In-Situ XPS Study on Adsorption Reaction of Dimethyl Sulfide on Pd Nanoparticle Surface*

M. Morihara, † K. Miura, T. Nomoto, and S. Yagi

Department of Quantum Engineering, School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan
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We have fabricated Pd nanoparticles (NPs) with clean surface and revealed the adsorption reaction of dimethyl sulfide (DMS) on Pd NPs/Ni(111) surface depending on the amount of deposited Pd NPs using in-situ X-ray Photoelectron Spectroscopy (XPS). As a result of XPS, DMS does not decompose on Ni(111) and bulk Pd surface. However, DMS dissociates into methanethiolate (MT; CH₃S⁻) and atomic S on Pd NPs/Ni(111). It is found that the activity of Pd NPs surface is higher than that of bulk Pd surface.

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I. INTRODUCTION

The regulation of automobile exhaust gas becomes more severe in these years, it is necessary to improve the performance of automobile catalyst. Automobile catalyst is composed of the platinum group metals (Pd, Rh and Pt) since these metals indicate the superior properties of the purification of the automobile exhaust gas [1–3]. Therefore, many researchers have been interested in the nanoparticles of automobile catalyst since it is effective to increase the specific surface area of the catalyst.

To apply the nanoparticle to the automobile catalyst, it needs to resolve two problems about the automobile catalyst; (1) surfactant molecules remain on the active sites of nanoparticle surface, which are fabricated by chemical reduction method [4–7] and (2) the performance of automobile catalyst is decreased by sulfur-containing molecules in gasoline fuel, known as “Sulfur Poisoning” [8, 9]. To clear these problems, it is necessary to fabricate Pd nanoparticles without surfactant molecules by the gas evaporation method [10, 11] and to reveal adsorption reaction of sulfur-containing molecules adsorbed on nanoparticle surface.

In our previous study, we have prepared Pd NPs deposited on poly crystalline Ni substrate. We revealed the dissociation reaction of DMS adsorbed on Pd NPs/poly crystalline Ni. It indicates that DMS adsorbed on Pd NPs surface dissociates. However, DMS adsorbed on bulk Pd and poly crystalline Ni does not decompose. Thus, the catalytic activity of Pd NPs is higher than that of bulk Pd [12]. Besides, it is not cleared that the dissociation reaction of DMS occurs on Pd NPs surface and/or Pd-Ni interface. Therefore, we have investigated adsorption reaction of DMS depending on amount of deposited Pd NPs using in-situ XPS.

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†Corresponding author: morihara.masayoshi@d.mbox.nagoya-u.ac.jp
condition and the annealing up to $\sim$1000 K by electron bombardment. The cleanness of Ni(111) surface was confirmed by XPS. The Pd NPs with clean surface were fabricated by the gas evaporation method using a research grade He gas (8.0 kPa) and deposited on Ni(111). The amount of Pd NPs was controlled by deposition time. This sample was cooled down to 90 K by liquid N$_2$ before dosing DMS molecule. The research grade DMS was admitted via a variable leak valve under a constant pressure of $1.0 \times 10^{-8}$ Torr. The exposure was kept up for 20 sec (0.2 L). During XPS measurement, the substrate temperature was kept at 90 K.

The XPS measurement was carried out by the MgK$_\alpha$ X-ray (1253.6 eV) and the hemispherical electron energy analyzer PHOIBOS 100-5ch (SPECS). The base pressure of the XPS measurement chamber was $3.0 \times 10^{-8}$ Pa. The XPS spectra of both Pd and Ni(111) 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.

III. RESULTS AND DISCUSSIONS

A. AFM images

Figures 1 (a), (b), (c) and (d) show the AFM images of Pd NPs. The particle size can be evaluated by the height value of the AFM analysis. Because the height value of the AFM has a good resolution in comparison with the horizontal value [4, 10]. 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. The layer thickness of deposited Pd NPs was estimated by decay of the Ni 2p$_{3/2}$ intensity of XPS measurement since the signal decay is related with the amount of Pd NPs. These images are corresponding to (a) 0.26, (b) 0.40, (c) 0.58 and (d) 0.90 layer of Pd NPs, respectively. The Pd NPs of 0.26 and 0.40 layer are dispersed very well. On the other hand, the Pd NPs seem to aggregate partly in 0.58 and 0.90 layer.

