

Characterization of Pd(PVP) nanoparticles studied by AFM, Pd L₃-edge and Cl K-edge NEXAFS

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(Received: November 28, 2007; Accepted: April 02, 2008)

We have fabricated Pd(PVP) nanoparticle and investigated the size and chemical state by Atomic Force Microscopy (AFM), and Pd L₃- and Cl K-edges Near-edge X-ray Absorption Fine Structure (NEXAFS) techniques. The average size of Pd(PVP) with standard deviation can be estimated to be 2.0±0.6 nm after annealing at 723 K. Furthermore, when the species is heated up to 1073 K, the size has been enlarged gradually. The NEXAFS spectrum for the as-prepared specimen shows that there is the ionic state of Cl⁻ in the Pd(PVP). This ionic state disappears by annealing more than 723 K. All Cl K-edge NEXAFS spectra have the specific peaks, which show the existence of the [PdCl₄]²⁻ state. After anneal up to 1073 K, the amount of 25 % chlorine atoms still remain in the nanoparticle as compared with the start species.

1. Introduction

Many kinds of metal nanoparticle are used for the catalytic applications in the past decade [1-5]. A nanoparticle composed by a precious metal (Pd, Rh and Pt) is used for the purification catalysis of the automobile emission gas. These nanoparticles have a good property for the purification effects. In these years, the regulation value for the emission gas has become severe. Moreover the reduction of the amount of precious metals has been demanded in the world. Therefore, the catalyst with nanoparticle having a large effect for the purification is much desired. Especially, Pd and Pt nanoparticles have been used as a DPF (diesel particulate filter) and are much in demand in recent years. Thus there are many reports about the applications of the nanoparticle focused on the DPF [6-8].

We have revealed that the changes of the particle size and the chemical state about the Rh(PVP) nanoparticles, which are fabricated by means of the reflux-flow method at 353 K [9,10]. In those studies, we have used the AFM

and NEXAFS measurements. Because both measurements are nondestructive, the same sample can be used for other experiments. It suggests that both two measurements are suitable for doing the combined measurement to the same sample.

In this paper, our purposes are to fabricate the Pd nanoparticle by means of similar method of our previous way for Rh(PVP), and to characterize the nanoparticle by the combined measurements of both AFM and NEXAFS techniques.

2. Experimental details

We have fabricated the Pd(PVP) nanoparticles with one kind of PVP (K-15, molecular weight of 10000) received by KISHIDA CHEMICAL CO., Ltd. The 5.0x10⁻² mmol palladium chloride received from Mitsunawa Chemicals Co., Ltd and 0.5 mmol PVP were dissolved into a mixture solvent of ethanol and distilled water (total volume: 70 ml). The Pd(PVP) nanoparticle colloidal solution was fabricated by the reflux-flow sys-

tem at 353 K for 2 hours. The reflux-flow system is composed of a magnetic stirrer with a heater, an Arlene type condenser and a chromel-alumel (K-type) thermocouple. We can confirm the formation of the Pd(PVP) nanoparticles, when the change of the solution color occurs from light orange to dark brown. We have prepared the nanoparticle thin film by the spin-coating method for the Pd(PVP) nanoparticles on the Ni or Si substrate (10×10 mm², 0.5 mm thickness) at 4000 rpm and heated at several temperatures in the air. Since the Si wafer has a very flat and smooth surface, we use it as a substrate for AFM measurements. However, if we use the Si wafer as the substrate for NEXAFS measurements, the Si wafer emits much fluorescence rays with energy of about 1700 eV. Those fluorescence rays obstruct NEXAFS measurements. Thus we use the Ni substrate for NEXAFS.

