Original Paper

Dissociation reaction of (CH$_3$)$_2$S adsorbed on Pd nanoparticles fabricated by gas evaporation method

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The Pd nanoparticles (NPs) with clean surface are fabricated by the gas evaporation method. We can control the particle size and the degree of dispersion of the Pd NPs. It is found that Pd NPs have the average diameter of 2.6 nm with the standard deviation of 1.1 nm. The chemical states of sulfur and Pd were analyzed by X-ray photoelectron spectroscopy (XPS). Judging from XPS results, dimethyl sulfide (DMS) does not decompose on the substrate surfaces of bulk Ni and Pd. However, DMS adsorbed on Pd NPs surface dissociates. Therefore, the catalytic activity of Pd NPs surface is superior to that of bulk Pd surface.

1. Introduction

The platinum group elements (Pd, Rh and Pt) play the role of the catalyst in the purification reaction of automobile exhaust gas [1-3]. These elements have the superior propeties of oxidizing carbon monoxide (CO) and hydrocarbon (C_xH_y) or reducing nitrogen oxide (NO_x). In these years, the regulation of automobile exhaust gas becomes more severe and it is important to improve the performance of the automobile catalyst. To clear this regulation, many researchers have been interested in the nanoparticle of automobile catalyst elements since it is effective to increase the specific surface area.

Most of the nanoparticles are fabricated by the chemical reduction method [4, 5]. Some kinds of polymer and thiol molecules are often used for this method as a capping molecule, which can prevent aggregation of nanoparticles. Since the surface of the nanoparticles is covered with the capping molecules, there is a possibility that the activity of the nanoparticles is decreased. Therefore we have paid attention to fabricate the nanoparticles with clean surface. In our previous study, Yagi et al. have fabricated the Pd NPs with clean surface by the gas evaporation method [6].

Many papers have been reported that the sulfur-containing molecules adsorbed on the several transition metal, which are used as an automobile catalyst, cause deactivation of catalytic performance [7-9]. How-

ever, there are few papers about the interaction between sulfur-containing molecules and nanoparticles with clean surface. We have reported the dissociation reaction of the DMS, which has a sulfur atom and a simple structure, by XPS.

2. EXPERIMENTAL DETAILS

Fig. 1 shows a photographic view of the in-situ XPS measurement system. This system is composed of the nanoparticle fabrication chamber and the XPS measurement chamber. This nanoparticle fabrication chamber was designed to be compact and portable size. Therefore, we can perform the in-situ measurement for the fabricated NPs at any fascilities, which locate at the outside of our laboratory. The polycrystalline Ni substrate (Nilaco Co. and 99.7 % purity) was mechanically polished using Al_2O_3 with 0.05 μm diameter to a mirror finish. The Ni substrate was cleaned by Ar^+ sputtering to remove the impurities of sulfur, carbon and oxygen under an ultra-high vacuum condition and the cleanness of the surface was confirmed by XPS. The Pd NPs with clean surface were fabricated by the gas evaporation method using a research grade He gas (8.0 kPa) and deposited on the Ni substrate in the nanoparticle fabrication chamber [6]. This sample was transferred to XPS measurement chamber under high vacuum condition and cooled down to 90 K by liquid N_2. The research grade DMS was admitted

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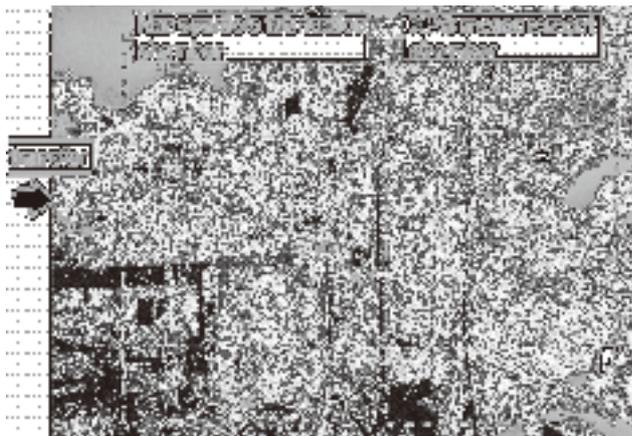
Fig. 1. In-situ XPS measurement system composed of nanoparticle fabrication chamber and XPS measurement chamber.

via a variable leak valve at a constant pressure of 2.0×10^{-8} Torr. The exposure was kept up for 25 sec (0.5 L).

