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Preparation and catalytic properties of palladium–(boron, phosphorus) thin films using an RF sputtering method

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Palladium–(boron, phosphorus) thin films have been prepared by an RF sputtering method. The palladium fcc structure was destroyed by adding boron or phosphorus and the palladium films finally became amorphous in structure. Boron, whose interaction with palladium was very weak, donated electrons to palladium, whereas phosphorus accepted electrons from palladium. The palladium–(boron, phosphorus) films showed high selectivity (above 97%) for the partial hydrogenation of diolefins (cyclopentadiene and 1,3-butadiene) and acetylene. The activity and the selectivity changed with the boron or phosphorus concentration. The changes in the selectivity were explained in terms of the ensemble and the ligand effect in the palladium films. It was found that the palladium–boron films with Pd_3B like structure and the amorphous palladium–phosphorus films were excellent for partial hydrogenation.

1. Introduction

Metal boride and metal phosphide are usually prepared by the reaction of an aqueous solution of metal salts with sodium borohydride and with sodium hypophosphite, respectively. For example, nickel boride and nickel phosphide are prepared by the reduction of nickel salts using $NaBH_4$ and NaH_2PO_2 in water or ethyl alcohol [1, 2]. However, palladium boride could not be prepared by a similar method, namely, the reduction of $PdCl_2$ using $NaBH_4$ [2]. The RF sputtering method is an excellent way to prepare alloy thin films [3]. The composition and film thickness are easily controlled by varying the sputtering conditions. The nickel–boron [4] and nickel–phosphorus [5] films with various boron or phosphorus concentration were prepared by the RF sputtering method because both nickel and a boron or a phosphorus atom are simultaneously deposited on the substrate from the gas phase. It is expected that the palladium–(boron, phosphorus) films are prepared as well.

On the other hand, it is well known that palladium is suitable for the partial hydrogenation of diolefins and acetylenes and exhibits high selectivity to monoolefins [6]. In recent investigations of the hydrogenation of acetylenes over supported palladium catalysts, it was found that the small particle size of palladium was favourable for the selective hydrogenation of phenylacetylene to styrene [7] and that the catalyst pretreatment decreasing the amount of surface hydrogen enhanced the selectivity from acetylene to ethylene [8]. Palladium alloy systems are often employed in order to enhance the properties of palladium by alloying. In the alloy systems, it would be necessary to consider catalysis by the alloys with regard to an ensemble and a ligand effect [9]. The ensemble size would affect the relative concentration of mono- and multi-adsorbed complexes of adsorbates, resulting in the apparent selectivity patterns in the hydrocarbon reaction. The ligand effect, namely, the effect caused by the electronic interaction between the active metal and the partner element, would influence the nature of the adsorption bond such as the bond strength. The ensemble and the ligand effect would often occur together and contribute to the changes in the nature and the concentration of the adsorbed complexes. It was reported for VIII/Ib alloys that no ligand effect existed on palladium–gold [10], palladium–silver [11] and palladium–copper [11] alloy surfaces for CO adsorption and on palladium–(gold, silver, copper) [12–14] alloy films for the electronic state measured by X-ray photoelectron spectroscopy (XPS) and that only the ensemble effect influenced the hydrocarbon conversion reactions. In metal–metalloid alloy systems, however, the electronic interaction between metal and metalloid has been confirmed in nickel–(boron, phosphorus) alloys [2, 4, 5]. Boron was found to act as the electron donor and phosphorus was the acceptor. It is expected that the electronic interaction is present in the palladium–(boron, phosphorus) films and that the alloying effects such as the ensemble and the ligand effect affect the catalytic properties of the palladium–(boron, phosphorus) films.

