

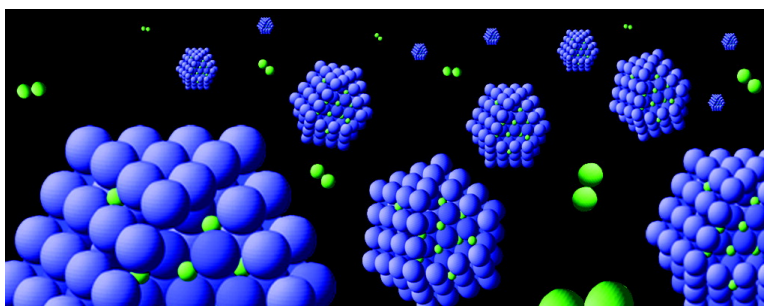
Communication

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## On the Nature of Strong Hydrogen Atom Trapping Inside Pd Nanoparticles

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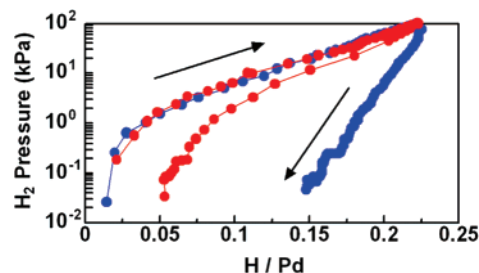
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Hydrogen storage alloys<sup>1</sup> provide one of the best ways to store hydrogen compactly and safely as a consequence of the stability of their hydride.<sup>2</sup> Recently, nanoparticles of such metals have attracted much attention, not only as electronic, magnetic, optical, and catalytic materials<sup>3,4</sup> but also as a new type of hydrogen storage alloys.<sup>5,6</sup> In particular, the hydride of bulk Pd has been intensively investigated because of its high hydrogen storage capacity. Consequently, Pd nanoparticles have been studied as a nanostructured model for the clarification of hydrogen storage properties of metal nanoparticles.<sup>6</sup>

It is reported that the hydrogen pressure–composition (PC) isotherm for Pd nanoparticles having a diameter of 2–4 nm shows a phase transition from solid solution to hydride.<sup>6a–c</sup> It is known that in reversing the process the curve does not completely return back to the starting point in the case of Pd nanoparticles,<sup>6a,b</sup> while for bulk Pd, it is completely reversible.<sup>2b</sup> The origin of this phenomenon has been a puzzle so far.<sup>6a–c</sup>

In this work, we have investigated the hydrogen absorption/desorption hysteresis by means of in situ powder X-ray diffraction (XRD) and solid-state <sup>2</sup>H NMR to clarify the location of hydrogen, surface or body, and its chemical form, molecular, atomic, or as hydride. The present results point out that strongly trapped hydrogen atoms exist inside the Pd nanoparticles due to a strong Pd–H bond formation, resulting in the incomplete recovery of the PC isotherm observed upon the desorption process.

Pd nanoparticles used in this work were prepared by a stepwise growth procedure using a chemical reduction method.<sup>7</sup> The nanoparticles were protected from oxidation by a protective coating of poly(*N*-vinyl-2-pyrrolidone) (PVP), while hydrogen can penetrate through.<sup>5a,6c</sup> Moreover, PVP does not show any adsorption of hydrogen.<sup>6c</sup> Therefore, PVP is a superior protective polymer to investigate the hydrogen storage properties of Pd nanoparticles. The mean diameter of the obtained Pd nanoparticles was found to be 6.1 ± 0.8 nm by transmission electron microscopy (TEM).<sup>8</sup> The hydrogen absorption/desorption behavior up to 101.3 kPa of hydrogen pressure was investigated by measurement of PC isotherms using an automatic PC isotherm apparatus (Suzuki Shokan Co., Ltd). The hydrogen PC isotherms at 303 and 373 K are shown in Figure 1. The hydrogen composition (H/Pd) increases with hydrogen pressure at both temperatures, which shows that Pd nanoparticles absorb hydrogen. The pressure of the plateau-like region, where solid solution (Pd + H) and hydride (Pd – H) phases coexist, was higher than that in bulk Pd; that is, the intermediate pressure of the plateau-like region in the hydrogen absorption



**Figure 1.** PC isotherms of Pd nanoparticles (blue = 303 K, red = 373 K). Isotherm was measured according to the directions of the arrows.

process is ca. 13.3 kPa both at 303 and 373 K,<sup>8</sup> while the equilibrium pressure for bulk Pd is only 2.7 kPa at 303 K and 36.0 kPa at 373 K.<sup>8</sup>

The hydrogen composition under 101.3 kPa of hydrogen pressure at 303 and 373 K was 0.22. In the desorption process, the composition is decreased to 0.15 under vacuum at 303 K and to 0.05 at 373 K. On the other hand, for bulk Pd, the PC isotherm is reversible.<sup>2b</sup> Similar incompleteness of hydrogen desorption in Pd nanoparticles was reported.<sup>6a–c</sup> Several explanations have been proposed for this difference between bulk and nanoparticle. One reasonable explanation is that a fraction of the hydrogen is atomic, which is strongly trapped at some positions of the particles, such as at the surface or inside, and it cannot be dissociated under vacuum at 303 K. To elucidate whether the hydrogen atoms are trapped inside the nanoparticle or on its surface, we performed in situ XRD measurements at the BL02B2 in SPring-8.<sup>8</sup>