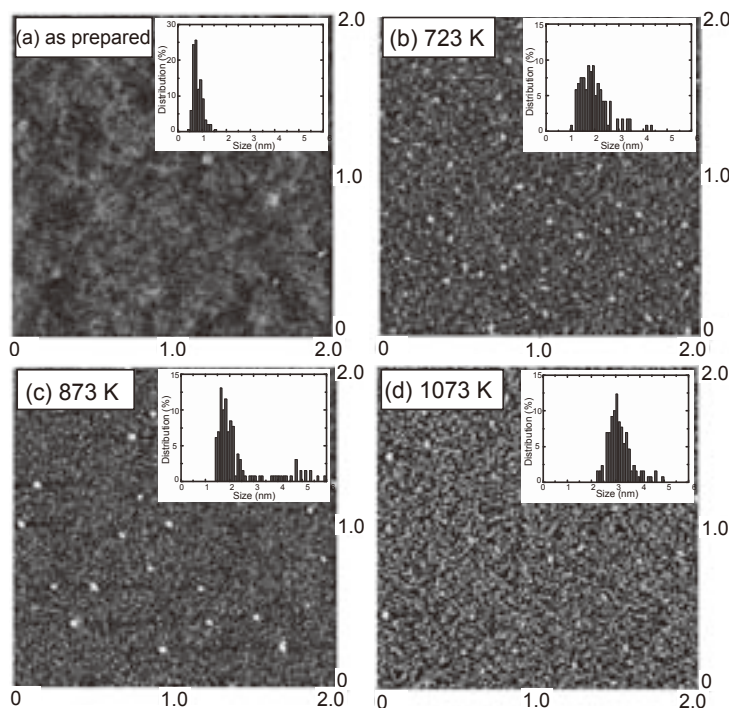
The AFM images for each Pd(PVP)/Si specimens were measured by NanoScope IIIa (Veeco Instruments) with non-contact tapping mode at Innovation Plaza Hiroshima JST. The morphology and the distribution of the particle size of the Pd(PVP) were estimated by analyzing the AFM measurements. The resolution of vertical value about AFM analysis is better than that of horizontal value. Thus we have analyzed the particle size using the vertical value.

The Near-edge XAFS (NEXAFS) spectra were carried out by yielding fluorescence X-rays with the atmospheric XAFS measurement system using He gas at the soft X-ray double crystal monochromator beamline BL-3 on Hiroshima Synchrotron Radiation Center (HSRC) [11-13]. The measurement energy range for Cl-K edge and Pd-L₃ edge were 2810 – 2850 eV and 3165 – 3190 eV, respectively. The photon energy was calibrated on the assumption that the first peak of K₂SO₄ appears at 2481.70 eV. The fluorescence yield detection was employed using an UHV-compatible gas-flow type proportional counter with P-10 gas (10 % CH₄ in Ar).

3. Results and discussion

3.1. AFM measurements

We have used AFM for the estimation of the particle size of Pd(PVP) nanoparticles. In general, a vertical value of AFM image has a little error bar in comparison with a horizontal one. Therefore, the particle size can be evaluated by the height value of the AFM analysis.



Figures 1(a)-(d). The AFM images with inset of the size distribution of the Pd(PVP) nanoparticles, which are (a) as-prepared, heating up to (b) 723 K, (c) 873 K and (d) 1073 K. Each scan size is 2×2 μm².

Figures 1(a)-(d) show the AFM images with inset of the size distribution of the Pd(PVP) nanoparticles, which are as-prepared, heating up to 723 K, 873 K and 1073 K. As reported about the Rh(PVP) nanoparticle by Ashida and Yagi *et al.*, since the nanoparticles with using PVP polymer are covered with the capping molecule, we can not obtain an exact particle size [9,10]. Because the PVP polymer decomposes at temperature higher than 673 K, reported by Ashida *et al.* [9], we have prepared the samples by heating at temperatures higher than 723 K.

Judging from each AFM measurements, the average particle sizes with standard deviation are estimated to be (a) 0.8±0.2, (b) 2.0±0.6, (c) 2.4±1.1 and (d) 3.3±1.1 nm, respectively. The estimated particle size about the as-prepared sample is a very small, it suggests that the average particle size is underestimated.

