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The Effect of the Heat Treatment of Pd Thin Film Alloy on the Hydrogenation of Olefins

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Pd–(B, P) thin film alloys have been prepared by an RF sputtering method. Before heat treatment, the selectivity for the partial hydrogenation of olefins increased with the increase in the B or P concentration in the Pd–(B, P) films. After the heat treatment, on the other hand, the selectivity for the partial hydrogenation was reduced over the Pd films with a low B or P concentration. However, in the case of the Pd films with a high B or P concentration, the selectivity was enhanced by the heat treatment. The high selectivity after the heat treatment was explainable in terms of the small ensemble size, the low electron density of Pd, and the appearance of a Pd_3B, $Pd_{4.8}P$, or Pd_5P_2 phase in the Pd films with a high B or P concentration. A sputtered film is known to have a columnar structure. This columnar structure was deduced to be controlled both by the alloying of Pd with B or P and by the heat treatment, so as to exhibit the high selectivity for the partial hydrogenation of olefins.

It is well-known that palladium shows a high selectivity in the hydrogenation of diolefins and acetylenes to monoolefins[1] and so is extensively utilized in industrial processes. Alloyed palladium catalysts are often used in order to enhance the properties of palladium by alloying, e.g., Pd–Pb,[2] Pd–Cu,[3–5] Pd–Au,[6] and Pd–Sn[7] alloys.

In a previous investigation,[8] boron (B) and phosphorus (P) were employed as partner elements of Pd alloys; Pd–(B, P) thin film alloys with various compositions of B or P could easily be prepared by changing the RF sputtering conditions. Since boron and phosphorus acted as the electron donor and the acceptor in the Pd alloys respectively, the electronic state of palladium could easily be modified by alloying with B or P. The palladium in the Pd–B alloys was in a high electron density, while the palladium in the Pd–P alloys was in a low density. The change in the electron density of Pd affected the selectivity for the partial hydrogenation of olefins. When the electron density of Pd was decreased by alloying by, for example, the Pd–P alloys, the selectivity was considered to be raised by the enhancement of the difference in the adsorption abilities of diene and monoene.[9] On the other hand, the ensemble effect in the alloy must be considered as well.[10] The ensemble size of Pd is invariably decreased by alloying with B or P, according to the results of investigations using the single-crystal surfaces of noble metals.[11–14] Since the small ensemble size of Pd caused a decrease in the number of adsorptive sites of hydrogen,[15] diolefins and acetylene were considered not to be readily hydrogenated up to paraffins, resulting in an enhancement of the selectivity for the partial hydrogenation. In the Pd–(B, P) alloys, the selectivity of the partial hydrogenation was controlled by the ensemble and by the ligand effect.

Thornton[16] reported that the structure of a sputtered film consisted of an aggregate of tapered columnar crystallites and that each column was separated by grain boundaries or voids so that the surface of film was not flat. The surface microstructure of the columnar crystallites is assumed to influence the catalysis by the film. Annealing by heat treatment would change the microstructure of the films. In this study, the effect of the heat treatment on the activity and the selectivity in the partial hydrogenation of olefins was examined in terms of the surface microstructure and the electronic state of the Pd film alloys.

Experimental

The Pd–(B, P) alloys were prepared using the RF sputtering method; the details of the film preparation were described in previous reports.[9,17] A Pd plate (99.95%) was used as a target for the sputtering. The 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 with a high purity of Ar (99.9995%) at a pressure of 0.05 Torr and $B_2H_6+H_2$ for the preparation of Pd–B films or a mixed gas of Ar and PH_3+H_2 for the preparation of Pd–P films. The glow discharge was carried out under various B_2H_6 or PH_3 partial pressures. The Pd thin film alloys were deposited on Pyrex glass substrates opposite the target. The average film thickness was 200 nm for all the Pd thin film alloys.

The hydrogenation of diolefins (cyclopentadiene and 1,3-butadiene) and acetylene was carried out over the Pd–(B, P) films at 273 K using a closed circulation system. The H_2/hydrocarbon ratio and the total pressure in the system were controlled to 6 and 140 Torr respectively. The products of the hydrogenation were analysed by means of a gas chromatograph (Shimadzu GC-8A) with a thermal conductivity detector. The columns used were a 3 m 2,4-dimethylsulfolane column for the hydrogenation of cyclopentadiene, a 5 m sebaconitrile column for 1,3-butadiene, and a 3 m activated charcoal column for acetylene. The heat treatment of the Pd thin film alloys was carried out at 573 K for 1 h in a vacuum ($<10^{-3}$ Torr (1 Torr=133.322 Pa)). The surface analysis and the hydrogenation activity and selectivity were examined again after the treatment. The surface analysis was performed using a Shimadzu VD-1 X-ray diffractometer and a Shimadzu ESCA-750 X-ray photoelectron spectrometer.

