

Surface Properties of Air-Exposed α -Ti-Pd Alloys via XPS and Cross-Coupling Reaction

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To identify the reasons why Ti-Pd alloys for hydrogen storage materials show good hydrogenation properties, X-ray photoelectron spectroscopy and the Suzuki-Miyaura cross-coupling reaction were used to investigate a small amount of Pd added Ti-Pd alloys. Pd in or on Ti oxide films is in a valence state of 0 (Pd^0). Catalytic activity was shown by Pd^0 in the Suzuki-Miyaura cross-coupling reaction. Therefore, the enhanced hydrogenation properties of Ti-Pd alloys for hydrogen storage materials is due to Pd^0 's catalytic activity in dissociating hydrogen molecules. In addition, the potential catalytic activity of Ti-Pd alloys was shown to be based on a Pd catalyst.

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1. Introduction

In the pursuit of hydrogen economy, several studies have explored the possibility of greater energy efficiency for hydrogen storage materials. Among the general hydrogen storage materials, Ti-based hydrogen storage materials are inexpensive and can absorb and desorb hydrogen at low pressures and temperatures.¹⁻³⁾ The advantages of Ti-based hydrogen storage materials are that it is practical and affordable for stationary applications.^{4,5)} Despite these advantages, Ti-based hydrogen materials generally need to be initially activated at high temperature in a vacuum because of their stable passive oxide film, which forms after exposure to air.⁶⁻⁸⁾ To mitigate this activation condition, some studies reported that Pd added Ti based materials (e.g., TiFe and $\text{Ti}_{33}\text{V}_{33}\text{Cr}_{34}$) showed an improvement in their initial activation property due to the catalytic effect of the presence of Pd on the material surface.⁹⁻¹¹⁾

According to its surface properties, Pd in or on Ti oxide films might assist in dissociating hydrogen molecules to hydrogen atoms. Based on this assumption, the outermost Pd may produce a catalytically active reaction site for molecular transformation. According to the Ti-Pd alloy corrosion model, a Pd crystallite layer was exposed on the surface of a Ti oxide film.¹²⁾ In this model, the outermost Pd crystallite layer should serve as a catalyst. Therefore, this study used X-ray photoelectron spectroscopy (XPS) and a Suzuki-Miyaura cross-coupling reaction¹³⁾ to investigate the surface properties of Pd, which was added to a Ti alloy (i.e., a Ti-Pd alloy).

2. Experimental Procedure

The Ti-Pd alloys were fabricated by an arc-melting method. Their initial activation properties were evaluated using a Sievert's type apparatus. The selected Pd concentrations were 0.2, 0.5, and 1.0 mol% (hereafter abbreviated as

Ti-Pd alloys: i.e., 0.2Pd, 0.5Pd, or 1.0Pd) because a small amount of Pd was also effective in decreasing the activation time.^{8,14)} An X-ray diffractometer (XRD) and XPS were used to investigate phase identification and chemical surface states. A Suzuki-Miyaura cross-coupling reaction between iodobenzene and 4-methylphenylboronic acid was conducted with air-exposed and hydrogenated Pd-Ti alloys as catalysts.

The cross-coupling reaction products were characterized using several analytical methods. Gas chromatography-mass spectrometry (GC-MS) and GC with flame ionization detection (GC-FID) analyses were performed in conjunction with a 0.22 mm \times 25 m capillary column (BP-5). ^1H NMR spectra were acquired at 400 and 100 MHz in CDCl_3 , with tetramethylsilane as the internal standard. Based on an internal standard, the reaction yields were estimated from the peak areas obtained during GC analyses. All starting materials were commercially available and used without any purification.