It is found that the average particle size is gradually growing along with the rise of annealing temperature. It is necessary to note that there are some nanoparticles, which have a large particle size of 5–6 nm, as annealing temperature of the substrate rises. This result is not obtained by our previous study about Rh(PVP) nanoparticles. It might depend upon the element kind, whether the nanoparticles grew up largely or not by heating the

specimens.

3.2. NEXAFS measurements

3.2.1. Cl-K edge NEXAFS

Figure 2 shows the Cl K-edge NEXAFS spectra of (a) PdCl₂ powder, (b) PdCl₂ aqueous solution, and (c)-(f) Pd(PVP) with annealing at several temperatures. All spectra were normalized to the edge-jump. There are four peaks (A), (B), (C) and (D), which are shown in Figure 2. The peak (A) can observe in spectra (a), (b) and (c) and is associated with the transition from the Cl 1s level to the lowest antibonding molecular orbital a_g(σ*) of the [PdCl₄]²⁻ state [14,15]. The peak at 2822.1 eV in the spectrum (b) is observed accurately at different peak position of (A). Because the chemical state of Cl in (b) is ionic state in the aqueous solution, this peak shows the Cl⁻ state. It is found that the chemical state of Cl in (c) is almost same as (a), since the peak positions are almost correspond to (a). Therefore, the Pd atoms of the nanoparticle have a chemical bonding with the Cl atom before annealing. Peak (A) disappears after annealing Pd(PVP) nanoparticles. This result suggests that there is no Cl⁻ state in the annealed samples of (d)-(f).

On the other hand, peaks (C) and (D) can be seen in all NEXAFS spectra though there is a difference of the peak intensity. Sugiura *et al.* has reported that the origin of those peaks are the square-planar complex ions of [MCl₄]²⁻ [14]. Here, M is the palladium. Hence, it is found that there are same structures of [MCl₄]²⁻ about Pd-Cl bonding in the Pd(PVP) nanoparticles. After annealing up to 1073 K, two peaks of (C) and (D) are still observed. It seems that the structure of [MCl₄]²⁻ is a very stable structure.

Peak B can be seen only in the spectrum of (f), annealed up to 1073 K. The origin of this peak is unknown. However, we think that peak (B) appears, if the chlorine atom receives one electron or less. A more detailed experiment is necessary in the future.

Figure 3 shows the Cl K-edge NEXAFS spectra for Pd(PVP) specimens which are (c) RT, and annealed at (d) 723 K, (e) 823 K and (f) 1073 K. All NEXAFS spectra are plotted by the agreement with each base line. The difference value between the post-edge at 2845 eV and the pre-edge at 2810 eV is the edge-jump value and means a total amount of Cl atoms. Therefore we can estimate the Cl amount of decrease in comparison with

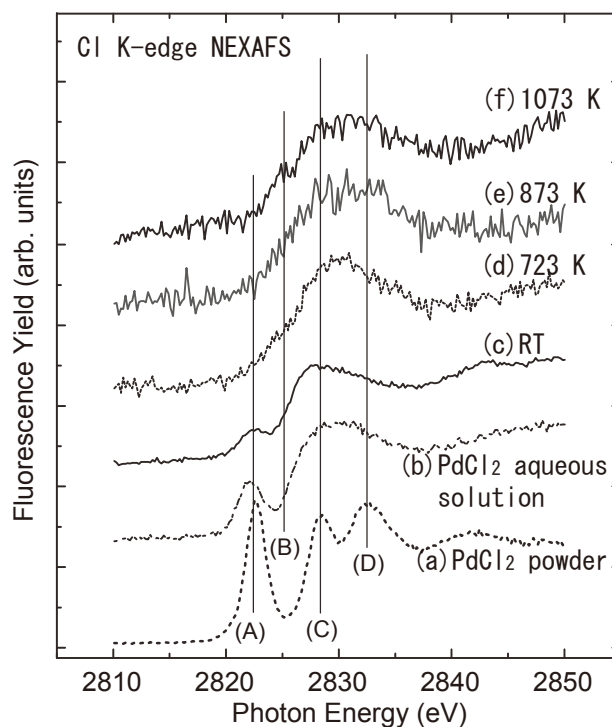


Figure 2. The Cl K-edge NEXAFS spectra of (a) PdCl₂ powder, (b) PdCl₂ aqueous solution, and (c)-(f) Pd(PVP) with annealing at several temperatures.