In this study, the preparation of palladium–(boron, phosphorus) films with various boron or phosphorus concentrations was attempted using the RF sputtering method. Their structure and electronic state were characterized by using X-ray diffraction (XRD) analysis and XPS with regard to the boron or phosphorus

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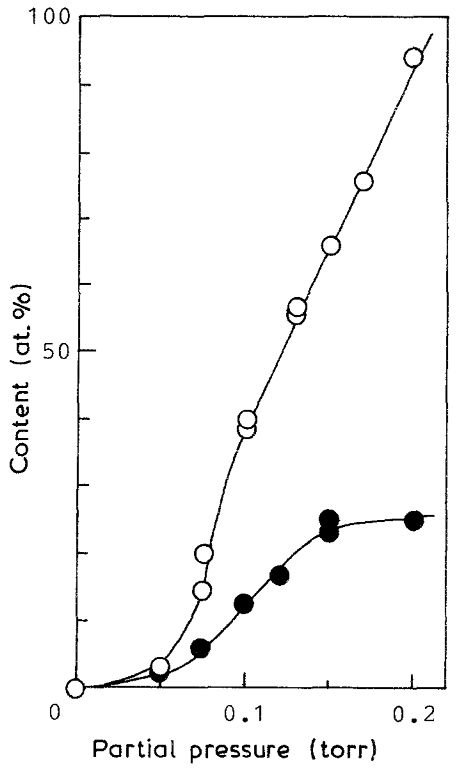

Figure 1 Plot of B (○) or P (●) concentration in palladium film alloys against $B_2H_6 + H_2$ or $PH_3 + H_2$ partial pressure.

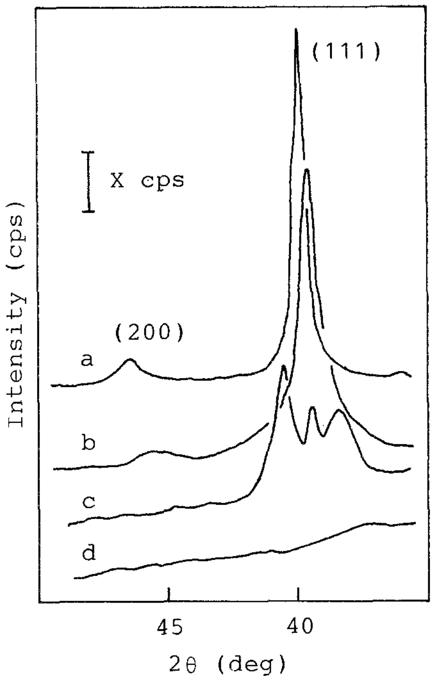

Figure 2 Cu $K\alpha$ X-ray diffraction patterns of the palladium–boron films. (a) Pd_{100}, (b) $Pd_{93}B_7$, (c) $Pd_{80}B_{20}$, (d) $Pd_{71}B_{29}$. Scale of peak intensity (X c.p.s.): (a) 1000, (b) 500, (c) 200, (d) 200.

concentration. The activity and the selectivity for the partial hydrogenation of diolefins (cyclopentadiene and 1,3-butadiene) and acetylene were investigated.

2. Experimental procedure

The palladium–(boron, phosphorus) films were prepared using the RF sputtering method. The detailed procedure of the film preparation has been described previously [3–5]. The target for the sputtering was a palladium plate (99.95%). Boron and phosphorus sources were B_2H_6 diluted with H_2(5.25 vol %) and PH_3 diluted with H_2 (5.37 vol %), respectively. The sputtering atmosphere was a mixed gas of a high purity of argon (99.9995%) at a pressure of 0.05 torr (1 torr = 133.3 Pa) and $B_2H_6 + H_2$ for a preparation of the palladium–boron films or a mixed gas of argon and $PH_3 + H_2$ for the preparation of the palladium–phosphorus films. The glow discharge was carried out on various B_2H_6 or PH_3 partial pressures. The palladium–(boron, phosphorus) films were deposited on a Pyrex glass substrate opposite the target. The film thickness was controlled to about 200 nm using a film thickness monitor with a quartz oscillator (Inficon XTM).

The hydrogenation of diolefins (cyclopentadiene and 1,3-butadiene) and acetylene were carried out over the palladium–(boron, phosphorus) films at 273 K using a conventional closed circulation system without any pretreatment. The ratio of hydrogen to hydrocarbon was 6 and the total pressure in the system was 140 torr. The products of the hydrogenation were analysed by a gas chromatograph (Shimazu GC-8A) with a thermal conductivity detector. Three packed columns were used in each hydrogenation. These were sebaconitrile 5 m used at 303 K for 1,3-butadiene, dimethylsulpholane 3 m at 303 K for cyclopentadiene, and activated charcoal 3 m at 423 K for acetylene.

