

## EXAFS Studies of Pd Nanoparticles-Abnormal elongation of bond distance

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Pd nanoparticles have been reported to exhibit abnormal behavior where the Pd lattice expands as the size of the Pd nanoparticles decreases. We measured X-ray absorption fine structure (XAFS) of Pd nanoparticles and confirmed that the Pd-Pd bond distance in small Pd nanoparticles with a diameter of 3 nm was elongated by 2% compared with that in Pd foil. The origin for the unusual bond elongation was discussed.

### 1 Introduction

Metal Nanoparticles (MNPs) have drawn much attention because of its fundamental and practical interests. In many MNPs show the contraction of metal-metal bonds. Yamauchi and Teranishi independently found that the Pd MNPs showed the lattice expansion.<sup>1</sup> We have invested this unique phenomenon using XAFS and confirmed the elongations of Pd-Pd distance.<sup>2</sup>

### 2 Experiment

MNP samples were prepared by a solution reduction method under inert atmosphere to avoid oxidation of the Pd PVP poly(*N*-vinyl-2-pyrrolidone)-protected MNPs reported elsewhere. We prepared three samples with different particle size. TEM images of the Pd PVP MNPs showed that the Pd MNPs had uniform structure with an average diameter of  $2.7 \pm 0.5$  nm,  $4.5 \pm 1.1$  nm, and  $7.6 \pm 2.3$  nm for the samples hereafter called Pd(3), Pd(5), and Pd(8), respectively. XAFS measurements were carried out in NW10A in PF-AR using a transmission mode.

### 3 Results and Discussion

Figure 1 showed the Fourier transforms of Pd samples with different particles sizes. The main peak could be assigned to Pd-Pd distance. The peak was shifted to the longer side in Pd(3) while Pd(8) had the peak at the same position as that of Pd foil, indicating that the Pd(3) had the expanded lattice. Table 1 summarized the curve fitting results. The Pd-Pd bond distances increased with the order of  $2.75 \text{ \AA}$  for Pd(8) <  $2.78 \text{ \AA}$  for Pd(5) <  $2.81 \text{ \AA}$  for Pd(3). We confirmed the bond elongation with the Pd(3). Pd(5) had the intermediate distance between the Pd(3) and Pd(8). Looking at longer distances we could find the 2nd to 4th shells well corresponding to those of the fcc Pd lattice indicating the crystal structure was maintained in Pd(3). The origin of the bond elongation was not clear yet. Pd easily creates the Pd hydride when Pd is exposed to hydrogen where Pd-Pd bond distance is

longer than the pure Pd foil keeping the fcc structure. However, the formation of Pd hydride can be rejected because of the following reasons. First, smaller nanoparticles can dissolve fewer hydrogen. In addition, Yamauchi found that the elongated Pd PVP MNPs could absorb hydrogen. Hydrogen-absorbed Pd PVP MNPs show less expansion with decreasing particle size than that found for the larger ones. Finally, the absorbed hydrogen can be easily removed under a hydrogen-free atmosphere. We measured MNP's XAFS under the N<sub>2</sub> atmosphere so that hydrogen should not be absorbed. Therefore hydride formation could not explain the bond elongation. We are still investigating the origin for the elongation of Pd-Pd distance

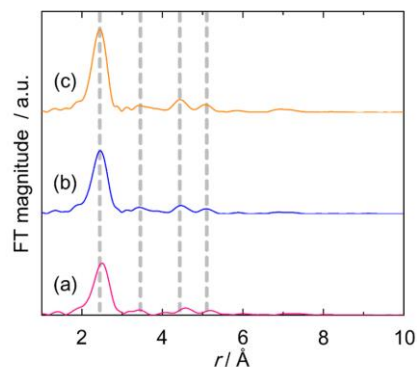


Figure 1. Fourier transforms of EXAFS spectra of a) Pd(3), b) Pd(5), and c) Pd(8). Gray dashed lines indicate the positions of the 1<sup>st</sup> to 4<sup>th</sup> peaks for Pd(8).

1M. Yamauchi, H. Kitagawa, *Synth. Met.* **2005**, *153*, 353.; T. Teranishi, M. Miyake, *Chem. Mat.* **1998**, *10*, 594.  
 2 Ohba et al. Chem Lett. in press

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**Table 1.** XRD and XAFS analyses of Pd PVP MNPs

|       | EXAFS    |                               |   |                 |                                    |                     |
|-------|----------|-------------------------------|---|-----------------|------------------------------------|---------------------|
|       | <i>N</i> | <i>r</i> <sub>Pd-Pd</sub> / Å | $\Delta\sigma^2 / 10^{-3} \cdot \text{\AA}^2$ | $\Delta E / eV$ | $C_3 / 10^{-4} \cdot \text{\AA}^3$ | <i>R</i> factor / % |
| Pd(8) | 9.2±1.0  | 2.75 ±0.02                    | 6.6 ±0.5                                      | 0 ± 3           | 0.1±1.0                            | 0.3                 |
| Pd(5) | 8.5±1.0  | 2.78 ±0.02                    | 7.4 ±0.6                                      | 0 ± 3           | 1.2±1.0                            | 0.3                 |
| Pd(3) | 8.3±1.0  | 2.81 ±0.02                    | 7.9 ±0.7                                      | 0 ± 3           | 0.8 ±1.0                           | 0.5                 |