Results and Discussion

Effect of the Heat Treatment on the Hydrogenation of Olefins. The highest activity in the hydrogenation was obtained over the pure Pd film. However, it steeply decreased with an increase in the B or P concentration. After the heat treatment, the hydrogenation activity decreased by about 1/3. This might be attributable to the decrease in the surface area resulting from the heat treatment.

The selectivity for the partial hydrogenation of cyclopentadiene to cyclopentene changed with the B or P concentration, as is shown in Figs. 1 and 2. Before the heat treatment, as is shown by the solid line, the selectivity was satisfactorily high, even for the pure Pd film, and it further increased with the enhancement of the B or P concentration. The selectivity reached 96.7% for the $Pd_{67}B_{33}$ film and 100% for the $Pd_{75}P_{25}$ film. After the heat treatment, as is shown by the broken line, a selectivity drop was observed for the Pd–B films below 20 atom% of B and for the Pd–P films below 10 atom% of P. However, the selectivity increased in the region of the higher B or P concentration and reached 98.4% for the $Pd_{67}B_{33}$ film and 99.5% for even the $Pd_{85}P_{15}$ film. The selective hydrogenation of cyclopentadiene is a significant process for the utilization of the C_5 fraction in naphtha-cracking products. In the study by Hirai et al.[18] using colloidal Pd supported on a chelate resin, 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 by Chaouki et

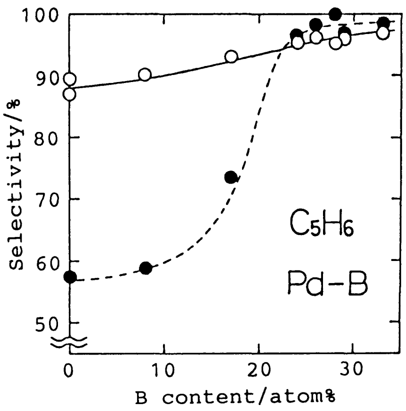

Fig. 1. Selectivity of the partial hydrogenation of cyclopentadiene as a function of the boron content.
—○—; before heat treatment. ---●---; after heat treatment.

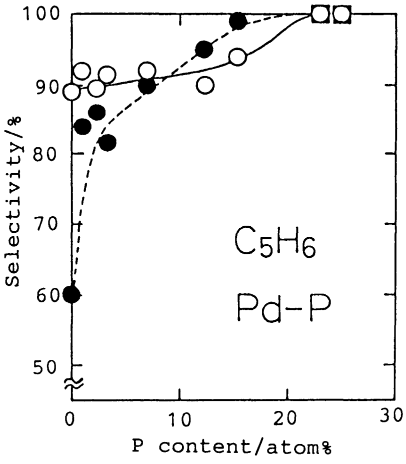

Fig. 2. Selectivity of the partial hydrogenation of cyclopentadiene as a function of the phosphorus content.
—○—; before heat treatment. ---●---; after heat treatment.

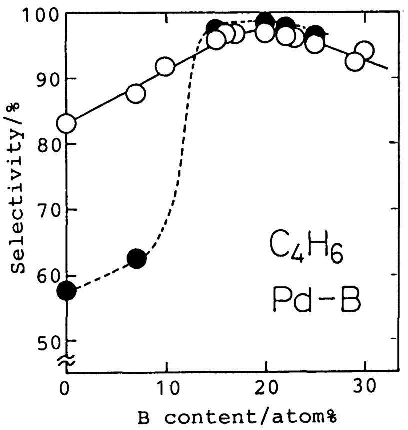

Fig. 3. Selectivity of the partial hydrogenation of 1,3-butadiene as a function of the boron content.
—○—; before heat treatment. ---●---; after heat treatment.

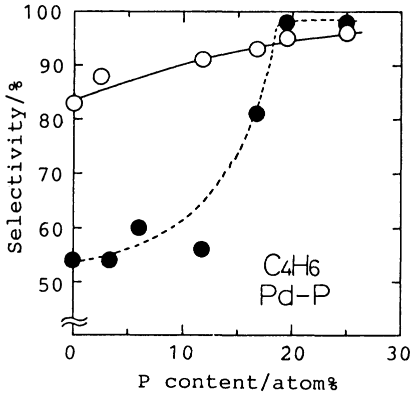

Fig. 4. Selectivity of the partial hydrogenation of 1,3-butadiene as a function of the phosphorus content.
—○—; before heat treatment. ---●---; after heat treatment.

al.[19] using the Cu/Al_2O_3 aerogel catalyst, the selectivity was about 100% for an integral plug flow reactor. Better results were obtained in our investigation in the gas phase.