The structure measurement of the palladium–(boron, phosphorus) films was performed by using Shimazu VD-1 X-ray diffractometer (CuKα radiation with 30 kV, 20 mA), while the surface composition and the electronic state of the palladium–(boron, phosphorus) films were investigated by a Shimazu ESCA-750 X-ray photoelectron spectrometer (MgKα radiation with 8 kV, 30 mA).

3. Results and discussion

3.1. Influence of sputtering atmosphere

The surface composition of the films was evaluated on the basis of the XPS peak area ratios of palladium-3d to boron 1s or phosphorus 2p levels. The variations of the surface composition with the partial pressure of $B_2H_6 + H_2$ or $PH_3 + H_2$ are shown in Fig. 1. The boron concentration in the palladium–boron films increased with increasing $B_2H_6 + H_2$ partial pressure and became about 90 at. % at 0.20 torr. On the other hand, the phosphorus concentration in the palladium–phosphorus films also increased with the enhancement of the $PH_3 + H_2$ partial pressure and reached about 25 at % at 0.20 torr. It was found that both the palladium–boron and the palladium–phosphorus films with various compositions were easily obtained. In a similar way to the nickel–(boron, phosphorus) system [4, 5], it is more difficult to dope phosphorus in palladium than boron.

3.2. Structure of the films

Figs 2 and 3 represent XRD patterns of the palladium–boron and the palladium–phosphorus films with various surface compositions, respectively. Two peaks due to Miller indices (1 1 1) and (2 0 0) of palladium fcc structure appeared at 40.3° and 46.5° in the pure palladium film. Below 15 at % of boron in the

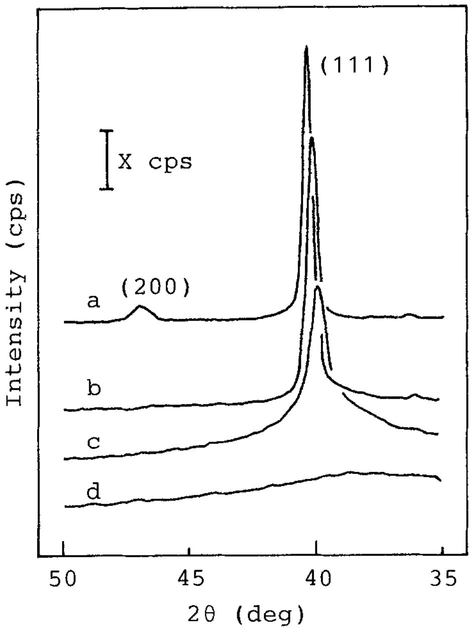

Figure 3 CuKα X-ray diffraction patterns of the palladium–phosphorus films. (a) Pd_{100}, (b) $Pd_{87}P_{12}$, (c) $Pd_{77}P_{23}$, (d) $Pd_{75}P_{25}$. Scale of peak intensity (X c.p.s.): (a) 1000, (b) 1000, (c) 500, (d) 500.

palladium–boron films, two peaks similarly appeared and the peak position shifted to the low angle of 2θ (Fig. 2b). This indicates that the structure of the palladium–boron films in this region is analogous to the palladium fcc structure and the larger lattice constant than palladium metal is due to the addition of boron. This is one of the results of the alloying of palladium with boron. Above 15 at % of boron, three small peaks typically appeared at 38.6°, 39.4°, and 40.5° (Fig. 2c). This peculiar structure is quite different from the palladium fcc structure. Pd_3B (B; 25 at %) and Pd_5B_2 (B; 28 at %) are known as stable palladium boride crystals. Stenberg determined the structure of these crystals [15]. Pd_3B and Pd_5B_2 were found to be orthorhombic and monoclinic with the unit cell, respectively. According to his report, the peculiar structure in this study may resemble Pd_3B rather than Pd_5B_2. The palladium–boron films with more than 20 at % of boron formed an amorphous structure indicated by no diffraction peaks (Fig. 2d).

Below 25 at % of phosphorus in the palladium–phosphorus films, only one peak appeared near the palladium (1 1 1) peak (Figs 3b and c). The peak position shifted to the lower angle of 2θ and the peak became smaller and broader with increasing phosphorus concentration. This is also evidence of alloying. Above 25 at % of phosphorus, the palladium–phosphorus films became amorphous (Fig. 3d).

