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Elongated Pd-Pd bond length in Pd nanoparticle

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1 Introduction

Contraction of metal-metal bond length in nanoparticles has been frequently reported. However, the Pd lattice in the small nanoparticle was elongated as shown in Fig.1 where the Pd nanoparticle diffraction peaks shifted to lower angles. The diffraction results in literature sometimes showed that Pd nanoparticles had longer Pd-Pd bond distances than the bulk.[1] From the lattice expansion reported in the literature, Pd should have about 0.280 nm for Pd-Pd bond distances while Pd-Pd distance in the Pd crystal should be 0.277 nm. In this paper we carried out XAFS studies on the Pd nanoparticles to confirm the bond elongation.

2 Experiment

The sample was prepared by solution reduction method and the resultant Pd colloid was deposited on the SiO_2 surface. The particle was further reduced with H_2 to increase the particle size. XAFS measurements were carried out after the H_2 reduction at indicated temperature.

In order to remove the absorbed and adsorbed H_2 we evaculated the sample under He with 200 ºC. Phase shift and amplitude functions were derived from Pd foil.

3 Results and Discussion

Fig.1 shows the XRD results. The broad peak position was a little shifted to the lower angle when reduced at 200 ºC indicating the expansion of Pd lattice.

Fig.2 showed the Fourier transforms of the XAFS oscillations. The peak height increases with the particle size indicating the increase of the particle size. At the same time the peak position was shifted to a shorter bond length. Table 1 shows the structure parameters determined by XAFS.

The smallest nanoparticles(reduced at 200ºC) had the Pd-Pd bond distance around 2.8 Å while that of the large Pd particles have around 2.77 Å. The expansion of the bond distance in nanoparticle was around 10 %, well corresponding to that derived from the diffraction data. The Pd-Pd distance was elongated when hydrogen was absorbed. However, our previous work showed that the elongation of Pd-Pd induced by hydrogen absorption was 2.84 Å, (nearly 20 %).[2] Thus it was not so large as that of hydrogen induced one. In addition to that we found the larger Debye Waller factor in the Pd with the elongated bond. We have not yet obtained the origin of the elongation of metal-metal distance but we confirmed the unique phenomenon of the elongation of Pd-Pd in the smaller nanoparticle.

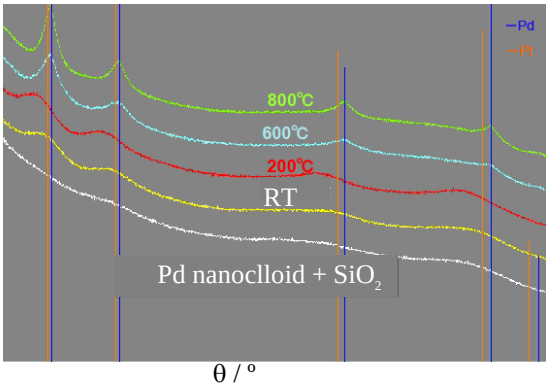

Fig. 1 XRD patterns of Pd particles, wit with various treatment temperature.

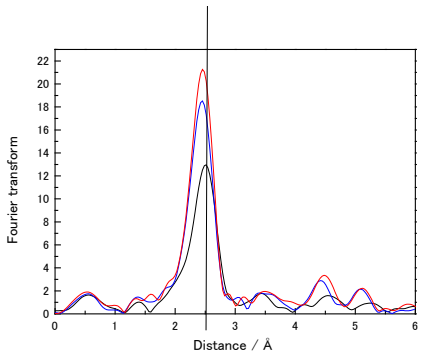

Fig. 2 Fourier transform of Pd nanoparticles treated with various temperature. (Black one 200 ˚C blue 600 ˚C and red 800 ˚C.)

Table 1 Curve Fitting results of Pd nanoparticles.

	N	R / Å	DW / Å	R / %
200 ˚C	8.4	2.80	0.096	0.76
600 ˚C	8.4	2.76	0.084	0.45
800 ˚C	9.2	2.76	0.083	0.22

1 M. Yamauchi, et al. *Synthetic Met* **2005**, *153*, 353; T. Teranishi, et al., *Chemistry of Materials* **1998**, *10*, 594.

2 T. Kubota,et.al., *Bull. Chem. Soc. Jpn.* **1999**, *72*, 673.

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