The selectivity for the partial hydrogenation of 1,3-butadiene to butenes altered with the B or P concentration, as is shown in Figs. 3 and 4. Before the heat treatment, the selectivity was at its maximum at 20 atom% of B in the Pd–B films, and the maximal selectivity was 97.1%. The selectivity in the Pd–P films increased monotonously with the P concentration until it reached 96.0% for the $Pd_{75}P_{25}$ film. After the heat treatment, similar results on the hydrogenation of cyclopentadiene were observed. The selectivity was reduced below 10 atom% of B for the Pd–B films and below 17 atom% of P for the Pd–P films. However, the selectivity was enhanced in the region of a higher B or P concentration, reaching 98.3% for the $Pd_{80}B_{20}$ film and 98.0% for the $Pd_{75}P_{25}$ film.

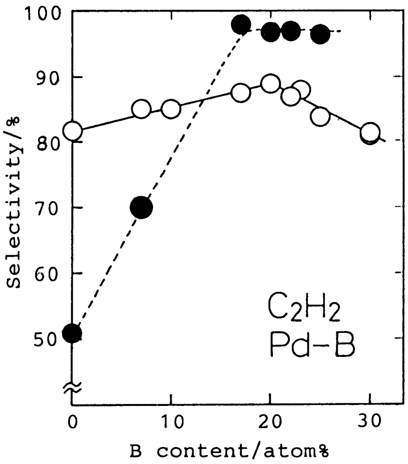

Fig. 5. Selectivity of the partial hydrogenation of acetylene as a function of the boron content. —○—; before heat treatment. ---●---; after heat treatment.

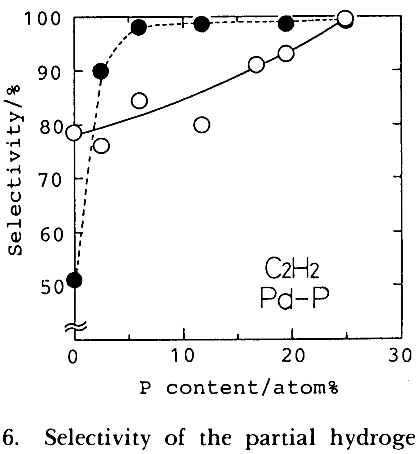

Fig. 6. Selectivity of the partial hydrogenation of acetylene as a function of the phosphorus content. —○—; before heat treatment. ---●---; after heat treatment.

The selectivity for the partial hydrogenation of acetylene to ethylene changed with the B or P concentration, as is shown in Figs. 5 and 6. With the Pd–B films, the selectivity before the heat treatment was at its maximum at 20 atom% of B, much as in the hydrogenation of 1,3-butadiene, and the maximal selectivity was 89.0%. In the case of the Pd–P films, the selectivity increased with the increase in the P concentration. After the heat treatment, analogous to the hydrogenation of cyclopentadiene and 1,3-butadiene, the selectivity dropped in the region of a lower B or P concentration. However, it was raised in a higher B or P concentration range. The selectivity reached 98.0% for the $Pd_{84}B_{16}$ film and 99.0% for the $Pd_{75}P_{25}$ film. The partial hydrogenation of acetylene has been investigated for the sake of the commercially significant ethylene formation and the purification of ethylene by hydrogenating the acetylene contaminant. A higher selectivity of ethylene was obtained over the Pd–(B, P) films after the heat treatment in comparison to the conventional supported Pd catalysts[20] and other Pd alloy catalysts.[2–6]

Change in the Film Structure. The structure of the Pd thin film alloys was investigated by using X-ray diffraction analysis (XRD). Below 15 atom% of B in the Pd–B films, two peaks appeared at about 40 and 46 degrees; they corresponded to the Pd(111) and Pd(200) faces respectively. Below 25 atom% of P in the Pd–P films, only one peak appeared at about 40 degrees. In this region, the structure of the Pd–(B, P) films was found to be analogous to Pd fcc structure. In the higher B or P concentration range, three small peaks typically appeared at 38.6, 39.4, and 40.5 degrees in the Pd–B films (Fig. 7), while no peak was recognized in the Pd–P films (Fig. 8). The peculiar structure in the Pd–B films was found to resemble the Pd_3B crystal,