3.3. Electronic state of the films

The surface state of the palladium–(boron, phosphorus) films was examined by XPS. All the binding energies (BE) were referred to the contaminant carbon (carbon 1s = 285.0 eV). In boron 1s level for the palladium–boron films, two peaks appeared at 188.8 and 192.6 eV. The former was assigned to boron interacting with palladium (B_I) and the latter was boron oxide (B_{II}, B_2O_3). Both intensities of B_I and B_{II} increased and a ratio of B_I/B_{II} decreased with increasing boron concentration. Peaks of palladium 3d5/2 and palladium 3d3/2 due to palladium metal appeared at 335.7 and 340.9 eV. The peak positions of boron 1s and palladium 3d5/2 were unaltered with the boron concentration (Fig. 4). The interaction of boron with palladium was not confirmed by the core level BE shifts. An electronic state of metal is estimated using not only a chemical shift of a core level but also the behaviour of a satellite peak of a core level in XPS, e.g., that of nickel 2p3/2 level for nickel–(boron, phosphorus) films [4, 5]. The small satellite peak of palladium 3d for the palladium–(boron, phosphorus) films, however, prevented this estimation. A valence band (v.b.) spectrum for palladium–(boron, phosphorus) films is mainly attributable to the palladium 4d band and would reflect the electronic state of palladium. Therefore, the v.b. spectra were measured for the palladium–(boron, phosphorus) films with various surface compositions. The v.b. spectra for the palladium–boron films changed a little in the shape with the boron concentration (Fig. 5). The shape of shoulder in the high BE side slightly changed. The position of the main peak was unaltered with the boron concentration. This implies that boron weakly electronically interacts with palladium in the palladium–boron films.

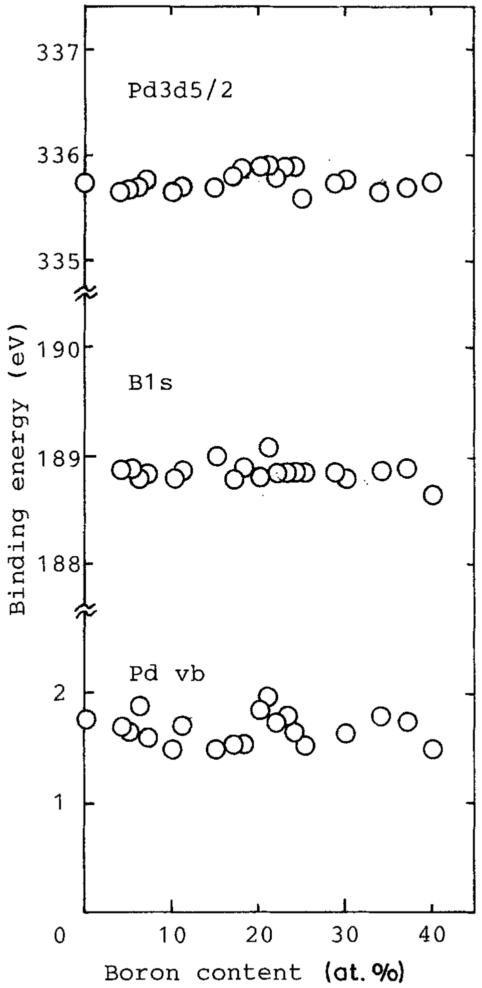

Figure 4 Dependences of the peak positions of palladium 3d5/2, boron 1s, and palladium v.b. on the boron concentration.

In order to assume the electron density of palladium in the palladium–boron films, the product distribution in the hydrogenation of 1,3-butadiene was measured.

