

STUDY ON STRUCTURAL CHANGE OF Pd NANOPARTICLES WITH HYDROGEN ABSORPTION/DESORPTION PROCESS

Hydrogen is the cleanest vector of energy, and holds promise for solving the current pollution problem by its use in zero-emission vehicles. To utilize hydrogen as a clean energy source, the development of an effective, safe and stable storage medium is required. Hydrogen-storage alloys can store hydrogen above room temperature because chemical interactions between the alloy and the hydrogen are sufficiently strong for hydrogen accumulation at the ambient temperature. Therefore hydrogen-storage alloys have been studied extensively as a hydrogen-storage medium for many years. However, there has been little research on the dynamics of the structural change following hydrogen absorption/desorption, although it is important for the development of practical hydrogen-storage alloys.

As a new type of hydrogen storage alloy, we have investigated mono-dispersed metal nanoparticles. It is well known that metal nanoparticles exhibit characteristic properties based on the quantum-size effect. Since the hydrogen-storage properties of metals are strongly related to their electronic states, novel hydrogen-storage properties are expected in metal nanoparticles. We have studied the hydrogen-storage properties of Pd nanoparticles, and they are different from those of bulk Pd [1].

In this study, we carried out *in situ* XRD measurements to investigate the dynamics of the structural change of Pd nanoparticles with hydrogen pressure. Poly(*N*-vinyl-2-pyrrolidone) (PVP)-protected Pd nanoparticles were prepared by stepwise growth [2].

A transmission electron microscopy (TEM) image of the prepared PVP-protected Pd nanoparticles is shown in Fig. 1, indicating that an almost constant size of particles was obtained. As shown in the inset, the obtained size distribution of particles is narrow, and this

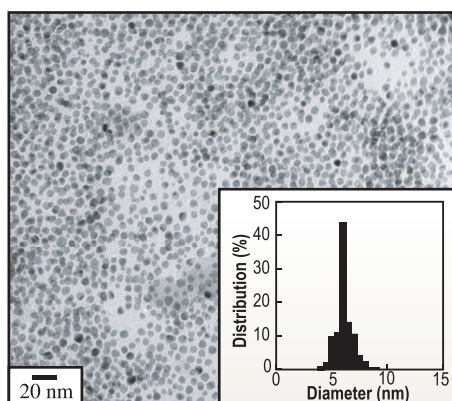


Fig. 1. TEM image of Pd nanoparticles.

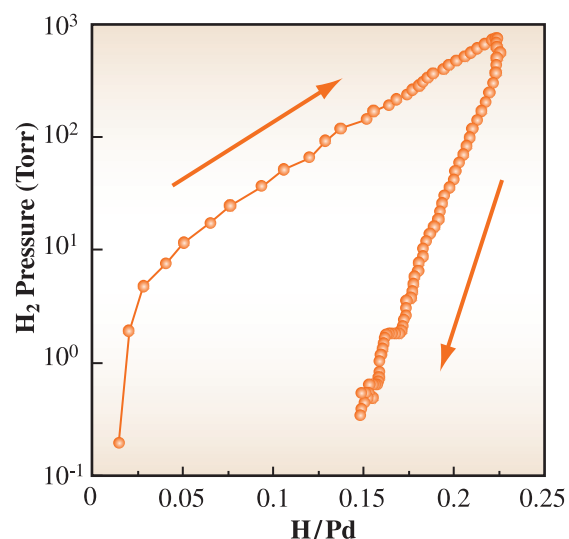


Fig. 2. PC isotherm of Pd nanoparticles at 303 K. The isotherm was measured according the directions of arrows.

indicates that mono-dispersed nanoparticles were synthesized. The mean diameter of the Pd nanoparticles was 6.1 ± 0.8 nm.

The hydrogen absorption/desorption behavior up to 760 Torr hydrogen pressure was investigated by measurement of the hydrogen pressure-composition (PC) isotherm using an automatic PC isotherm apparatus (Suzuki Shokan Co., Ltd.). The hydrogen PC isotherm at 303 K observed for the Pd nanoparticles is shown in Fig. 2. The hydrogen composition (H/Pd) increases with hydrogen pressure, which shows that Pd nanoparticles absorb hydrogen. The ratio of H/Pd at 760 Torr was 0.22. In the desorption process, the total amount of H/Pd decreases with hydrogen decompression, and it is 0.15 at 0 Torr, i.e., the amount did not return to zero under vacuum.

