in the extent of contamination on the catalyst surface, since additions of NaOH and CH_3COOH modify the catalytic activities and selectivities of NiB catalysts.[7]

The Ni $2p_{\frac{3}{2}}$ binding energy for nickel metal in NiB catalyst was consistent with those for DNi and bulk nickel metal (852.2±0.2 eV). With other metal-boride catalysts, the binding energies of Co $2p_{\frac{3}{2}}$, Fe $2p_{\frac{3}{2}}$, Pd $3d_{\frac{5}{2}}$ and Pt $4f_{\frac{7}{2}}$ levels for the metals in Co, Fe-, Pd- and Pt-B catalysts were 778.2, 706.4, 335.6 and 71.7 eV, respectively, and were in good agreement with those for the corresponding pure metals.

The surface oxidation of nickel metal was observed as shown in fig. 1. The fraction of nickel metal in the total surface nickel was estimated by deconvoluting the Ni $2p_{\frac{3}{2}}$ spectra to metal (852.2 eV) and oxide peaks (855.7 eV, satellite splitting; 6.1 eV). The X.p.s. data for the oxide peak agrees well with those for NiO obtained by us and reported by Vedrine *et al.*[23] The metal fractions thus obtained are listed in table 1 for various NiB catalysts. NiB catalysts showed a comparable degree of surface oxidation except for the catalysts prepared from nickel formate (≈15 %) and nitrate (≈0 %), which were deeply oxidized and showed only a little activity for hydrogenation reactions. On the other hand, in the cases of CoB catalysts, cobalt formate provided a good catalyst, while cobalt acetate did not. These facts indicate that the choice of a precursor salt is an important factor in obtaining an active metal boride catalyst.

Regarding surface boron, two kinds of boron were found on the NiB (P-1) catalyst prepared from acetate salt, as is shown in fig. 1. The binding energies of the B 1*s* level were 188.2 and 191.7 eV. These boron species are designated B-I and B-II, respectively. The NiB catalysts prepared from other nickel salts in water or in ethyl alcohol showed similar spectra to those in fig. 1 and the B 1*s* binding energies for B-I and B-II boron species were identical in the NiB catalysts within the reproducibility of the binding energy (±0.3 eV). Co- and Fe-B catalysts showed similar B 1*s* spectra except for a slightly different B 1*s* binding energy for B-I boron from that in NiB catalyst. The B 1*s* binding energies for B-I boron are summarized in table 2 for the metal boride catalysts studied in this work.

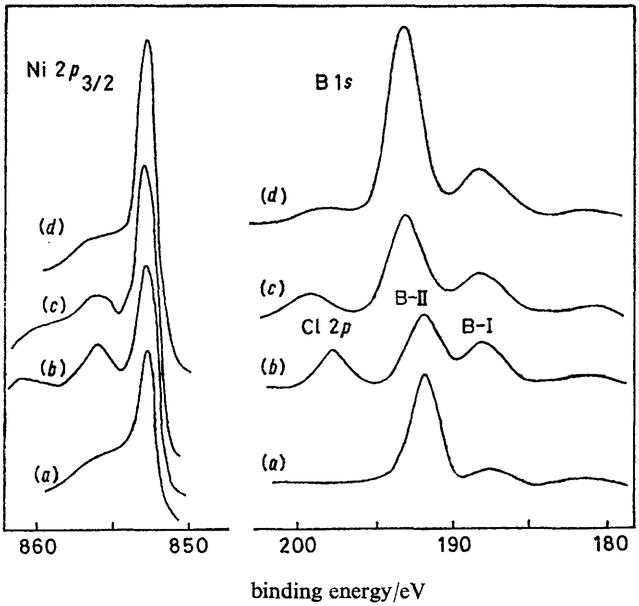

FIG. 1.—X-ray photoelectron spectra of Ni $2p_{\frac{3}{2}}$ and B 1*s* levels for NiB(P-1) catalyst prepared from nickel acetate at 30°C, (*a*) unwashed, (*b*) washed 3 times with water and subsequently 3 times with 99 % ethyl alcohol, (*c*) evacuated at 200°C for 1 h, (*d*) evacuated at 400°C for 1 h.