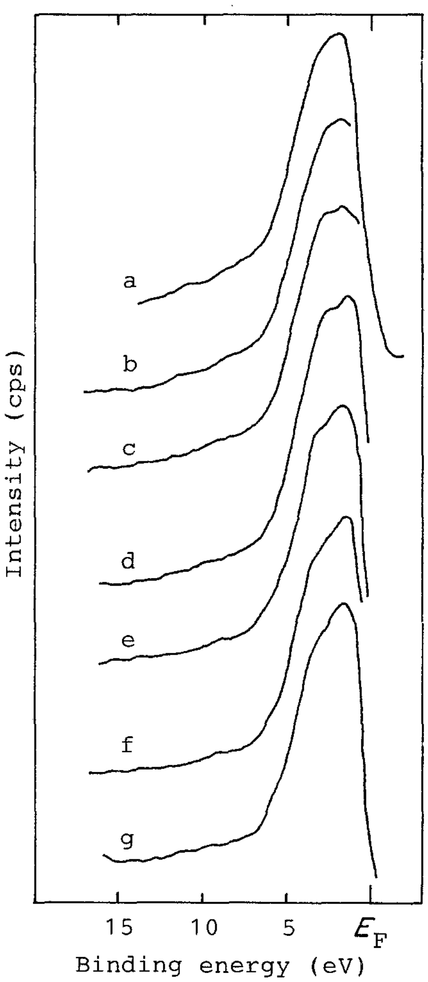

Figure 5 X-ray photoelectron spectra of palladium v.b. for the palladium–boron films. (a) Pd_{100}, (b) $Pd_{96}B_4$, (c) $Pd_{93}B_7$, (d) $Pd_{89}B_{11}$, (e) $Pd_{80}B_{20}$, (f) $Pd_{70}B_{30}$, (g) $Pd_{60}B_{40}$.

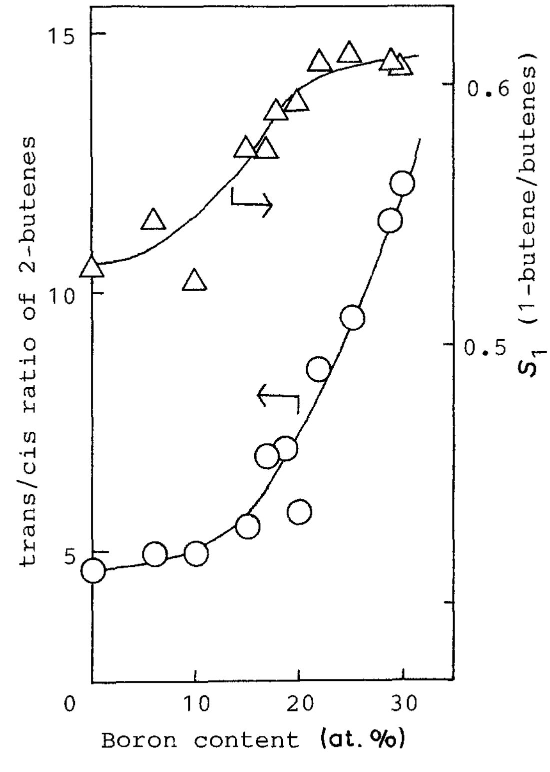

Figure 6 Dependences of trans to cis ratio of 2-butenes and S_1 in the hydrogenation of 1,3-butadiene on the boron concentration.

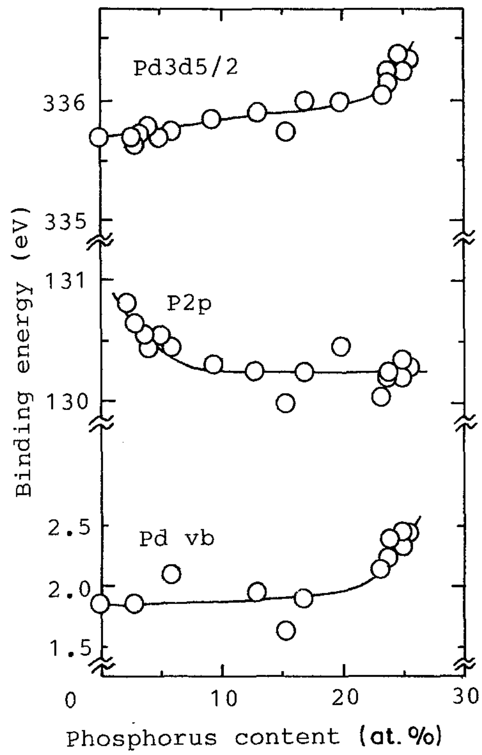

Figure 7 Dependences of the peak positions of palladium 3d5/2, phosphorus 2p, and palladium v.b. on the phosphorus concentration.

the distribution was estimated at 0% conversion of 1,3-butadiene. Fig. 6 shows dependences of a trans–cis ratio in 2-butenes and a selectivity of 1-butene in butenes (S_1) on the boron concentration. The trans–cis ratio and S_1 increased with increasing boron concentration. The distribution of butenes in the hydrogenation of 1,3-butadiene is presumed to be influenced by the electronic state of palladium. The monotonous increases of the trans–cis ratio and S_1 suggest the enhancement of the electron density of palladium. These results are supported by the studies using nickel alloy catalysts [4, 16].

