Alternation of the Pd Lattice in Nano-Sized-Pd/ZrO$_2$ Composite during Hydrogen Absorption

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Abstract. Structural analysis of high Deuterium absorbed 5 nm Pd particles in dispersed ZrO$_2$ has been carried out using XAFS techniques. X-ray absorption spectra around the Pd K-absorption edge were observed and analyzed. The Pd-Pd bonding distance in the fcc Pd lattice was enlarged by 0.08 ~ 0.09 Å during absorption of deuterium, and it completely reverted to its original state with the release of deuterium while maintaining the crystal lattice symmetry. These changes provide evidence that deuterium locates not on the surface of the Pd particle, but rather within the Pd crystal lattice. XANES spectra clearly indicate that any change in the oxidation state of Pd are not observed, resulting in no reaction of the absorbed Deuterium atoms with Pd atoms. This paper reports the alternation of Pd lattice in nano-sized composite during hydrogen absorption. The possible models of deuterium position in the Pd lattice are also discussed.

Keywords: Hydrogen absorption, Nano-composite materials, XAFS.

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INTRODUCTION

Much study on hydrogen storage materials has been examined to apply for power portable electronic devices using fuel cells. In the search for new materials, nanostructured materials sometimes yield anomalous effects due to their unique nanometer-scale structure. The nano-composite material consisting of ZrO$_2$ and Pd is one of those, in which Pd nanoparticles are formed with the size of about 5 nm through oxidizing amorphous Zr$_{65}$Pd$_{35}$ alloy. We have already confirmed that specific amount of deuterium atoms per unit Pd cell are absorbed through exothermic process and that the absorbing process is reversible. In order to elucidate the absorbing process we have adopted XAFS techniques. As deuterium atoms are too light to detect the XAFS signals, we are compelled to take indirect way to observe the Pd-Pd distance instead of direct Pd-H distance for finding the deuterium position in Pd unit cell. The radial distribution function shows that the first peak corresponding to the first neighbor of Pd (Pd-Pd distance) increases according to filling with hydrogen. The results of XAFS analysis indicate that the bonding distance of Pd-Pd elongates by 0.08 Å through absorbing deuterium atoms. The elongation is uniform and isotropic within the analysis limitation of XAFS method. In addition, the lattice change proceeds while holding the Pd lattice (f.c.c.) symmetry and it is reversible completely. Possible position of absorbed deuterium atom are also be discussed.

EXPERIMENTAL

Zr$_{65}$Pd$_{35}$ was prepared from a mixture of pure Zr and Pd metals by melting in an Ar atmosphere, and Pd particles embedded in ZrO$_2$ were obtained by oxidizing the amorphous Zr$_{65}$Pd$_{35}$ alloy at 553 K for 24 h in air. To obtain the nano-sized-Pd/ZrO$_2$ composite, the above Pd particles embedded in ZrO$_2$ were baked at 423 K for 48 h in vacuum (10$^{-7}$ Torr). Details of the preparation of these nanocomposite materials are described in Ref. [1,2]. The as-prepared nano-sized-Pd/ZrO$_2$ composites were treated for XAFS measurements as follows. First, they were introduced into a quartz vessel with a gap of 50-100
μm and thickness of 1.0 mm with the assistance of supersonic apparatus. To remove some of the adsorbed atoms or ions, the material in the vessel was kept in a vacuum of 8 x 10⁻⁷ Torr at about 400 K for 24 hours (denoted as Vac hereafter). D₂ gas was injected into Vac at 0.2 MPa at room temperature (D₁st) and then the vessel was evacuated to 8 x 10⁻⁷ Torr at 400 K (D-Vac). Finally D₂ gas was again injected into the vessel at 0.2 MPa at room temperature (D₂nd).

X-ray absorption spectra at the Pd K-edge using synchrotron radiation were measured at BL19B2 (SPring-8), BL10B(PF) and NW10A(PF) in a transmission mode at 295K. The X-rays were monochromatized by a Si(111) double crystal. Incident and transmitted X-rays are detected by ion chambers filled with 50%Ar and 50%N₂ gases, and 100%Ar gas, respectively. Glass with a total thickness of 2 mm reduced the incident X-rays to about half at the Pd K-edge threshold energy (24.35 keV). The Pd K-edge data were analyzed using the Rigaku REX2000 code. Backgrounds were subtracted from the pre-edge region using an extrapolated Victoreen-plus-constant type function, and the XAFS oscillations \( \chi(k) \) were extracted using cubic spline baseline functions. Fourier transforms were performed on the normalized \( \chi(k) \) with \( k^3 \) weighting of a Hanning window in the region \( k = 1.2–15.0 \) Å⁻¹. Curve fitting was carried out using a single shell model in the range filtered from 1.83 to 3.03 Å in R for Pd-Pd.