In fig. 2, the X.p.s. data of B 1*s* level for Pd- and Pt-B catalysts are shown. Another kind of boron was observed around 182 eV (182.3 eV for PdB and 181.5 eV for PtB) in addition to B-I and B-II species. This boron peak is assigned to a separate boron species, since the intensity is too strong to attribute it to the Al $K\alpha_{3,4}$ satellite of the B-II boron peak in both catalysts. This boron species is denoted B–H.

In order to characterize these boron species in metal boride catalysts, the binding energies of B 1*s* level for some boron compounds are presented in table 3. These values are in good agreement with those reported in the literature.[24]

The B 1*s* binding energies for B-I boron depend on the metal species as summarized in table 2. However, they were independent of the precursor salts, reduction temperature (13-40°C) and the amount of $NaBH_4$ used during preparation ($NaBH_4$/metal salt = 1-6 for NiB). Therefore, the state of B-I boron is characteristic of the respective metal in metal boride catalysts. In addition, the chemical shifts for B-I boron from elementary boron are not large enough for us to attribute B-I boron to boron oxides. Consequently, it is reasonable to assign the B-I species to boron combined with the metal in metal boride catalysts. Comparing the B 1*s* binding energies for B-I species with that for elementary boron, it is immediately concluded that the B-I boron species are positively charged. These findings indicate that the electron densities on the metals in metal boride catalysts are increased by electron transfer from B-I boron to the metals. In the cases of metal-rich boride compounds, such as NiB, Ni_2B, CoB, Co_2B and FeB, similar behaviour of boron has been reported on the basis of magnetic susceptibility, electron conductivity, ^{59}Co n.m.r. and high resolution Bremsstrahlung isochromat measurements.[25-28] These measurements imply considerable filling of metal 3*d* bands by electron transfer from boron to metal.[28] Our results show the presense of similar interactions between boron and metal in metal boride catalysts just as in crystalline stoichiometric metal borides, although metal boride catalysts are amorphous in structure.[7, 15, 16]

TABLE 2.—BINDING ENERGY OF B 1*s* LEVEL FOR BORON BONDED TO METAL IN METAL BORIDE CATALYST (C 1*s* = 285.0 eV)

metal	binding energy /eV
Ni	188.2
Co	188.2
Fe	187.9
Pd	189.1
Pt	188.4

With regard to B-II boron, it may be supposed, on the basis of the binding energy (191.7 eV), to be deposited BO_2^- ion, which results from the hydrolysis of $NaBH_4$. Pd- and Pt-B catalysts contain B–H boron which shows very low B 1*s* binding energies. It is reasonable to assign B–H boron to BH_3^- or BH_4^- adsorbed on Pt or Pd metal. The formation of BH_3^- adsorbed on metal is assumed to occur during the hydrolysis of borohydride.[29] Furthermore, large negative chemical shifts are expected for these borohydride ions;[30] the borohydride complexes of Pd and Pt are reported to be rather stable.[31]

The surface concentrations of boron (the average content in the surface layer of the catalyst) were estimated from the peak area intensities of Ni $2p_{\frac{3}{2}}$, Co $2p_{\frac{3}{2}}$, Fe $2p_{\frac{3}{2}}$, Pt $4f_{\frac{7}{2}}$ or Pd $3d_{\frac{5}{2}}$ and B 1*s* levels, although the procedures may be only semi-quantitative in complex systems such as metal boride catalysts described here. The atomic sensitivities were obtained by measuring the X-ray induced spectra of the following compounds; BN, $Ni(NO_3)_2$, $K_2Ni(CN)_4$, $NiCl_2$, $Co(NO_3)_2$, $Fe(NO_3)_2$, H_2PtCl_6 and $PdCl_2$ and are tabulated in table 4, together with the values reported by Scofield[32] and Wagner[33] for comparison. Differences in the relative atomic sensitivities among workers, particularly for transition metals, are considered to be due mainly to differences in the evaluation methods of the base lines and so the peak area intensities. The surface concentration of boron and the respective fractions of B.I, B-II and B–H species in the boron are summarized in table 1.