Pure Ti buttons were prepared by arc-melting pure sponge Ti (99.7 mass%) prior to making the Ti-Pd alloys. Alloys of x mol% Ti-Pd (where x = 0.2 Pd, 0.5 Pd, or 1.0 Pd) were subsequently produced by arc-melting the pure Ti buttons with varying quantities of pure Pd sheets (99.95 mass%) under Ar using a water-cooled copper hearth. Each alloy was remelted at least 10 times to promote the homogeneity of the composition. A milling machine was used to obtain flake-like specimens from Ti-Pd alloy ingots. In addition, an abrasive cutting machine was used to prepare plate-type specimens for XPS analyses, followed by mechanical polishing with waterproof SiC papers (from #320 to #800) and a 0.04 μm colloidal silica suspension in ultrapure water. After mechanical polishing, the specimens were immediately ultrasonically cleaned while immersed in acetone, using at least three 600 s cleaning sessions. Both flake and plate specimens were stored in a desiccator for at least 86.4 ks to generate a stable surface oxide film.

The hydrogenation properties of the materials prior to activation were examined with a Sievert's type apparatus by heating 500 mg samples in a stainless-steel reactor from

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ambient temperature to 673 K at 5 K min⁻¹ at an initial hydrogen pressure of 3.0 MPa. XPS analyses were performed using Al K α radiation with a 1486.6 eV excitation source. The take-off angle for photoelectron detection was 45° from the specimen surface. Photoelectron peak intensities were estimated by subtracting the background from the spectra according to Shirley's method. Peak fitting and integration of the spectra were performed using a commercial software package (CasaXPS; Casa Software, Teignmouth, UK). Depth profiles were obtained via Ar gas sputtering at a SiO₂-equivalent sputtering rate of 1.2 nm min⁻¹.

Phases were identified both before and after hydrogenation using XRD with Cu K α radiation at a tube voltage of 30 kV and a tube current of 15 mA.

In the Suzuki–Miyaura cross-coupling reaction, a mixture of iodobenzene (**1**, 102 mg, 0.5 mmol), 4-methylphenylboronic acid (**2**, 102 mg, 0.75 mmol), K₂CO₃ (138 mg, 1.0 mmol), and 1.0Pd (24 mg, 0.5 mmol) as the catalyst was stirred in methanol (1 mL) at 393 K for 24 h under Ar. The conversions and yields were estimated from peak areas obtained from GC analysis, based on an internal standard (tridecane). The product, **3**, was obtained in quantitative yield in each case. Following one trial (Table 1, entry 3), the product was isolated by column chromatography (70–230 mesh silica gel, n-hexane/ethyl acetate = 100/1) in 94% yield (79 mg).

White powder, m.p. 47–48°C (lit.¹ 46–47°C), ¹H NMR (400 MHz, CDCl₃, TMS): δ (ppm) = 7.57 (d, 2 H, J = 7.2 Hz), 7.48 (d, 2 H, J = 8.2 Hz), 7.41 (t, 2 H, J = 7.7 Hz), 7.30 (t, 1 H, J = 7.2 Hz), 7.23 (d, 2 H, J = 8.3 Hz), 2.38 (s, 3 H). MS (EI): m/z (%): 168 (100) [M+1], 167 (67), 165 (26), 152 (25), 115 (8).

3. Results and Discussion

The representative relationship between the hydrogen-to-metal ratio and reaction time profile is shown in Fig. 1. After hydrogen was introduced and the reactor heated to 673 K, the hydrogen was slightly absorbed at approximately 0.2 in H/M, which was followed by drastic absorption. The samples were taken out of the stainless-steel reactor before and after the drastic hydrogen absorption reaction. The sample was composed of only α -Ti before the drastic hydrogen absorption

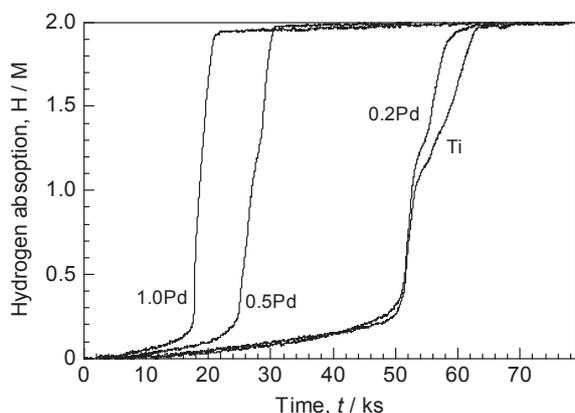


Fig. 1 Relationship between reaction time and hydrogen-to-metal ratios of Ti, 0.2Pd, 0.5Pd, and 1.0Pd.