The XPS measurement was carried out by the Mg Kα X-ray (1253.6 eV) and the hemispherical electron energy analyzer PHOIBOS 100-5ch (SPECS). The base pressure of the XPS measurement chamber was 3.0×10^{-8} Pa. The XPS spectra of both Pd and Ni substrates were obtained as reference data under same experimental condition.

Atomic force microscopy (AFM) observations were carried out under atmospheric condition by using Nanoscope IIIa (Veeco) by tapping mode.

3. RESULT AND DISSCUSSION

Fig. 2(a) and (b) show the AFM image and the size distribution of Pd NPs, respectively. It reveals that Pd NPs form a dispersed phase on substrate, since the Pd NPs are not aggregated each other. Furthermore, a shape of Pd NPs is almost spherical. The particle size can be evaluated by the height value of the AFM analysis [4-6]. As a result of AFM observation, it is found that Pd NPs have the average diameter of 2.6 nm with the standard deviation of 1.1 nm.

Fig.3 shows a summary of S 2p XPS spectra for multilayer, DMS adsorbed on Ni, Pd and Pd NPs. The peak position of both DMS/Ni and DMS/Pd spectra are corresponding to that of multilayer (163.8 eV). In previous studies, DMS does not decompose on the single crystal Ni(100) and Ag(111) surface at 90 K [10,11]. Judging from these results, DMS adsorbed on Ni and Pd substrate does not decompose. The peak position of DMS/Pd NPs/Ni

spectrum is lower than that of others spectra. Nomoto et al. have studied the chemical states of DMS adsorbed on Rh(100) using XPS measurement, where DMS dissociates into methanethiolate (MT: CH$_3$S-) at 163.2 eV [12]. As a result of DMS/Pd NPs/Ni spectrum deconvolution, DMS adsorbed on Pd NPs undergoes the dissociation into MT.

Fig.4 shows a summary of C 1s XPS spectra for multilayer and DMS/Pd NPs/Ni. These spectra have been already subtracted from the background spectrum, which is measured before the exposure of DMS. The results for DMS/Ni and DMS/Pd, not shown in Fig.4, indicate that DMS does not decompose on those surfaces. Therefore, their results are corresponding to those of S 2p XPS. The peak position of DMS/Pd NPs/Ni spectrum is different from that of multilayer. Thus, we have carried out the deconvolution same as S 2p results. From the deconvolution result, it is found that DMS adsorbed on Pd NPs surface dissociates. The adsorbed species have three
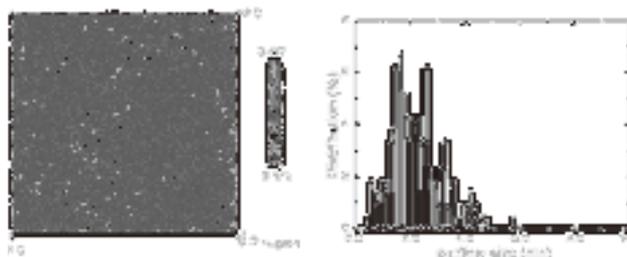

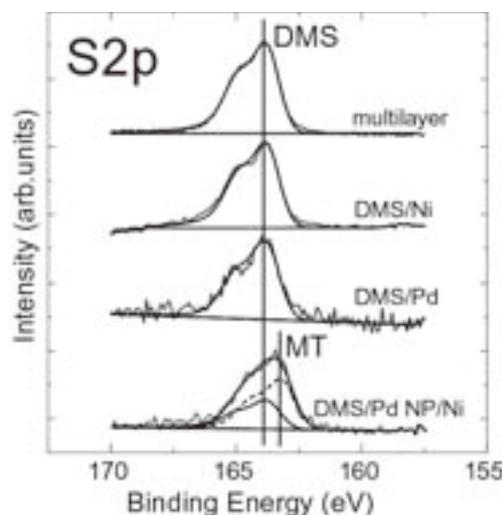Fig. 2. (a) AFM image of Pd NPs and (b) the size distribution of Pd NPs.