From table 1, the surface content of B-I boron, which is bonded to nickel or cobalt metal, is seen to depend strongly on precursor salts and solvents. The preparation temperature also varied the B-I boron concentration (B-I/Ni metal = 0.37 at 13°C for the NiB (P-1) prepared from nickel acetate). However, the molar ratio of metal salt to $NaBH_4$ ($NaBH_4$/metal salt = 1-6) caused no major changes in the surface composition of the catalyst. It is noteworthy that the (P-2) method provides catalysts containing a considerably lower surface B-I boron content than the (P-1) method. With regard to the total boron content, however, the B/Ni atomic ratio for NiB catalysts was almost invariant ($\approx$0.5) with preparation procedure and was consistent with the bulk composition of NiB catalyst (B/Ni $\approx$ 0.5).[34-37] These findings facilitate interpretation of Brown's results on the differences between NiB(P-1) and (P-2) catalysts in hydrogenation selectivity.

In table 1, it is also seen that the amount of surface boron combined with metal (B-I/metal) decreased in the following order; NiB> CoB> FeB$\gg$ PtB, PdB. The

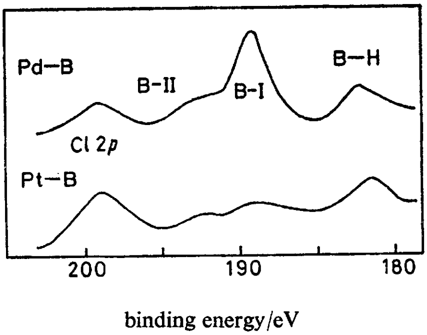

FIG. 2.—X-ray photoelectron spectra of B 1*s* level for PdB and PtB catalysts after washing.

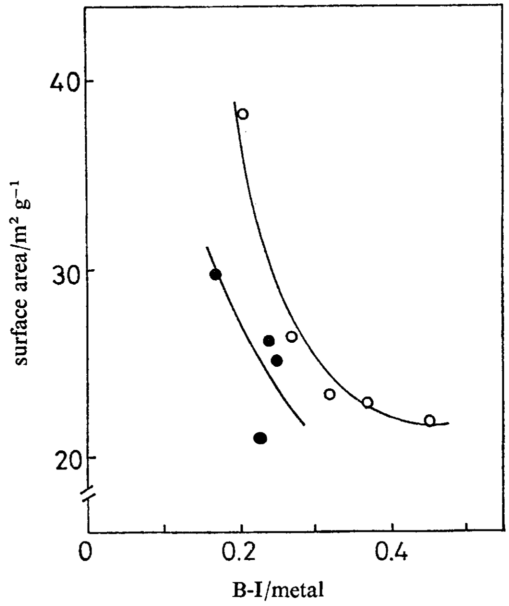

FIG. 3.—Correlations between surface areas (m^2 g^{-1}) and B-I surface contents for NiB (○) and CoB (●) catalysts.

extremely small concentration of boron in PdB catalyst is in good agreement with the results reported by Chen *et al.*[38]

On comparing the surface areas and B-I/metal ratios for Ni- and Co-B catalysts, it is evident that the surface areas depend on the surface content of B-I boron, as shown in fig. 3. It is supposed that the relative rates of the metal salt reduction with $NaBH_4$ and the decomposition of $NaBH_4$ determine the surface content of B-I boron and surface area of the catalyst. The pH values of aqueous solutions (8.52 mmol/50 cm^3 H_2O) were 7.2, 6.2, 5.6 and 5.1 at 30°C for $Ni(CH_3COO)_2$, $NiSO_4$, $NiCl_2$ and $Ni(NO_3)_2$, respectively. The surface content of B-I boron decreased with reduction of pH value and, therefore, with increasing rate of hydrolysis of $NaBH_4$, although the total boron content (B-I + B-II) did not change so much with the metal salt used. With $Ni(NO_3)_2$, even the nickel salt could not be reduced, probably due to vigorous hydrolysis of $NaBH_4$ in the strong acidic solution.

TABLE 3.—BINDING ENERGY OF B 1*s* LEVEL FOR BORON COMPOUND (C 1*s* = 285.0 eV)

compound	binding energy /eV
amorphous boron	187.5
BN	190.2
$NaBO_2$	192.1
B_2O_3	193.0
$B(OH)_3$	193.0

Heat-treatments of NiB(P-1) were carried out in vacuum (1×10^{-5} Torr) at 200 and 400°C (fig. 1). The intensity of the B-II boron photoelectron spectrum was increased considerably and the B 1*s* binding energy increased to 193.0 eV, indicating transformation of B-II boron to B_2O_3 or $B(OH)_3$, as judged by the binding energy (table 3). The B-I content was decreased slightly, whereas the binding energy was not changed (188.2 eV). After evacuation at 200 and 400°C for 1 h, the amount of total boron was increased by 55 and 63 %, respectively, accompanying the reduction of nickel oxide to metal, as is shown in fig. 1. These facts imply a transfer of oxygen from nickel to boron, to form boron oxides.