The structure of the Pd nanoparticles was investigated by X-ray powder diffraction method using synchrotron radiation with 51.148 pm wavelength at beamline BL02B2. The X-ray diffraction patterns of the sample sealed in a glass capillary were measured *in situ* under controlled hydrogen pressure in the range 0-760 Torr [3]. Figure 3 shows the *in situ* X-ray diffraction (XRD) patterns of the Pd nanoparticles upon the processes of absorption and desorption of hydrogen. Under vacuum (0 Torr), Pd nanoparticles showed the diffraction pattern from a face centered cubic (fcc) lattice, as for bulk Pd. With increasing hydrogen pressure, diffraction peaks of the Pd nanoparticles shifted continuously to the lower-angle side, indicating that

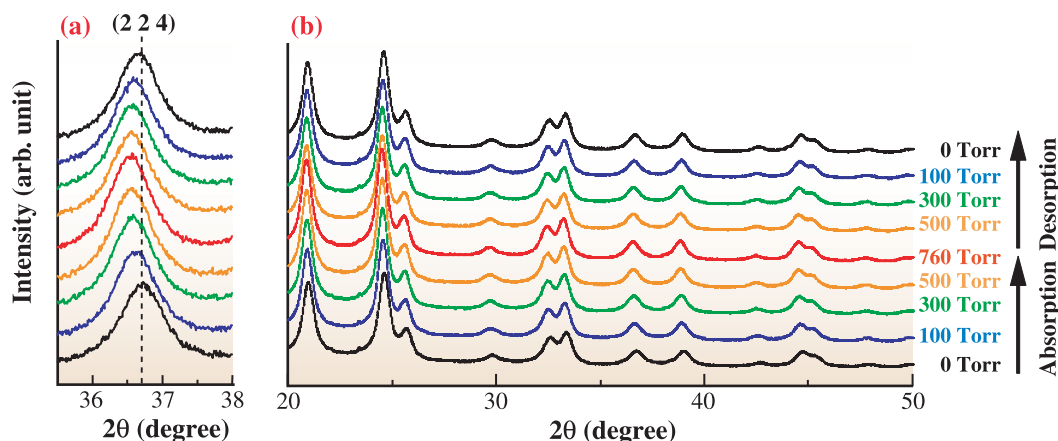


Fig. 3. *In situ* synchrotron XRD patterns for Pd nanoparticle during hydrogen absorption/desorption at 303 K.

hydrogen atoms enter the inside of the Pd lattice and expand it. With decreasing hydrogen pressure, the diffraction peaks of the Pd nanoparticles were shifted continuously to the higher-angle side.

The lattice constant under various hydrogen pressures was estimated by Le Bail fitting to the diffraction patterns, shown in Fig. 4. It can be seen that the lattice constant increases with hydrogen pressure. The lattice constant under a hydrogen pressure of 760 Torr is larger by 0.018 Å than the constant under vacuum, and the extent of lattice expansion for the Pd nanoparticles is smaller than that for the Pd bulk. The lattice constant decreases with hydrogen decompression, and the lattice constant at 0 Torr is larger by 0.006 Å than that of pristine sample, indicating that the lattice constant does not completely revert to the same position as in the pristine sample. Additionally, it should be noted that the lattice constant shows a hysteresis in the course of hydrogen absorption/desorption as observed in the PC isotherm, i.e., the lattice constant during the desorption process is larger than that during the absorption process. The behavior of the hydrogen-pressure dependence of the lattice constant is very similar to that of the PC isotherm, demonstrating that the hydrogen-storage behavior of Pd nanoparticles is correlated with the volumetric change of the Pd nanoparticles. From this result, the incomplete return of the PC isotherm in during desorption process suggests that some of the hydrogen atoms remain as a hydride (Pd-H) in the Pd lattice. Generally, for hydrogen storage alloys, hydrogen absorption/desorption is a first-order phase transition. For example, bulk Pd absorbs hydrogen at 20 Torr and completely desorbs it at 8 Torr at 303 K. Therefore, the existence of hydrogen atoms partially remaining in the Pd lattice under vacuum strongly implies that there exist absorption sites in the Pd nanoparticle with different stability from those of the bulk.

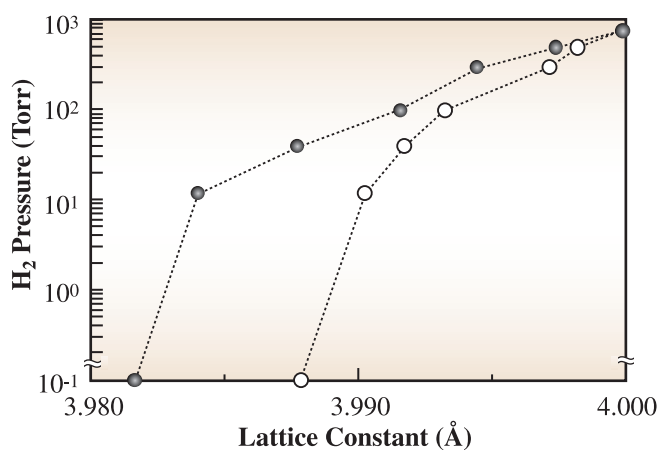


Fig. 4. Hydrogen pressure dependence of lattice constant of Pd nanoparticles (closed circles: absorption, open circles: desorption) obtained by fitting of XRD patterns.

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