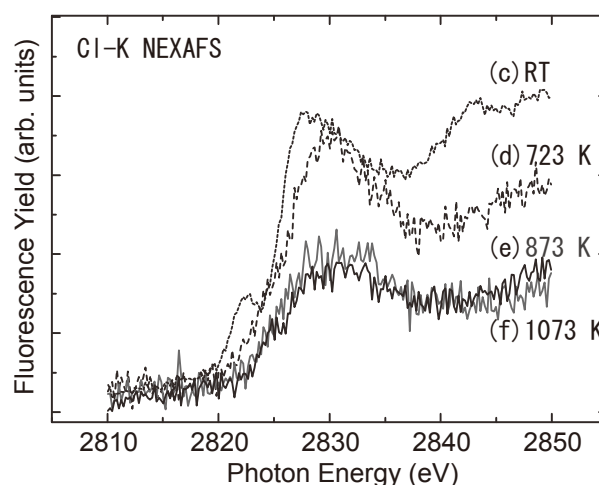


Figure 3. The Cl K-edge NEXAFS spectra for Pd(PVP) specimens which are (c) RT, and annealed at (d) 723 K, (e) 823 K and (f) 1073 K.

the edge-jump values. The edge-jump values decrease with raising the annealing temperature. Those results indicate that some of chlorine atoms desorb from the sample. But the chlorine atom for 1073 K specimen remains about 25 %, (edge-jump value (1073 K)/edge-jump value (RT) %), in comparison with the start specimen of RT. In our previous study for Rh(PVP) nanoparticle, the residual chlorine atoms have decreased to less than 10 % [10]. There is a big difference about the amount of the residual chlorine atoms between Pd(PVP) and Rh(PVP). It is thought that this difference depends upon a stability of chlorine atom in the nanoparticles. Actually, the NEXAFS spectrum for Rh(PVP) has no peak such as (C) and (D) shown in Figure 2. This result seems to show the chlorine atom has no structure of $[\text{RhCl}_4]^{2-}$ state in Rh(PVP) nanoparticle.

3.2.2. Pd-L₃ edge NEXAFS

Figure 4 shows the Pd L₃-edge NEXAFS spectra of (a) PdCl₂ powder, (b) Pd bulk, (c) Pd nanoparticle on Ni substrate (by dry process), (d) PdCl₂ aqueous solution, and (e)-(h) Pd(PVP) annealed at several temperatures. All spectra were normalized to the edge-jump. There are two peaks (A) and (B), which are shown in Figure 4. Since the peak (A) is corresponding to (b)Pd bulk peak, the peak (A) can be assigned to the metal Pd⁰ state. On the other hand, the peak (B) is same as the peak position of (c) Pd nanoparticle, which is fabricated by the gas evaporation method with He gas [16]. Yagi *et al.* [16] and Miura *et al.* [17] have reported that the surface of the Pd nanoparticle is easily oxidized by the exposure to the air at room temperature. Therefore, the peak (B) shows that there is the oxidized state in Pd(PVP) nanoparticle. However, the peak of (d) Pd aqueous solution has a same position of (B). In the aqueous solution, the Pd atom can exist in the state of the Pd²⁺. In other words, the Pd²⁺ state is equal to the same state of the oxidized state. Thus, it is found that most of Pd atoms in Pd(PVP) nanoparticle take the Pd²⁺ state, regardless of the substrate temperature. Such results was not seen for Rh(PVP) nanoparticle [9,10]. The Rh L₃-edge NEXAFS spectra show that the peak position shifts to the lower energy side with annealing in the air. When Pd(PVP) nanoparticle is compared with the result of Rh(PVP), it has been understood that Pd can not easily reduce with annealing in the air.