NiP CATALYST

The X.p.s. data on the P 2*p* level for NiP catalysts are presented in fig. 4. The Ni $2p_{\frac{3}{2}}$ signals were very similar to those for NiB catalysts in fig. 1. The Ni $2p_{\frac{3}{2}}$ binding energy for metal (852.2 eV) was consistent with those for bulk nickel metal and for the metal in NiB catalyst. Based on the X.p.s. data for $Ni(OH)_2$ (Ni $2p_{\frac{3}{2}}$; 856.2 eV, satellite splitting; 5.9 eV, which values are consistent with those reported in the literature),[23] the oxidized nickel (Ni $2p_{\frac{3}{2}}$; 856.1 eV, satellite splitting; 5.6 eV) in the NiP catalyst surface is considered to be hydroxide, which contrasts with the NiB catalyst. It is evident from fig. 4 that there exist two kinds of phosphorus in the catalyst surface. The higher binding energy peak (P 2*p*; 134.0 eV) is assignable to oxidized phosphorus such as PO_4^{3-} on the basis of the binding energy. The P 2*p* peak at the binding energy of 129.7 eV is shifted negatively by 0.7 eV from red phosphorus (P 2*p*; 130.4 eV). Similar negative shifts have been reported for MnP (0.8 eV) and CrP (1.3 eV) by Pelavin *et al.*[39] and for CuP_2 (0.3 eV) and Cu_3P (0.4 eV) by Nefedov *et al.*[40] Therefore, the phosphorus having lower P 2*p* binding energy in NiP catalyst surface can be attributed to the one bonded to nickel metal. The phosphorus in the NiP catalyst interacts with the nickel metal as in metal phosphide compounds in spite of the amorphous structure. Similar interactions between boron and nickel metal in amorphous NiB catalyst have been discussed above. The negative shift for phosphorus indicates that the phosphorus withdraws electrons from the nickel metal and, hence, that the electron density on the nickel metal is decreased by electron transfer between phosphorus and the nickel metal in contrast to NiB catalysts, in which the electron density on the nickel metal is supposed to be increased by the electron donating nature of boron.

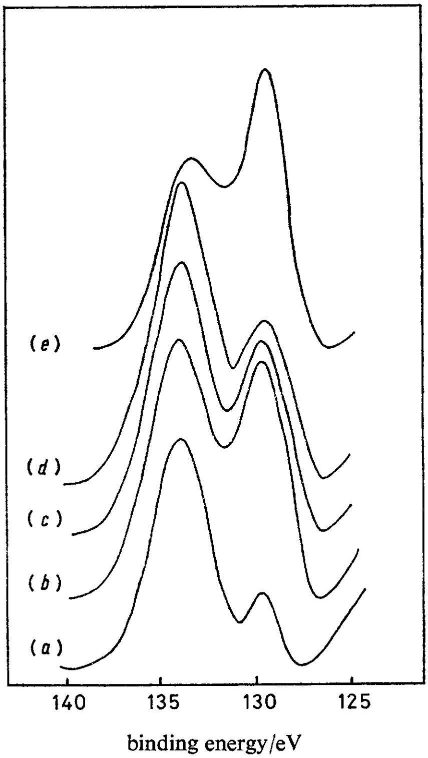

FIG. 4.—X-ray photoelectron spectra of P 2*p* level for NiP catalyst, (*a*) NiP-2, (*b*) NiP-1, (*c*) NiP-1 evacuated at 200°C for 1 h, (*d*) NiP-1 evacuated at 400°C for 1 h, (*e*) NiP-1 treated with 0.5 mol dm^{-3} HCl for 30 min.

It will be instructive to examine the preparation effects of NiP catalyst, NiP-1 and NiP-2, in connection with the NiB catalyst. The X.p.s. peak area intensity ratios of P 2*p* and Ni $2p_{\frac{3}{2}}$ levels were corrected to atomic ratios by using the relative atomic sensitivity of the P 2*p* and Ni $2p_{\frac{3}{2}}$ levels, determined from the photoelectron spectra for a standard compound; $Ni_3(PO_4)_2$ (table 4). As shown in fig. 4 and table 5, preparation effects were apparently observed. In both NiP and NiB catalysts, the catalysts prepared in water contain more promoter (boron and phosphorus) combined with metal than those prepared in alcoholic solutions. Furthermore, the surface area of NiP-2 was larger than that of NiP-1, in agreement with the NiB catalyst (fig. 3).