RESULTS AND DISCUSSION

The particle size of dispersed Pd in ZrO₂ has been measured to be about 5 nm by SEM image. We have confirmed the reproducible formation of nano-sized Pd particle dispersed in ZrO₂. The characteristics of D₂/H₂ absorption into the nano-sized-Pd/ZrO₂ composite have been described in Ref. [1,2,3], as well as the microstructure. Fig. 1 shows XAFS oscillation parts of the specimens for the nano-sized-Pd/ZrO₂ composite specimens, D₁st, D-Vac, D₂nd and Pd-black. Commercial Pd-black was used as a reference. They are extracted from the absorption spectrum with standard procedure of XAFS analysis, and are multiplied by \( k^3 \). The XAFS oscillation for all spectra shows a maximum amplitude in the k range from 8 to 10 Å⁻¹ and that of D₁st is identical with that of D₂nd. However, that of Pd-black has two times larger than that of D-Vac. Fig. 2 shows Fourier transformation of Fig. 1. It is noticed that the dominant peak around 2.4 Å clearly shifts to shorter distance by evacuating the specimen from D₁st to D-Vac, and that the re-injection state (D₂nd) completely shows elongation to the same distance of D₁st. The both RDF of D₁st and D₂nd completely overlap. The dominant peak corresponds to the first neighbor of Pd in fcc Pd lattice; Pd-Pd shell. This suggests absorbing deuterium produces the expansion of Pd lattice and its expansion could be isotropic because the peak appears to be a singular peak. Essentially, the contribution of Pd-D shell should have been observed in around 1.2-1.7 Å although its intensity is too light to detect.

![Figure 1](image1.png)

**FIGURE 1.** XAFS oscillation parts of the specimens D-absorbed (D₁st), D-desorbed (D-Vac), D-reabsorbed (D₂nd) and Pd-black specimens. They are extracted from the absorption spectrum.

![Figure 2](image2.png)

**FIGURE 2.** Fourier transformation of Figure 1’s spectra. Note that the both RDF of D₁st and D₂nd completely overlap.

Curve-fitting and quantitative analysis were carried out to get more precise physical information and the results are summarized in Table 1. Absorption
of deuterium enlarges Pd-Pd bonding distance by 0.08~0.09 Å and it completely reverted to its original state with the release of deuterium. In addition, since one shell model yields good fitting, the expansion occurs while maintaining the crystal lattice symmetry. This is obvious evidence to indicate local structural change in hydrogen absorbing materials.

**TABLE 1.** Structure parameters for the nano-sized-Pd/ZrO₂ composites obtained from the curve-fitting using one shell (Pd-Pd). The R range used is from 1.83 to 3.03Å: \( d = \text{Pd-Pd distance}, \sigma = \text{the Debye-Waller factor}, \text{M.F.P. denotes mean free path}.\)

<table>
<thead>
<tr>
<th></th>
<th>C.N.</th>
<th>(d) (Pd-Pd) / Å</th>
<th>(\sigma) / Å²</th>
<th>M.F.P.</th>
<th>R / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>D₁ˢᵗ</td>
<td>12.0</td>
<td>2.82</td>
<td>0.080</td>
<td>3.69</td>
<td>1.69</td>
</tr>
<tr>
<td>Pd-black</td>
<td>12.0</td>
<td>2.74</td>
<td>0.069</td>
<td>4.58</td>
<td>1.29</td>
</tr>
<tr>
<td>D-Vac</td>
<td>12.0</td>
<td>2.73</td>
<td>0.075</td>
<td>3.63</td>
<td>1.27</td>
</tr>
<tr>
<td>D₂ⁿᵈ</td>
<td>12.0</td>
<td>2.82</td>
<td>0.082</td>
<td>3.72</td>
<td>2.02</td>
</tr>
</tbody>
</table>

Fig. 3 shows normalized the XANES region around the Pd K-edge threshold for all specimens. The insignificant difference in the XANES spectra among the specimens indicates that the valence of Pd is the same. Chemical bonding between Pd and deuterium does not occur in association with the change of oxidation state. Therefore, the nano-sized Pd cluster can maintain the chemical state against deuterium absorbing. This may be related to the reason why this nano-composite material can easily absorb and desorb deuterium.

Positioning of hydrogen atoms into octahedral or tetrahedral holes or a combination of the two in the fcc Pd lattice, allows the number of hydrogen limit to be 1, 4, 6 and 8 in Pd unit lattice. From the obtained Pd-Pd bonding distance for D₁ˢᵗ, an interstitial octahedral and tetrahedral space calculated to be 1.18 Å and 0.64 Å, respectively. It may be reasonable for deuterium to be located in the octahedral sites. However, considering a spherical shape of 1s orbital of deuterium, it is likely for a local lattice unstability to occur and octahedral site will be unstable. Therefore, the position of deuterium should be displaced slightly from octahedral along <111> direction in order to obtain the stable site potentially. On the other hand, we have investigated the difference spectrum of D-Vac and D₁ˢᵗ in which difference of scattering due to existing deuterium must be included. We are under progress by using differential Fourier analysis, or first principle calculation.

**CONCLUSION**

For nano-sized-Pd/ZrO₂ composites, X-ray absorption spectra around Pd K-absorption edge are observed and analyzed and deuterium absorbing behaviors are investigated.

- The bonding distance of Pd-Pd elongates by 0.08~0.09 Å through absorbing deuterium atoms. The elongation is uniform and isotropic within the analysis limitation of XAFS method.
- Deuterium locates not on the surface of Pd particle, but in Pd crystal lattice. In addition, the change proceeds while maintaining the Pd lattice (f.c.c.) symmetry and it is reversible.
- Possible positions of absorbed deuterium are discussed.

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**REFERENCES**