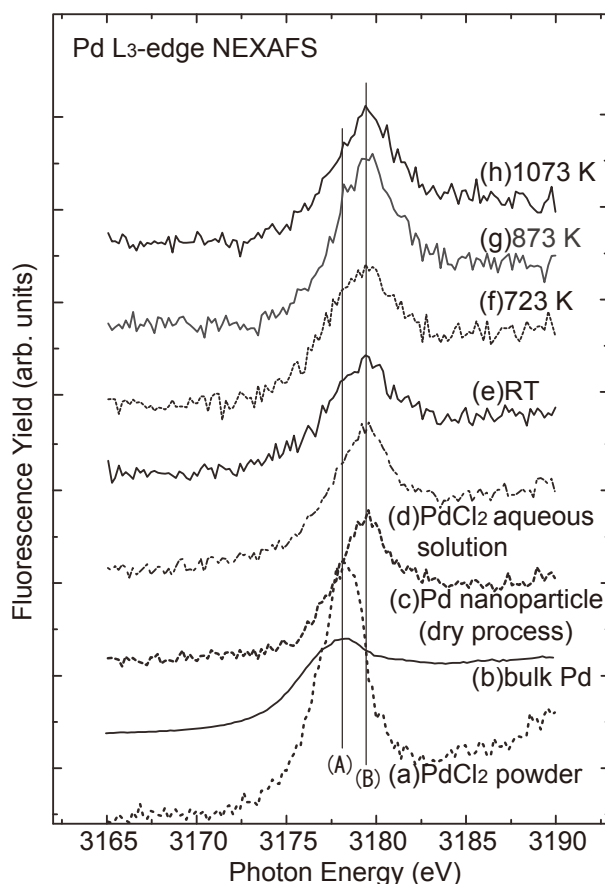


Figure 4. The Pd L₃-edge NEXAFS spectra of (a) PdCl₂ powder, (b) Pd bulk, (c) Pd nanoparticle on Ni substrate (by dry process), (d) PdCl₂ aqueous solution, and (e)-(h) Pd(PVP) at several temperatures.

4. Conclusion

We have synthesized Pd(PVP) nanoparticle with use of PVP(K-15) by the reflux-flow method. If the existence of the PVP as the capping molecule is taken into consideration, the size of Pd(PVP) nanoparticle is underestimated for the as-prepared specimen. Therefore, the real particle size of Pd(PVP) nanoparticle can be evaluated after annealing at 723 K in the air. The average size of Pd(PVP) with standard deviation is estimated to be 2.0 ± 0.6 nm. The particle size has been gradually enlarged with raising the annealing temperature. We have investigated the chemical state of Pd(PVP) nanoparticle by means of Pd L₃- and Cl K-edges NEXAFS. The spectrum for the as-prepared specimen shows that there is the ionic state of Cl⁻ in the Pd(PVP) nanoparticle. This ionic state disappears by annealing more than 723 K. There are two peaks at around 2830 eV, which suggest the existence of the $[\text{PdCl}_4]^{2-}$ state in the nanoparticle. Those

peak shapes can not be observed in the NEXAFS spectra of Rh(PVP) nanoparticles, which have been fabricated in our previous study. After anneal up to 1073 K, the amount of 25 % chlorine atoms still remain in the Pd(PVP) nanoparticle as compared with the start species. It is thought that the chlorine atoms can not be easily removed from Pd(PVP) nanoparticle by annealing in the air.

5. Acknowledgements

This work was supported by the Grant-in-Aid for Research from the Ministry of Education, Science and Culture, Japan (Nos. 19008872 and 15360358), 21-Century COE "Isotope Science and Engineering from Basics to Applications" and JST Innovation Plaza Hiroshima/Tokai. This study was performed under the approval of HSRC Program Advisory Committee (Nos. 05-A-15, 05-A-16 and 06-A-26).

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