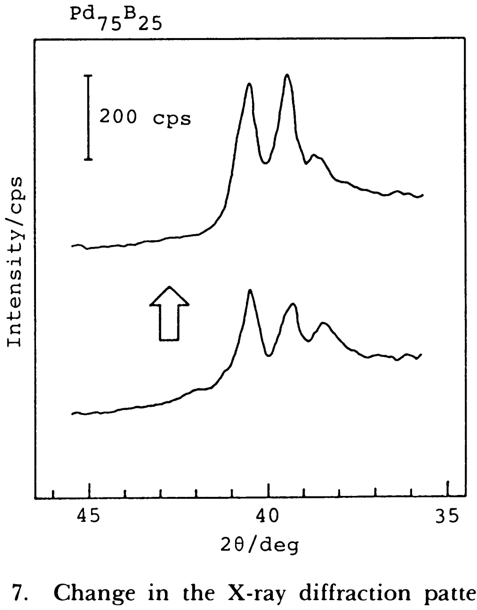

Fig. 7. Change in the X-ray diffraction pattern of $Pd_{75}B_{25}$ film by the heat treatment.

one of the stable palladium boride crystals,[21] whereas the structure of the Pd–P films was an amorphous structure.

Table 1 tabulates the changes in the peak positions and the full widths at half maximum (FWHM) of the XRD peak attributable to the Pd(111) face for the Pd–(B, P) films with the low B or P concentration upon heat treatment. After the heat treatment, the XRD peaks of the Pd fcc-like structure in the lower B or P concentration range increased in its intensity and became narrower. This indicates that Pd fcc structure develops in the Pd–(B, P) films with a low B or P concentration after the heat treatment. On the other hand, the small three peaks in the Pd–B films with a high B concentration increased a little at the same position after the heat treatment (Fig. 7). This reveals that the Pd_3B-like structure of the Pd–B film with a high B concentration grows slightly after the treatment. In the Pd–P films with a high P concentration, new six peaks appeared—at 33.0, 37.5, 38.2, 39.2, 40.0, and 43.0 degrees—after the heat treatment (Fig. 8). These peaks indicate the appearance of new crystalline Pd–P phases. The structure of the Pd–P film is assumed to be a mixed phase of the $Pd_{4.8}P$[22] and the Pd_5P_2[23] crystals, which are the stable palladium phosphide crystals. In the region of a high B or P concentration, the Pd alloy crystal was found to grow after the heat treatment, especially the amorphous structure in the Pd–P film crystallized. No growth of Pd fcc structure or separation of a Pd phase and a B or P phase were observed after the treatment in the region of a high B or P concentration.

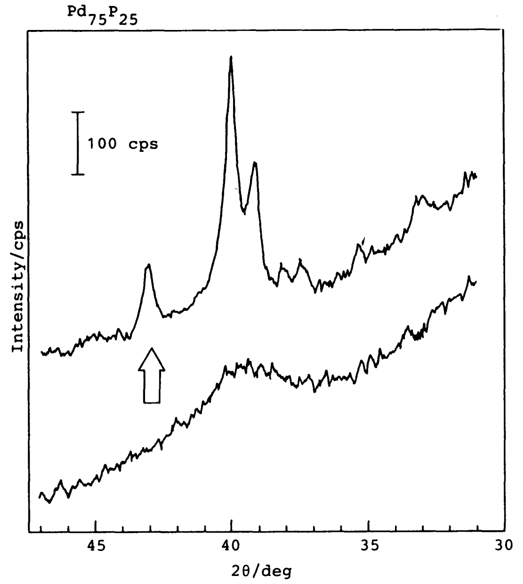

Fig. 8. Change in the X-ray diffraction pattern of $Pd_{75}P_{25}$ film by the heat treatment.

Change in the Film Composition and the Electronic State. The surface composition and the electronic state were evaluated by the use of an X-ray photoelectron spectroscope (XPS) equipped with an Ar-ion gun. The films were etched by Ar^+ for 30 sec, viz., by about 6 nm. The film composition was evaluated on the basis of the XPS peak area ratios of Pd3d5/2 to B1s or P2p level. The film composition and the binding energies (BE) of the surface and the bulk were compared before and after the heat treatment. These results are tabulated in Table 2. BE was

Table 1. Alterations in the XRD Peak Position and the Full Width at Half Maximum (FWHM) of the Pd(111) Face by the Heat Treatment

	Before		After	
	2θ/deg	FWHM/deg	2θ/deg	FWHM/deg
Pd_{100}	40.1	0.64	40.1	0.58
$Pd_{94}B_6$	40.0	0.65	40.1	0.60
$Pd_{87}B_{13}$	39.7	0.85	39.8	0.78
Pd_{100}	40.1	0.64	40.1	0.58
$Pd_{94}P_6$	39.7	0.67	39.8	0.63
$Pd_{88}P_{12}$	39.7	0.92	39.9	0.85