TABLE 4.—ATOMIC SENSITIVITY RELATIVE TO N 1*s* LEVEL

level	atomic sensitivity		
	Scofield [a]	Wagner [b]	this work
B 1*s*	0.27	0.35	0.38
P 2*p*	0.66	1.00	1.00
N 1*s*	(1.00)	(1.00)	(1.00)
Fe $2p_{3/2}$	6.01	4.36	2.33
Co $2p_{3/2}$	7.01	—	2.85
Ni $2p_{3/2}$	8.12	9.09	3.84
Pd $3d_{5/2}$	5.27	—	2.77
Pt $4f_{7/2}$	4.81	4.73	1.69

[a] Ref. (32); [b] ref. (33).

TABLE 5.—SURFACE CHARACTERIZATION OF NiP CATALYST

catalyst	treatment	surface area/m^2 g^{-1}	metal [a] /%	P_T/M [b]	P/P_T [c]	P /metal [d]
NiP-1	fresh	89	62	0.68	0.47	0.52
	evacuated at 200°C for 1 h		71	0.70	0.37	0.37
	at 300°C		71	0.73	0.35	0.36
	at 400°C		68	0.75	0.35	0.36
	treated with 0.5 mol dm^{-3} HCl		73	0.71	0.64	0.62
NiP-2	fresh	119	47	0.92	0.16	0.31

[a] Fraction of metal in total surface metal; [b] total phosphorus/total metal in surface; atomic ratio; [c] phosphorus bonded to metal/total phosphorus; [d] concentration of phosphorus bonded to metal; atomic ratio.

Heat-treatments of NiP-1 catalysts in vacuum induced an enhancement of P 2*p* X.p.s. intensity of the oxidized phosphorus and a decrease in the surface content of phosphorus associated with the nickel metal. The behaviour of phosphorus is very similar to that of boron in NiB catalyst. The transfer of oxygen on nickel to phosphorus was observed similarly to NiB catalyst.

SURFACE STATE AND HYDROGENATION ACTIVITY

In both NiB and NiP catalysts, the surface concentrations of boron and phosphorus combined with nickel metal are considerably altered by the preparation method, solvent and precursor salt used. It is thus interesting to examine the effects of boron and phosphorus on the hydrogenation activities of NiB and NiP catalysts. The specific activity is defined as the activity per unit surface area of nickel metal (cm^3 s.t.p. H_2 min^{-1} m^{-2} of nickel metal), where the surface area of nickel metal is estimated from the fraction of nickel metal in the surface nickel (tables 1 and 5).

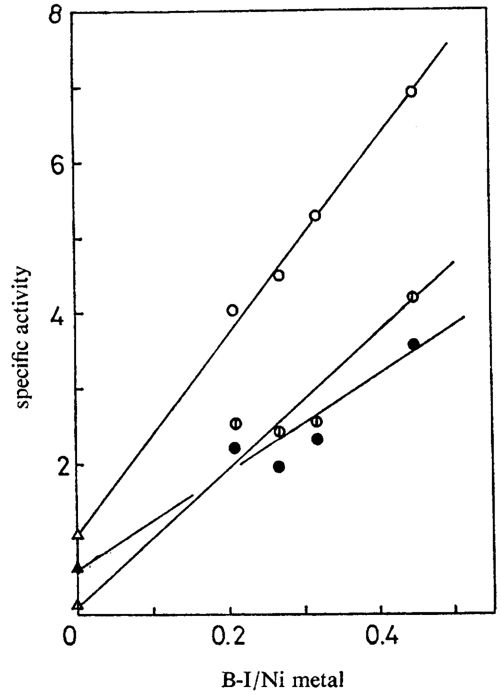

FIG. 5.—Specific activities (cm^3 s.t.p. H_2 min^{-1} m^{-2} of Ni metal) of NiB catalyst for styrene (○), cyclohexene (●) and cyclo-octene (⦶) hydrogenations at 30°C as a function of B-I boron content in the catalyst surface, triangle; DNi.