In the phosphorus 2p level for the palladium–phosphorus films, only one peak appeared at about 130 eV which was assigned to phosphorus interacting with palladium. A peak due to phosphorus oxide was hardly evident. The BE of phosphorus 2p shifted from 130.6 to 130.2 eV with increasing phosphorus concentration. On the other hand, the BE of palladium 3d5/2 was 335.7 eV in the pure palladium metal. Its BE in the palladium–phosphorus films gradually increased with increasing phosphorus concentration and steeply increased to 336.2 eV near 25 at % of phosphorus (Fig. 7). This suggests that phosphorus interacts with palladium and that phosphorus accepts electrons from palladium, resulting in the low electron density of palladium. Fig. 8 shows the v.b. spectra for the palladium–phosphorus films with various compositions. Below 15 at % of phosphorus, the v.b. spectra were similar to that for the palladium–boron films. The position of the main peak was also unchanged with the phosphorus concentration. At 25 at % of phosphorus, the peak position, however, shifted to the higher BE side and the peak became narrower. This phenomenon was not observed for the palladium–boron films. The shape of the v.b. spectra for $Pd_{75}P_{25}$

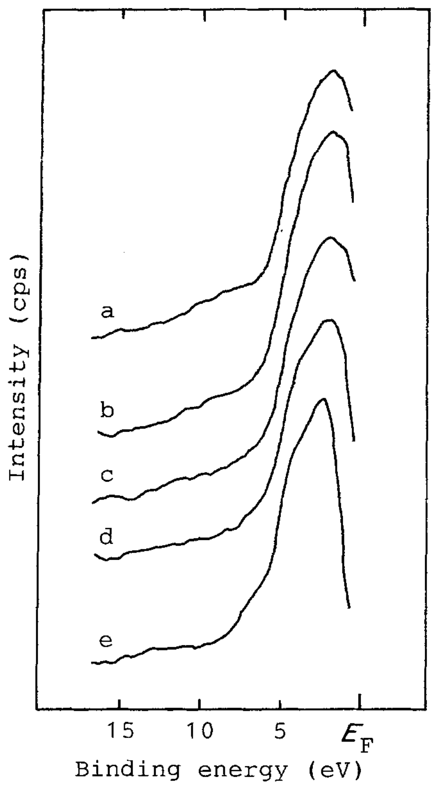

Figure 8 X-ray photoelectron spectra of palladium v.b. for the palladium–phosphorus films. (a) Pd_{100}, (b) $Pd_{98}P_2$, (c) $Pd_{94}P_6$, (d) $Pd_{88}P_{12}$, (e) $Pd_{75}P_{25}$.

film suggests the low electron density of palladium in view of the core level BE shifts.

V.b. spectra of palladium for many palladium alloys in XPS were investigated by Fuggle *et al.* [17]. Partner elements in the alloys were, for example, Al, Ti, V, Ta, La, Th, and Ce and were more electropositive than palladium. In their study, the v.b. spectra shifted to the higher BE side and their full widths at half maximum (FWHM) became narrower with increasing second element concentration. For instance, the BE of v.b. was 4.8 eV and its FWHM was 1.8 eV for $PdAl_3$ alloy. They suggested that such changes indicated the filling of the palladium 4d bands. These observations are in disagreement with our results for the palladium–phosphorus films. This reason may be contributed to the difference between metal and metalloid as the second element.

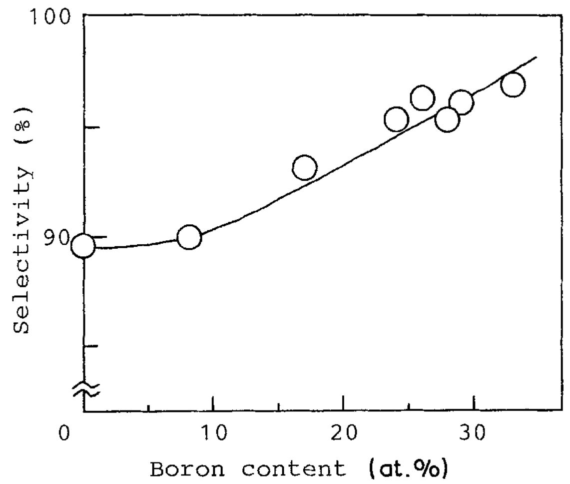

Figure 9 Dependence of the selectivity for the partial hydrogenation of cyclopentadiene over the palladium–boron films on the boron concentration.