Fig. 3. S 2p in-situ XPS spectra for multilayer, DMS/Ni, DMS/Pd and DMS/Pd NPs/Ni.
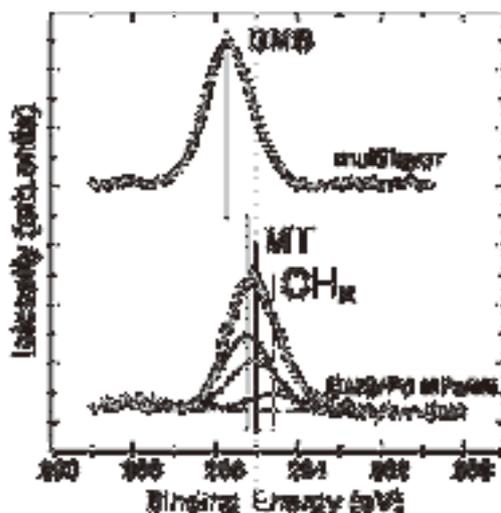
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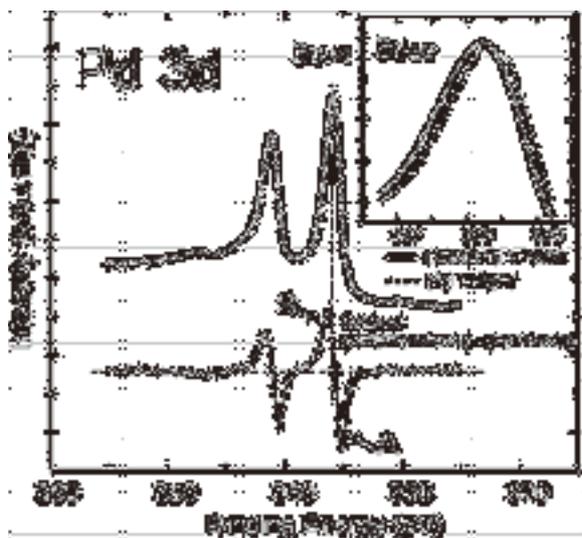Fig. 4. C 1s in-situ XPS spectra for multilayer and DMS/Pd NPs/Ni.

Fig. 5. Pd 3d in-situ XPS spectra.

chemical states; DMS, MT and CH$_x$ (x>1). Thus, it indicates that the activity of Pd NPs surface is higher than that of bulk Pd surface.

Fig. 5 shows Pd 3d XPS spectra for DMS/Pd NPs/Ni, Pd NPs/Ni and subtracted spectrum of (DMS/Pd NPs/Ni) – (Pd NPs/Ni). The inset in Fig. 5 indicates the enlarged figure of the Pd 3d$_{5/2}$ peak top area, and the peak intensities and positions are mutually different. In subtracted spectrum, there are two peaks around the Pd 3d$_{5/2}$ peak (shown as A and B). Chaplin et al. have reported that the peak position of Pd 3d shifts to higher binding energy

side when sulfur-containing molecules are adsorbed on Pd surface [13]. Therefore, the origin of peak B is due to Pd bonded with sulfur at Pd NPs surface. Besides, the peak A can be assigned to Pd, which has no interaction with DMS.

4. Conclusion

We have fabricated the Pd NPs with clean surface by the gas evaporation method and have investigated the dissociation reaction of DMS on Pd NPs surface by in-situ XPS measurement. At 90 K, DMS adsorbed on Ni and Pd substrate does not decompose. On the other hand, DMS adsorbed on Pd NPs surface dissociates into MT. Therefore, these results indicate that the activity of Pd NPs surface is higher than that of bulk Pd surface.

5. Acknowledgements

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