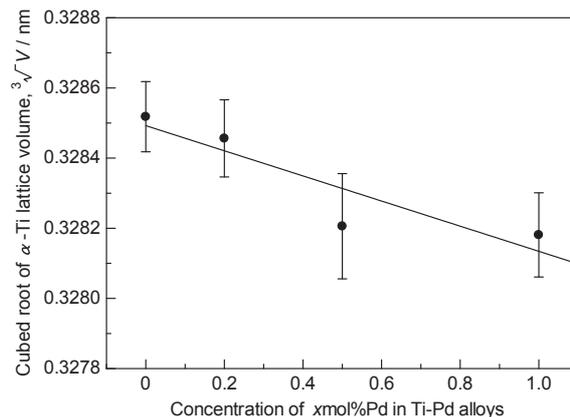


Fig. 2 Cube root of α -Ti lattice volume with Pd concentration in Ti–Pd alloys.

reaction, thereafter the sample transformed into Ti hydride (TiH_{1.924}). As Pd concentrations increase, Ti–Pd alloys show a trend of rapid transformation into Ti hydride.

The lattice parameters of α -Ti were calculated from their XRD profiles. The cube root of α -Ti lattice volume decreased with increase in Pd concentration (Fig. 2). Because the atomic radius of Pd (0.137 nm) is smaller than that of Ti (0.147 nm),¹⁵ this resulting decrease in the α -Ti lattice volume can be accounted for in the formation of a substitutional solid solution alloy.

The Ti 2p spectra of Ti and 1.0 Pd were divided into four peaks, which correspond to the valence states of 0 (Ti⁰), 2 (Ti²⁺), 3 (Ti³⁺), and 4 (Ti⁴⁺), respectively. The Ti spectra corresponded well to air-exposed Ti alloy for approximately 1 week.¹⁶ The peaks were deconvoluted based on their full width at half maximum results. Figure 3 shows the XPS Ti 2p spectra of mirror-polished Ti and 1.0Pd. When these two spectra were compared, the Ti⁰-related shoulder was detected in Ti, whereas the peak was not detected in 1.0Pd. Figure 4 shows the relationship between the ratio of integrated intensity of Ti⁰ peak in Ti as a function of Ar gas sputtering time. The sputtering rate was equivalent to a SiO₂ sputtering rate of 1.2 nm min⁻¹. In this region, the ratio of Ti⁰ in Ti was higher than that in 1.0Pd. In addition, the ratio in Ti gradually increased at 180 s whereas that in 1.0Pd was increased at

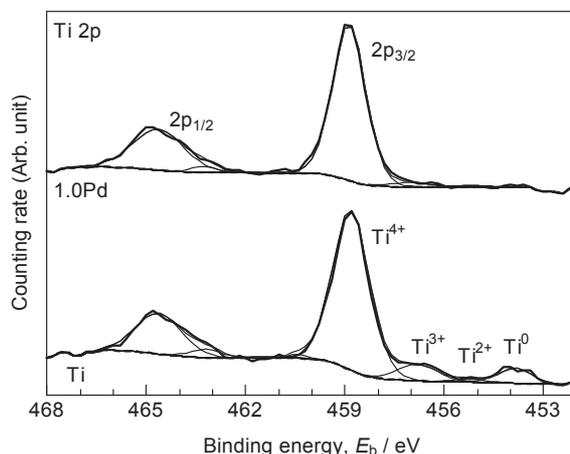


Fig. 3 Ti 2p spectra from mirror-polished Ti and 1.0Pd.