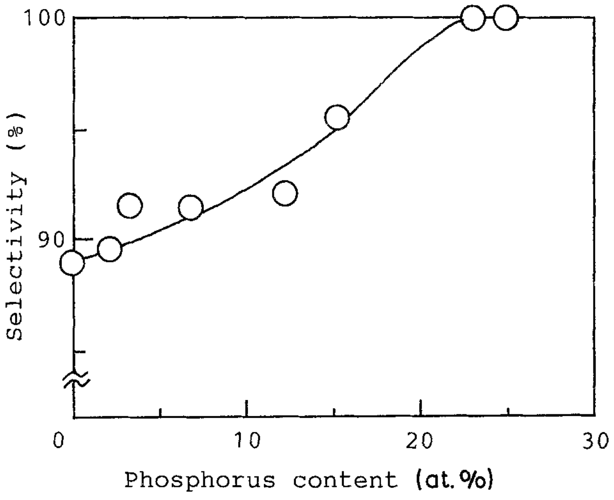

Figure 10 Dependence of the selectivity for the partial hydrogenation of cyclopentadiene over the palladium–phosphorus films on the phosphorus concentration.

3.4. Hydrogenation of olefins

A surface area of the film was too small to be measured by a BET method. Then, the geometrical surface area of the substrate ($9.7\,cm^2$) was substituted for the real surface area of the films. The highest activity per surface area was obtained over the pure palladium film and it was $1.2 \times 10^{-8}\,mol\,sec^{-1}\,cm^{-2}$ in the hydrogenation of 1,3-butadiene, $8.5 \times 10^{-9}\,mol\,sec^{-1}\,cm^{-2}$ in that of cyclopentadiene, and $6.2 \times 10^{-10}\,mol\,sec^{-1}\,cm^{-2}$ in that of acetylene. The activity steeply monotonously decreased with the enhancement of the second element (boron, phosphorus) concentration.

The selectivity for partial hydrogenation was evaluated by the extrapolation to 0% conversion of the product distribution curve. Figs 9 and 10 show dependences of the selectivity for cyclopentene on the second element concentration in the hydrogenation of cyclopentadiene over the palladium–boron and the palladium–phosphorus films, respectively. The selectivity was satisfactorily high (about 90%) even over the pure palladium film and further monotonously increased with increasing second element concentration. The selectivity reached 96.7% over $Pd_{67}B_{33}$ film and 100% over $Pd_{75}P_{25}$ film. In a study using a colloidal palladium supported on a chelate resin [18], the selectivity for the partial hydrogenation of cyclopentadiene was 97.1% for a batch reactor in a liquid phase and 96% in a gas phase using a closed circulation system. In another study using a $Cu–Al_2O_3$ aerogel catalyst [19], the selectivity was 100% for an integral plug flow reactor. The better results are obtained in our investigation in the gas phase.

Fig. 11 shows dependences of the selectivity for butenes in the hydrogenation of 1,3-butadiene and that for ethylene in the hydrogenation of acetylene on the boron concentration over the palladium–boron films. In the hydrogenation of 1,3-butadiene, the selectivity raised with increasing boron concentration below 20 at % of boron and dropped above 20 at % of boron in contrast with the case of cyclopentadiene.

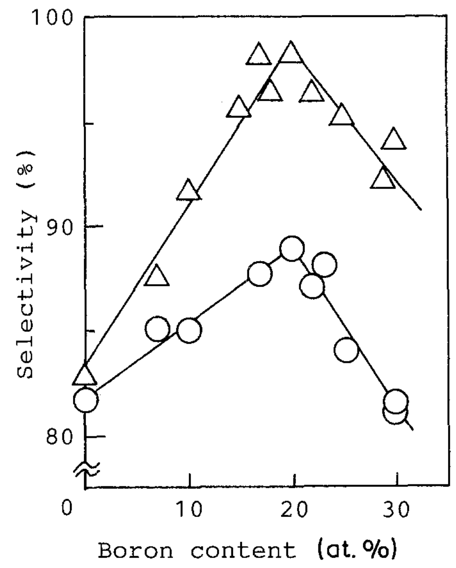

Figure 11 Dependence of the selectivity for the partial hydrogenation of 1,3-butadiene (△) and acetylene (○) over the palladium–boron films on the boron concentration.