Table 2. Alterations in the Film Composition and the Surface Satate for Pd–(B, P) Films by the Heat Treatment

Pd–B		Surface			Bulk		
		Comp.	Pd3d5/2	B1s	Comp.	Pd3d5/2	B1s
Low	Before	$Pd_{96}B_4$	335.7	188.9	$Pd_{94}B_6$	335.7	188.8
	After	$Pd_{91}B_9$	335.6	188.8	$Pd_{93}B_7$	335.7	188.8
Middle	Before	$Pd_{68}B_{32}$	335.5	188.8	$Pd_{78}B_{22}$	335.7	188.7
	After	$Pd_{51}B_{49}$	336.0	188.9	$Pd_{64}B_{36}$	335.9	188.7
High	Before	$Pd_{35}B_{65}$	335.5	188.9	$Pd_{63}B_{37}$	335.7	189.0
	After	$Pd_{16}B_{84}$	336.6	188.2	$Pd_{31}B_{69}$	336.5	188.7
Pd–P				P2p			P2p
Low	Before	$Pd_{77}P_{23}$	335.6	130.4	$Pd_{97}P_3$	335.7	130.6
	After	$Pd_{91}P_9$	335.5	130.4	$Pd_{97}P_3$	335.7	130.7
	Before	$Pd_{66}P_{34}$	335.8	130.1	$Pd_{83}P_{17}$	336.0	130.2
	After	$Pd_{80}P_{20}$	335.9	130.4	$Pd_{83}P_{17}$	335.9	130.3
Middle	Before	$Pd_{66}P_{34}$	336.2	130.2	$Pd_{76}P_{24}$	336.2	130.2
	After	$Pd_{70}P_{30}$	336.7	130.4	$Pd_{76}P_{24}$	336.2	130.4

corrected by the use of a contaminant carbon (C1s=285.0 eV).

In the Pd–B films with a low B concentration, little enrichment of boron to the surface was observed. However, the extent of enrichment increased with the increase in the B concentration. The surface composition of Pd was only 16 atom% in a high B concentration. On the contrary, the surface enrichment of phosphorus in the Pd–P films was not as notable as that of boron. In the region of a low P concentration, the somewhat high P concentration at the surface was attributable to the adsorption of PH_3 on the surface, for the P concentration steeply reduced after only 5 s etching. It was found that the mobility of P in the film was smaller than that of B.

The BE of the Pd3d5/2 level for the Pd–B films was unchanged by the heat treatment in a low B concentration. However, the BE in a high B concentration shifted to the higher BE side after the heat treatment. This obviously indicates that the electron density of Pd in the Pd–B films with a high B concentration becomes lower after the heat treatment, although B donates electrons to Pd before the heat treatment. On the other hand, the BE of the Pd3d5/2 level for the Pd–P films was increased with the enhancement of the P concentration even before the heat treatment. After the heat treatment, it was slightly shifted to the higher BE side in a high P concentration. The electron density of Pd was also found to decrease further in the Pd–P films with a high P concentration after the heat treatment.

Model of the Pd Thin Film Alloy. The following model may explain the above results. As has been described above, the selectivity for the partial hydrogenation of olefins over the Pd alloys can be explained in terms of the ensemble and the ligand effect. The smaller ensemble size and the lower electron density of Pd for the Pd thin film alloys would result in the higher selectivity of the partial hydrogenation.

In a lower B or P concentration range, it can readily be supposed that the surface defects, i.e., the grain boundaries in the columnar structure, etc., are decreased by the heat treatment and that the columns are collapsed to large ones. Therefore, the ensemble size of Pd on the surface of the film would become larger, resulting in the decrease in the selectivity of the partial hydrogenation. Because the electronic state of Pd is unchanged by the heat treatment in a low B or P concentration, the decrease in the selectivity seems to be mainly caused by the increase in the ensemble size of Pd. In a higher B or P concentration range, B or P prevents the growth of the column during the heat treatment because the proportion of B or P is increased in the film. The ensemble size, therefore, would be almost unaltered, even after the heat treatment. This is supported by the results of XRD. The Pd_3B, $Pd_{4.8}P$, and Pd_5P_2 phases formed by the heat treatment may exhibit a high selectivity of the partial hydrogenation. Furthermore, the results of the XPS measurement suggest that the high selectivity after the heat treatment is attributable to the low electron density of Pd in the region of a higher B or P concentration.

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