Pd nanoparticles showed a diffraction pattern corresponding to the metallic face-centered-cubic (fcc) lattice under different hydrogen pressures. The positions of the diffraction peaks were shifted continuously to the lower-angle side in response to hydrogen pressure.<sup>8</sup> The hydrogen pressure dependencies of the lattice constants at 303 and 373 K were determined by Le Bail fitting to the diffraction patterns and are shown in Figure 2. It can be seen that the lattice constants increase with hydrogen pressure, indicating that Pd atoms within the lattice are forced apart. This can only be a consequence of hydrogen atoms essentially penetrating the inside of the Pd lattice and expanding it. The lattice constant for a hydrogen pressure of 101.3 kPa at 303 K is increased by 0.018 Å relative to the value under vacuum. The lattice constant decreases with hydrogen desorption, and the lattice constant at 0 kPa and 303 K is larger by 0.006 Å than that of the pristine sample, indicating that the lattice constant does not completely return to the same value as in the pristine sample; that is, the lattice constant shows a hysteresis in the course of hydrogen absorption/desorption. This hysteresis behavior is almost the same as that observed in the PC hydrogen adsorption isotherm at 303 K. The lattice constant under vacuum at 373 K is slightly smaller by 0.002 Å than that in

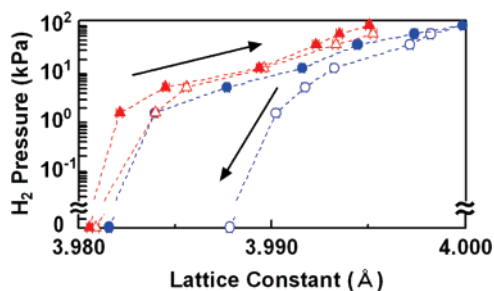
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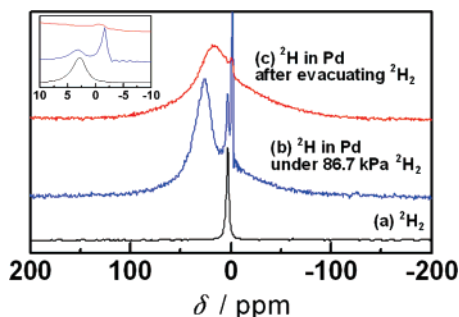
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**Figure 2.** Lattice constants of Pd nanoparticles obtained by fitting of XRD patterns (● absorption at 303 K; ○ desorption at 303 K; ▲ absorption at 373 K; △ desorption at 373 K). Lattice constants were plotted according to the directions of the arrows.



**Figure 3.** Solid-state  $^2\text{H}$  NMR spectra for (a)  $^2\text{H}_2$  gas, the sample of Pd nanoparticles (b) under 86.7 kPa of deuterium gas (c) after evacuating deuterium gas at 303 K. Inset shows expanded spectra.

the pristine sample at 303 K, implying that the disarranged Pd lattice as prepared is ordered by hydrogen absorption/desorption at 303 K.<sup>9</sup> The lattice constant at a hydrogen pressure of 101.3 kPa at 373 K is larger by only 0.014 Å than the value under vacuum and does almost revert to the same value as in the pristine sample at this temperature, indicating that the lattice of the particles is altered along with hydrogen pressure at 373 K. The hysteresis in the lattice constants upon hydrogen absorption/desorption at 373 K is much smaller compared to that at 303 K. The hysteresis of the lattice constant observed for Pd nanoparticles upon the hydrogen absorption/desorption process is similar to that in the PC isotherm, demonstrating that the incomplete recovery of the PC isotherm in the desorption process at 303 K is intrinsic and is related to the hydrogen atoms being strongly trapped inside the Pd lattice, not on the surface.

In order to confirm the hydrogen being trapped inside Pd nanoparticles at 303 K, we performed a solid-state  $^2\text{H}$  NMR measurement for Pd nanoparticles.<sup>8</sup> In the spectrum for  $^2\text{H}_2$  gas (Figure 3a), only a sharp line at 3.0 ppm was observed. In the  $^2\text{H}$  NMR spectra of the samples of Pd nanoparticles under a deuterium pressure of 86.7 kPa (Figure 3b), a broad absorption line at 26.9 ppm and sharp absorption lines at 2.9 and  $-1.5$  ppm were observed, attributing the broad component to absorbed deuterium atoms inside the Pd lattice as hydride (Pd–H) and the sharp components at 2.9 and  $-1.5$  ppm to free  $^2\text{H}_2$  gas and deuterium atoms diffusing and/or exchanged for free deuterium on the Pd surface, respectively.<sup>10</sup> For the spectra of Pd nanoparticles exposed to  $^2\text{H}_2$  gas to a pressure of 86.7 kPa and subsequently evacuated at 303 K (Figure 3c), it should be noticed that the broad signal (centered at 13.4 ppm) of deuterium atoms inside the Pd lattice is still observed while the sharp signal ( $-0.9$  ppm) for deuterium atoms on the Pd surface is considerably reduced due to no existence of free  $^2\text{H}_2$  gas (inset, Figure 3), indicating that hydrogen is retained inside the Pd lattice.

From these results, we conclude that hydrogen atoms are strongly trapped and stabilized in the lattice of Pd nanoparticles, compared

to bulk Pd, resulting in the incomplete recovery of the PC isotherm observed at 303 K. Moreover, the XRD peaks for the Pd nanoparticles were attributed to a single fcc phase, showing that hydrogen is not localized in some part of each nanoparticle but is distributed over the whole of the particle. Strong hydrogen trapping phenomenon observed in Pd nanoparticles provides clues not only for the development of hydrogen storage materials but also for clarification of the catalysis mechanism associated with hydrogen and Pd nanoparticles.

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**Supporting Information Available:** Experimental details, TEM image, PC isotherms, and XRD patterns. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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