The maximal selectivity was 97.1%. In the hydrogenation of acetylene, the selectivity had a maximum at about 20 at % of boron in analogy with the case of 1,3-butadiene and the maximal selectivity was 89.0%.

The change in the selectivity for the partial hydrogenation is assumed to be explained by the ensemble and the ligand effect of the palladium–(boron, phosphorus) films. According to the investigations using the single crystal surfaces of noble metals [10, 11, 20, 21], it is readily supposed that the ensemble size of palladium becomes small when boron or phosphorus is even slightly added to the pure palladium film. This is also suggested by the steep decrease in the hydrogenation activity with the boron or phosphorus concentration. Since the small ensemble size of palladium causes the decrease of the number of the adsorptive site of hydrogen [22], diolefins and acetylene are considered not to be readily hydrogenated up to paraffins. The formation of monoolefins would be eventually promoted, resulting in the enhancement of the selectivity for the partial hydrogenation.

For the ligand effect, when the electron density of palladium is decreased by alloying such as the palladium–phosphorus film alloys, the adsorption ability of diene becomes much larger than that of monoene [4]. Therefore, diene would adsorb on palladium in preference to monoene. The adsorbed monoene, which is produced by the hydrogenation of diene, would be apt to be replaced by diene. The high selectivity for the partial hydrogenation is finally obtained.

In the hydrogenation of 1,3-butadiene and acetylene over the palladium–boron films, the ensemble effect preferentially seems to influence the selectivity below 20 at % of boron. The selectivity was considered to be increased by the decrease of the ensemble size of palladium in this region. However, since the electron density of palladium increased in the palladium–boron films, the high electron density of palladium decreased the selectivity above 20 at % of boron. Therefore, the maximal selectivity was obtained in the hydrogenation of 1,3-butadiene and acetylene over the palladium–boron films. However, the selectivity to cyclopentene in the hydrogenation of cyclopentadiene monotonously increased with increasing boron concentration. The adsorption ability of cyclopentadiene is known to be much larger than that of cyclopentene because of the very large K_D/K_E ratio, which K_D and K_E are the adsorption equilibrium constants of cyclopentadiene and cyclopentene, respectively [18]. Therefore, the electronic state of palladium is presumed to be unlikely to influence the selectivity for the partial hydrogenation of cyclopentadiene. In the palladium–phosphorus films, both the changes in the ensemble size and the electronic state of palladium is deduced to be favourable for partial hydrogenation. Accordingly, a better selectivity for cyclopentene over the palladium–phosphorus films was obtained than over the palladium-boron films. In this way, the alteration in the selectivity could be explainable by the ensemble and the ligand effect of the palladium–(boron, phosphorus) films.

4. Conclusions

The palladium–(boron, phosphorus) thin films with various composition were prepared by the RF sputtering method. Palladium fcc structure is broken by adding boron or phosphorus to palladium and palladium–boron films above 29 at % of boron and the palladium–phosphorus films above 25 at % of phosphorus become amorphous. Boron, which very weakly interacts with palladium, donates electrons to palladium in the palladium–boron films, resulting in the high electron density of palladium. Phosphorus accepts electrons from palladium in the palladium–phosphorus films, resulting in the low electron density of palladium. The palladium–(boron, phosphorus) films show a very high selectivity for the partial hydrogenation of diolefins and acetylene. In particular, the palladium–boron films have a peculiar structure (Fig. 2c) which shows the high selectivity for partial hydrogenation of 1,3-butadiene and acetylene. The change in the selectivity can be explained by the ensemble and the ligand effects, that is, the structure and the electronic state of the palladium–(boron, phosphorus) films. The high selectivity for partial hydrogenation is attributable to the small ensemble size of palladium and its low electron density. Therefore, the alloying of palladium with phosphorus may be preferable for the partial hydrogenation of diolefins.

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