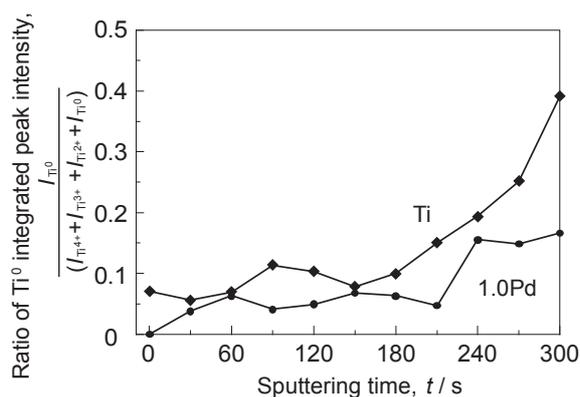


Fig. 4 Relationship between ratio of integrated intensity of Ti^0 peak as a function of Ar gas sputtering time for pure Ti and 1.0Pd.

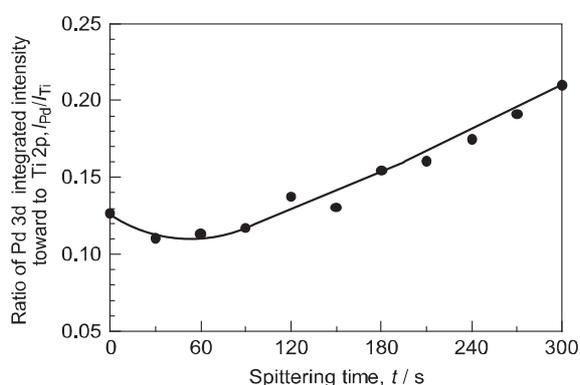


Fig. 5 Ratio of Pd 3d spectra integrated intensity toward to Ti 2p intensity as a function of Ar gas sputtering time.

240 s. These results suggest that Ti oxide layer of 1.0Pd was thicker than that of Ti because the two samples were mechanically polished at the same time and stored in the same condition. Figure 5 shows the ratio of Pd 3d spectra integrated intensity to Ti 2p intensity as a function of Ar gas sputtering time. The Pd concentration temporarily decreased with increased sputtering time and Pd concentration subsequently increased. Figure 6 shows the Pd 3d spectra in 1.0 Pd at mirror polished, and at 150 s and 300 s of Ar gas sputtering. While 0.5 Pd and 0.2 Pd were also investigated, an adequate intensity of peaks was not detected. For example, the peak intensity on 1.0Pd at mirror polished was very small. As shown in Fig. 6, a valence state of 0 (Pd^0) was detected. After 300 s of Ar gas sputtering, the Pd^0 peak slightly shifted into a positive binding energy state. This positive binding energy shift was also observed in amorphous Ti-Pd alloys.¹⁷⁾ According to the XPS analysis, the positive binding energy shift in Pd occurred with increased alloying Ti concentrations because of the decreased Fermi levels at Pd sites.¹⁷⁾ On the one hand, Pd exists as a substitutional solid solution in α -Ti (Fig. 2) and the Pd 3d doublets shift toward higher binding energy sides in internal areas of Ti (Fig. 6), which suggests that the internal Pd was alloyed with Ti. On the other hand, the Pd 3d doublets on the surface are at a lower binding energy and Ti is oxidized. According to these Pd 3d doublets shifts, Pd might be dealloyed from Ti and Ti oxidized on or in the surface oxide film. As mentioned above, XPS can detect

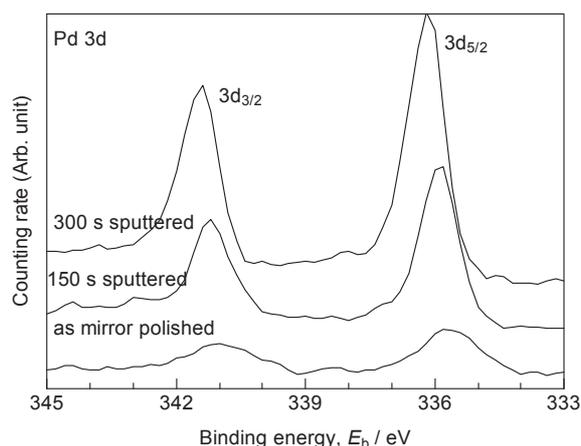


Fig. 6 Pd 3d spectra in 1.0Pd at mirror polished, and at 150 s and 300 s of Ar gas sputtering.

the surface region of the sample; however, the outermost surface could not be analyzed. To identify the presence of Pd^0 , a cross-coupling reaction was conducted with Ti-Pd alloys.