Thinking about the reaction site, these are three possible reaction sites. They are Ni(111), Pd NPs surface and Pd-Ni interface. If the deposition of Pd NPs increases, the surface area of Ni (111) decreases and the surface area of Pd NPs increases. The area for Pd-Ni interface, however, it depends upon the degree of the aggregation of Pd NPs. The ratio of those reaction sites can be changed since the amount of deposited Pd NPs can be controlled. It leads the difference about dissociation reaction of DMS, because it is known that adsorption reaction is related with the kind of element and the reaction site [13, 14]. Therefore, we can reveal the reaction sites through the discussion of XPS results.

B. S 2p XPS

Figure 2 shows a summary of S 2p XPS spectra for multilayer, Ni(111), bulk Pd and different amount of deposited Pd NPs. The peak positions of DMS/Ni(111) and DMS/bulk Pd spectra are corresponding to that of multilayer. Judging from these results, DMS adsorbed on Ni(111) or the bulk Pd substrate does not decompose. However, the peak position of DMS/Pd NPs/Ni(111) is different from those spectra. As a result of the spectrum deconvolution of DMS/Pd NPs/Ni(111), DMS dissociates into MT and atomic S. Therefore, the activity of Pd NPs surface is higher than that of the bulk Pd. This result is corresponding to previous our study [12]. It is found that the dissociations reaction of DMS adsorbed on different amount of deposited Pd NPs are different. Figure 3 shows the existence ratio of adsorbed species depending on the amount of deposited Pd NPs.

![Figure 2: S 2p XPS spectra for multilayer, Ni(111), bulk Pd and different amount of deposited Pd NPs.](image)

**FIG. 2**: S 2p XPS spectra for multilayer, Ni(111), bulk Pd and different amount of deposited Pd NPs.

![Figure 3: The existence ratio of adsorbed species depending on the amount of deposited Pd NPs.](image)

**FIG. 3**: The existence ratio of adsorbed species depending on the amount of deposited Pd NPs.
tion sites, which are Ni(111), Pd NPs surface and Pd-Ni interface. The dissociation reaction of DMS occurs on Pd NPs surface and/or Pd-Ni interface, since DMS adsorbed on Ni(111) does not decompose. Judging from the spectrum for multilayer Pd NPs, the existence ratio of atomic S increases clearly and that of MT decreases compared with the spectrum for 0.90 layer. As the amount of deposited Pd NPs is larger, the number of active sites of Pd NP increases. Those behaviors are similar to those of the existence ratio of atomic S. Thus, it is assumed that atomic S is formed on Pd NPs surface. Those active sites are composed of the step edge and defect of the nanoparticle surface.

C. C 1s XPS

Figure 4 shows a summary of C 1s XPS spectra for multilayer, DMS adsorbed on Ni(111), bulk Pd and different amount of deposited Pd NPs. The background spectrum, which is measured before the exposure of DMS, has been already subtracted from the raw spectra. DMS adsorbed on Ni(111) or bulk Pd does not decompose. However, DMS adsorbed on Pd NPs decomposes into MT and CH$_x$ ($x > 1$). It is found that the existence ratio of DMS decrease and that of MT increases, when the amount of deposited Pd NPs becomes large. Additionally, the existence ratio between DMS and MT is the same as S 2p result. Therefore, the analysis of C 1s has good agreement with S 2p result.

IV. CONCLUSION

We have studied the adsorption reaction of DMS on Pd NPs/Ni(111) surface depending upon the amount of deposited Pd NPs with in-situ XPS. DMS on Ni(111) and bulk Pd surface does not decompose. However, DMS adsorbed on Pd NPs dissociates into MT and atomic S. Thus, the activity of Pd NPs surface is higher than that of bulk Pd surface. Additionally, it is found that dissociation reaction of DMS depends on the amount of deposited Pd NPs and atomic S is formed mainly on the Pd NPs surface.

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