Fabrication and characterization of Pd Nanoparticles

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A size and condensation controlled Pd nanoparticle is reported. The Pd nanoparticles are prepared by a gas condensation method with He gas, so called dry process. A fabrication of the nanoparticle by means of the dry process is an excellent way, because there are little contaminations on the most lateral surface of the nanoparticle than the nanoparticle by the wet process. Characterizations by TEM and AFM show that the fabricated Pd nanoparticle has a spherical shape, a few nm size in diameter and highly dispersed on the substrate. It is found that there are two chemical states in the Pd nanoparticle. One is an oxidized part at the surface and the other is a bulk part. [DOI: 10.1380/ejssnt.2006.258]

Keywords: Palladium; nanoparticle; TEM; AFM; XPS; NEXAFS

I. INTRODUCTION

For the application to exhaust gas catalysis, it is important to reveal the structure, chemical state, surface reaction and charge transfer at the nanoparticle surface of the magnetic materials and the functional gas-sensors. The catalytic application of metal nanoparticles has been evaluated by several research groups in the past decade [1–4]. Most of the metal nanoparticles in the size range of 1-10 nm can be prepared in the colloidal state by chemical reduction of appropriate metal salts in solution [5–7]. However, their most lateral surface are covered with the surfactant molecules to prevent aggregation with each particle. It seems that the surfactant molecules act as a contaminant and prevent the surface catalytic reaction.

Platinum group metals (Pd, Pt and Rh) are well known as an excellent element for automobile exhaust gas catalyst [8]. These metals are utilized in the catalytic converter as an active component for reducing the emission of hydrocarbons, carbon monoxide, and nitrogen oxides. However automobile catalyst loses its activity by means of agglomeration and growth of the metal particle size. There are few reports about the automobile catalyst using nano-size (1-2 nm in diameter) controlled particle by means of other than wet process. Nobody knows the catalytic activity and agglomeration for the nano-size, such as 1-2 nm, controlled particles.

In this study, we pay attention to the palladium metal nanoparticle as the first step. Our aims are to produce Pd nanoparticle of controlled size and the condensation on the substrate surface by means of the non-colloidal methods, and characterize its nature by several techniques. Here we report the fabrication method of Pd nanoparticle, morphological investigation by transmission electron microscopy (TEM) and atomic force microscopy (AFM) observations. Moreover the physical and chemical properties have been studied by X-ray photoelectron spectroscopy (XPS) and near-edgeX-ray absorption fine structure (NEXAFS) measurements.

II. EXPERIMENTAL DETAILS

A. Fabrication of Pd nanoparticle

Pd nanoparticles were fabricated by the gas condensation method using a high purity He gas (4N5) in the Pd evaporation chamber, as shown in Fig. 1. The Pd nanoparticles were grown at several kPa of He gas and transferred to the adsorption chamber through the stainless pipe. The base and working pressures in the adsorption chamber were less than 1 × 10⁻⁵ Pa and 1 × 10⁻¹ Pa, respectively. The Pd source (rod-shape, 4N) in the evaporation chamber was set in a tungsten basket. The transferred Pd nanoparticles were adsorbed on a Si wafer surface. The Si wafer was n-type and <100> orientation.
Adsorption chamber
Transfer pipe port
Evaporation chamber

FIG. 1: Photographic view of the gas condensation chamber for fabrication of Pd nanoparticles. This chamber consists of three parts of an adsorption chamber, a transfer port and an evaporation chamber.

tion, and cleaned only by ultra sonic wave with ethanol solution. The size of the Pd nanoparticle was controlled by both the resistive heating power of the tungsten filament and the He gas pressure in the evaporation chamber. The amount of the Pd nanoparticle was controlled by an exposure time. We prepared four samples under different He pressure conditions of 3, 6, 10 and 18 kPa.

B. Transmission electron microscopy characterization

TEM experiments were carried out to study the fine structure and morphology of the Pd nanoparticles adsorbed on a microgrid (Quantifoils-Cu) as a support material, using JEOL JEM3000F at 300 kV. The microgrid was set in the adsorption chamber together with the Si wafer substrate. A sample for the TEM measurement was prepared by controlling the exposure time for a few seconds to prevent the formation of a multi-particle on the substrate.

C. Atomic force microscopy characterization

The surface morphology of the Pd nanoparticle was studied by an AFM observation using Veeco Instruments (Nanoscope III-a), operated in the non-contact tapping mode and under the atmospheric pressure condition. The model (RTESP) made of phosphorus (n-type) Si was used as a cantilever. The scan rate and the pixel size were 0.5 Hz and 512 x 512 pixels, respectively. Since a dark brown spot is clearly observed for over 8 min exposure, it is found that Pd nanoparticles overlap each other and construct a thin multilayer.

D. X-ray photoelectron spectroscopy analysis

Chemical states of the Pd nanoparticle were investigated by a surface analysis system equipped with a SPECs PHOIBOS 100-5ch concentric hemispherical analyzer and a dual Mg/Al X-ray source. High-resolution XPS spectra were obtained in the fixed analyzer transmission mode with a pass energy of 20 eV and an unmonochromatized AlK radiation (1486.6 eV) was operated at 300W and 15 kV.

E. Near-edge X-ray absorption fine structure analysis

Pd L\textsubscript{3}-edge NEXAFS spectra were obtained at the double crystal monochromator beamline BL-3 in the Synchrotron Radiation Center of Hiroshima University (HiSOR: 700 MeV) [9, 10]. Since the BL-3 equipped double InSb(111) crystals, we could use a photon energy of 1800-4100 eV region. This energy range covered the Pd L\textsubscript{3}-edge region. All NEXAFS spectra were obtained by means of fluorescence yield detection using a gas-flow type fluorescence proportional counter with P-10 gas. As an escape and a penetration depths for fluorescent X-rays are over 10 nm in this photon energy region, it is possible to obtain all the chemical states of the nanoparticles adsorbed on the substrate. All samples were set inside of the special XAFS measurement system under atmospheric pressure condition with He gas [11].