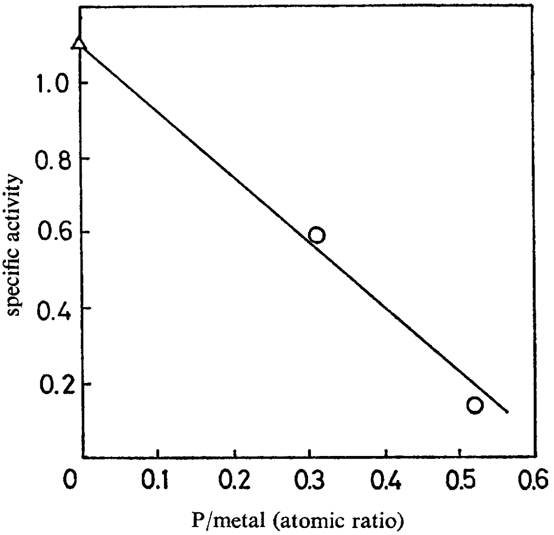

FIG. 6.—Specific activity (cm^3 s.t.p. H_2 min^{-1} m^2 of Ni metal) of NiP catalyst for styrene hydrogenation at 30°C as a function of surface content of phosphorus bonded to nickel metal, triangle; DNi.

In fig. 5, the specific activities of NiB catalysts for the hydrogenations of styrene, cyclohexene and cyclooctene are shown as a function of B-I/Ni metal ratio, that is, the concentration of boron bonded to nickel metal. The specific activities were found to increase linearly with increasing B-I content. No better relation was obtained between the specific activity and total boron/Ni metal, total boron/total Ni, and so on. This implies a promoting effect of B-I boron for the hydrogenation reactions. The promoting effect of B-I boron is considered to be attributed to the increasing 3*d* electron density of the nickel metal with increasing B-I concentration, since it is reported with metal-rich borides that the number of 3*d* electrons per metal increases as the boron content increases (*e.g.*, 8.2 for Fe_2B and 8.9 for FeB, 9.2 for Co_2B and 9.7 for CoB).[28] The increased electron density on nickel metal is considered to weaken the adsorption strengths of reactants such as styrene, which is an electron donor and adsorbs much stronger than hydrogen (zero reaction order for styrene, first order for hydrogen), resulting in the reduction of the self-poisoning effects by the adsorbed reactants. The high resistance of NiB catalysts to poisons [2, 3] can be explained successfully in terms of the increased 3*d* electron density of the nickel metal in NiB catalysts.

With regard to the NiP catalyst, the specific activities decreased with increasing phosphorus content in the surface (fig. 6), in contrast to NiB catalysts. It is considered, based on similar discussions to NiB catalyst, that the negative promoting or deactivating effect of phosphorus is to be ascribed to the reduced 3*d* electron density on the nickel metal by electron transfer from the metal to phosphorus. The electron deficient nickel metal results in a stronger and, therefore, more unfavourable adsorption strength of styrene for the hydrogenation. As a matter of fact, the adsorption equilibrium constants of substituted acetophenone in the hydrogenation reactions are increased in the following order;[8] NiB(P-1) < DNi < NiP-1. These facts strongly confirm the reasonableness of the X.p.s. results and the nature of the promoting effects of boron and phosphorus in NiB and NiP catalysts. Accordingly, in the cases of NiB and NiP catalysts, the positive (negative) promoting effect of boron (phosphorus) can be attributed mainly to the electronic modification of the nickel metal by boron (phosphorus).

SUMMARY

Surface characterisation of NiB and NiP catalysts leads to the following conclusions: (1) boron bonded to nickel metal in NiB catalysts donates electrons to the nickel metal, resulting in electron rich metal. (2) On the other hand, phosphorus combined with nickel metal in NiP catalyst creates electron deficient metal by withdrawing electrons from the metal. (3) In both NiB and NiP catalysts, preparation methods affect the surface concentrations of boron and phosphorus, surface area and specific activity for a catalytic reaction. (4) The positive (negative) promoting effect of boron (phosphorus) on the specific hydrogenation activity can be ascribed predominantly to the modification of the 3*d* electron density on the nickel metal.

The change in 3*d* electron density on the nickel metal induced by boron or phosphorus will modify the selectivities of the nickel catalyst for hydrogenation reactions. Concerning this problem, we are carrying out further experiments including Raney nickel and Urushibara nickel catalysts for more precise discussions.

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