Table 1 shows the conversion rate of iodobenzene (**1**) and the yield rate of 4-methylbiphenyl (**3**) using Ti-Pd alloys, hydrogenated Ti-Pd alloys, and Ti and Pd as a catalyst. The reaction is shown as follows:

Table 1 Catalytic activity of Ti-Pd alloys in the Suzuki-Miyaura cross-coupling reaction.



Entry	Catalyst	Conv.	Yield (%) ^d
1	Ti	<1	n.d.
2	Ti (Hydrogenated)	<1	n.d.
3	0.2 Pd	>99	94 (94) ^b
4	0.2 Pd (Hydrogenated)	>99	95
5	0.5 Pd	>99	>99
6	0.5 Pd (Hydrogenated)	>99	>99
7	1.0 Pd	>99	98
8	1.0 Pd (Hydrogenated)	>99	>99
9	Pd	>99	>99

Reaction conditions: **1** (0.5 mmol), **2** (0.75 mmol), catalyst (0.5 mmol), and K_2CO_3 (1.0 mmol) in MeOH (2.0 mL) at 393 K for 86.4 ks under Ar. a GC yield based on **1**. b Isolated yield.

The Ti-Pd alloys, hydrogenated Ti-Pd alloys, and Pd catalyst gave 4-methylbiphenyl (**3**) in high yield (Table 1). However, the cross-coupling reaction did not proceed in the mixture with pure and hydrogenated Ti. It should be noted that the reaction with Ti-Pd alloy turned out to produce the compound (**3**) at a high yield despite the low occupancy of

Pd site on the surface because the Pd existed with Ti oxide. According to this assumption, an extremely small amount of Pd could work as an active site for the cross-coupling reaction because the catalytically active site was equivalent to less than 0.2% of that for iodobenzene (**1**). In addition, the Ti–Pd alloys did not need pretreatment. Heterogeneous Pd catalysts generally need pretreatment at high temperature under H₂ or Ar for reduction of Pd particles and for removal of sulfur contaminants and the oxygen-containing functional group on the surface due to initial materials such as Pd halide as metal particles and inorganic oxide as a carrier.¹⁸⁾ In addition, heterogeneous Pd catalysts are conventionally synthesized by deposition–precipitation and impregnation methods.¹⁹⁾ During the Suzuki–Miyaura cross-coupling reaction, Pd⁰ was oxidized to Pd²⁺ by the oxidative addition of iodobenzene. The Pd²⁺ was subsequently subjected to transmetalation, which was followed by reductive elimination to give 4-methylbiphenyl as products.¹³⁾ From the above mechanism, the cross-coupling reaction could proceed with the Pd⁰ species. Because the Ti–Pd alloys did not need pretreatment, the Pd⁰ was stably present in or on Ti oxide film.

4. Conclusions

The hydrogenation process of adding a catalytically active element to Ti-based materials with rapidly hydrogenated oxide film has been demonstrated. Despite the thick oxide film of 1.0Pd in Ti–Pd alloy, its hydrogenation rate was faster than that of Ti. XPS analysis detected catalytically active Pd⁰ in the oxide film on 1.0Pd. The Pd⁰ existed on the outermost surface of Ti–Pd alloys because the Suzuki–Miyaura cross-coupling reaction proceeded quantitatively. Therefore, the Ti–Pd alloys can be considered to rapidly transform into Ti hydride because the valence state of Pd⁰ could work dominantly as a catalyst for molecular hydrogen dissociation.

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