III. RESULTS AND DISCUSSIONS

A. Transmission electron microscopy studies of Pd nanoparticles

The results of TEM studies of the Pd nanoparticles deposited on the microgrid show that the Pd nanoparticles have spherical shape and well-dispersed situation, as shown in Figs. 2(a) and (b). There is no multi-particle situation for Pd nanoparticles. Judging from the size distribution, not shown here, the size of the Pd nanoparticles (about 200 counts) are in the region of 1-4 nm in diameter under all He pressure conditions. The estimated average size of Pd nanoparticles are approximately 2 nm in diameter, which is in agreement with the size discussed in Section 3.2.

As can be expected from the obtained image of the fringes for the Pd nanoparticle shown in Fig. 2(b), the Pd nanoparticles exist as single crystallite. The estimation of those fringe spacing is carried out for the TEM image in
Fig. 2(b). The fringe spacing is obtained to be 0.226 ± 0.05 nm. Since Pd lattice constant in a face-centered cubic (fcc) structure at room temperature is 0.389 nm, the spacing value is 0.225 nm. These values are very similar to each other. Therefore it is found that fabricated Pd nanoparticles have the fcc structure.

B. Atomic force microscopy characterization

The AFM images for the Si wafer surface, as a substrate, and Pd nanoparticles fabricated at 10 kPa He pressure are shown in Figs. 3(a) and (b), respectively, and together with the distribution histogram obtained at (c) 6 kPa and (d) 10 kPa. Because an error is very large along the side direction in AFM measurements, the size of the nanoparticle is estimated by means of the value of the height direction. It is found that the averaged sizes of Pd nanoparticles are approximately 1.1 nm in diameter under 6 kPa condition and 1.9 nm in diameter under 10 kPa condition, respectively. These sizes are consistent with the results of TEM measurements. The FWHM (Full Width at Half Maximum) of the distribution curve is about 1-2 nm. Thus our gas condensation method has a good controllability for the well-dispersed fabrication.

These results imply that the nanoparticle sizes depend
FIG. 4: Pd 3d XPS spectra obtained for Pd nanoparticles with different exposure time.

on the He gas pressure in the evaporation chamber. In other words, if the nanoparticles are fabricated under low or high He gas pressure condition, the produced nanoparticles have a small or large diameter size, respectively. Due to the collision between Pd and He atoms, the mean free path of the evaporated Pd atom is not long distance under the high He gas pressure condition. Therefore the sizes of Pd nanoparticles grow large under the high He gas pressure condition.

C. X-ray photoelectron spectroscopy analysis

Figure 4 shows the Pd 3d XPS spectra for Pd nanoparticles prepared with different deposition time for several minute under 6 kPa conditions. Those investigated positions are also shown in Fig. 4 as an inset. The position (a) corresponds to the longest exposure time of Pd nanoparticles, and (b), (c) and (d) to the gradually decreased amount of the Pd nanoparticles. There are two peaks at higher binding energy side of main peaks as satellite. The satellite peak intensity gradually increases as the adsorbed amount of Pd nanoparticle decreases. The peaks obtained in (b), (c) and (d) at 337.6 and 342.9 eV are attributed to Pd 3d_{5/2} and 3d_{3/2} spin-orbit doublet peaks indicating that Pd is in a highly ionic Pd^{2+} state, whereas the peaks in (a) at 335.4 eV and 340.5 eV corresponding to bulk like Pd are in the zerovalent state [12–14]. These results mean that almost all the Pd nanoparticles inside stably exist in the metallic Pd^{0} state and the Pd atoms at the lateral surface of nanoparticle are in the oxidized Pd^{2+} state.

D. Near-edge X-ray absorption fine structure analysis

Figure 5 shows the Pd L_{3}-edge NEXAFS spectra for Pd nanoparticles prepared with different deposition time for several minute under 6 kPa conditions. Those investigated positions are also shown in Fig. 5 as an inset. The measurement position of (a) has a dark brown color with the Pd nanoparticles for 8 min exposure. The peak of (A) observed at 3176.6 eV is only measured at the position of (a). It seems that the Pd L_{3}-edge NEXAFS at position (a) is almost near the bulk Pd spectrum. On the other hand, the peak (B) observed at 3177.1 eV is measured in the positions (b), (c) and (d). The width of the peak (B) observed in the positions (b), (c) and (d) is slightly wider than peak (A). This means that those peaks do not consist of only a single peak component. These results are consistent with the XPS results. At the low exposure position, the Pd nanoparticles do not aggregate each other. Therefore the lateral surface of the nanoparticles, which is the oxidized chemical state, is observed at (b), (c) and (d). Moreover the peak (C) observed at 3180.7 eV is shown only in the spectrum (d). Since this peak is located at higher energy side in comparison with the peak (B), this peak seems to be assigned to more oxidized chemical state.
such as $\text{Pd}^{(2+6)}$.

IV. CONCLUSION

Morphological and chemical characterizations for fabricated the Pd nanoparticles have been carried out by TEM/AFM and XPS/NEXAFS techniques, respectively. TEM and AFM have revealed nano-sized scale particles exist as the single crystallite and the spherical shape on the substrate. XPS and NEXAFS analyses have also revealed that there are two chemical states on the Pd nanoparticles. One is the metallic bulk state of $\text{Pd}^0$ and the other is the oxidized state of $\text{Pd}^{2+}$ and/or $\text{Pd}^{(2+6)}$. The oxidized states are dominant in the case of the monodispersed nanoparticle sample.

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