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Paper

Fabrication of Rh Nanoparticle and Adsorption Reaction with DMS Studied by NEXAFS and XPS

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We have studied the adsorption reaction of DMS on the Rh nanoparticle fabricated by the gas evaporation method by using AFM, XPS and NEXAFS techniques. The AFM result shows that we can fabricate the Rh nanoparticle which has a small diameter with a small distribution and high dispersion of it by the gas evaporation method with the Rh wire as an evaporation source. The Rh L_3-edge NEXAFS spectra indicate that the surface and bulk of Rh nanoparticle is stable in the chemical state of Rh^0 despite the exposure to air. The Rh 3d XPS and S K-edge NEXAFS results show the lower degree of oxidized Rh nanoparticle has the stronger bonding with atomic S than the more oxidized one.

1. Introduction

The concerns over the environmental preservation are growing and the requirement for improvements in the purification of automobile exhaust gas is increasing every year all over the world. Platinum-group metals (Rh, Pd and Pt) are currently used as the catalyst for removal of toxic substances (NO_X, HC and CO) emitted by the combustion of fossil fuel. However, there is a problem that needs to be solved, a catalytic deterioration known as sulfur poisoning. This is caused by remaining sulfur-containing molecules in the automobile fuel on the surface of catalyst. These remaining molecules prevent a purification reaction of the toxic substances on their surface [1]. Despite the many reports on sulfur poisoning, it remains unclear things about the adsorption reaction of the sulfur-containing molecule on the surface of catalyst. Therefore, we have researched the adsorption reaction of the sulfur on Rh that possessed remarkable resistance and healing ability against the sulfur poisoning [2-4].

In our previous study, we have revealed the adsorption reaction with dimethyl sulfide (DMS: $(CH_3)_2S$) on the Rh(100) single crystal surface [2]. It is supposed that the more step-edge structures exist on the Rh surface, the higher reactivity against the decomposition of DMS into atomic S is caused. It is expected that the Rh nanoparticle possesses higher reactivity than the Rh single crystal surface because the surface of the nanoparticle has more step-edge structures than single crystal. Furthermore, we have investigated the DMS adsorption on the Rh(PVP) nanoparticles fabricated by chemical reduction method that is possible to mass-produce at a low price and practically used for fabricating the automobile exhaust catalyst [5,6]. The results of these studies show the polyvinylpyrrolidone (PVP) using as a surfactant influences the dissociation reaction of DMS. To clarify the adsorption reaction between the Rh nanoparticle and DMS, there is a need to fabricate the Rh nanoparticle by means of the method that has been free from the surfactant.

Thus, we have employed gas evaporation method that enabled to fabricate nanoparticles with clean surface in the previous study [7]. In this method, a pure metal is heated and evaporated by using a tungsten basket, and the metal nanoparticles are synthesized under inactive gas environment. However, the tungsten is mixed in the metal nanoparticles in the case of fabricating the nanoparticle of the metal with high melting point. To fabricate the Rh nanoparticle which is almost free from impurities, we used a Rh wire with high purity as evaporation source and heated itself by resistive heating. The purpose of this

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study is to reveal the adsorption reaction of DMS on the Rh nanoparticles by using atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS) and near edge X-ray absorption fine structure (NEXAFS) techniques.

2. Experimental

We fabricated the Rh nanoparticle with clean surface by gas evaporation method. Fig. 1 shows a schematic view about chambers for the fabrication of Rh nanoparticles with this method and photos of the lower chamber and the Rh wire as the evaporation source. The lower one was filled with the high-purity He gas under a pressure of 50 Torr. In this one, evaporating metals aggregated with each other by collision with He atoms and losing their kinetic energies, and the metal nanoparticles were synthesized. These nanoparticles were transported through a narrow stainless steel pipe (the outside diameter is 1/8 inches) via the upper one under vacuum environment of about 10^{-2} Torr and deposited on a substrate. The Rh wire with a purity of 99.93 % as an evaporation source was purchased from Tanaka Kikinzoku and the diameter of this wire was 0.3 mm^{ϕ}. The Rh nanoparticles were deposited on the Si single crystal substrate for the AFM measurement. To compare with the results of our previous study, the samples for the XPS and NEXAFS measurements were prepared by depositing Rh nanoparticles evenly on the Ni polycrystalline substrate annealed at 723 K in air [6]. The Rh nanoparticles on Si and Ni were fabricated under same conditions, which assured that the both Rh nanoparticles possessed same distributions of diameter and dispersion.
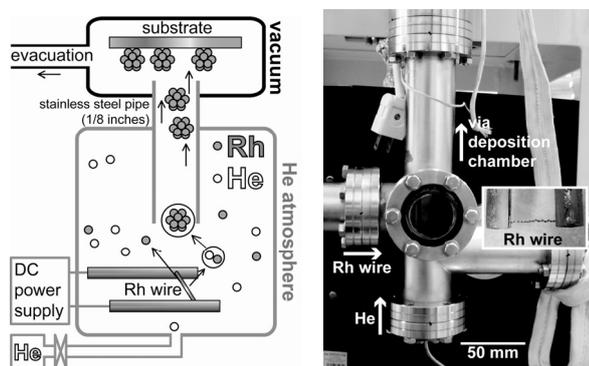
Fig. 1. A schematic view about chambers for the fabrication of Rh nanoparticles with gas evaporation method and photos of the lower one and the Rh wire as the evaporation source.

The chamber for the deposition of nanoparticles was connected to the XPS measurement chamber and it enabled to carry out the in-situ XPS measurement with the MgKα X-ray (1253.6 eV) and the hemispherical electron analyzer (PHOIBOS100-5ch, SPECS). Subsequently, the sample was exposed to DMS under a constant pressure of 2.0×10^{-8} Torr after cooling down to 90 K. The exposure was kept up for 25 sec (0.5 L). The particle sizes were evaluated by AFM measurement for the height value of the particles. The AFM measurement was carried out by NanoScope III-a (Veeco Instruments) with tapping mode. The ex-situ NEXAFS measurement for Rh L_3-edge and S K-edge was done at the double-crystal soft X-ray XAFS focusing beamline BL-10 on Ritsumeikan University SR Center by total electron yield (TEY) method with sample drain current and fluorescence yield (FY) method with silicon drift detector [8].

3. Results and Discussions
AFM results

The AFM image and average diameter of the Rh particles were shown in Fig. 2. The light color points in the image show the Rh particles, and the estimated average diameter and standard deviation of them were 1.2±0.3 nm. This result shows that we can fabricate the Rh nanoparticle which has a small diameter with a narrow distribution and high dispersion of it by the gas evaporation method with the Rh wire as an
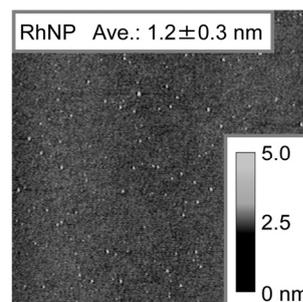
Fig. 2. The AFM image and average diameter of the Rh particles.

evaporation source.

Rh L_3-edge NEXAFS results

Fig. 3 shows the ex-situ Rh L_3-edge NEXAFS spectra for the Rh nanoparticle (RhNP) and standard samples (Rh bulk and Rh_2O_3) with FY and TEY method. The peak position of RhNP was lower than that of Rh_2O_3 at 3006.2 eV and corresponds that of Rh bulk at 3005.2 eV in the results with FY and TEY methods. These results

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show that the surface and bulk of Rh nanoparticle fabricated by the gas evaporation method is stable in the chemical state of Rh^0 despite exposure to air.
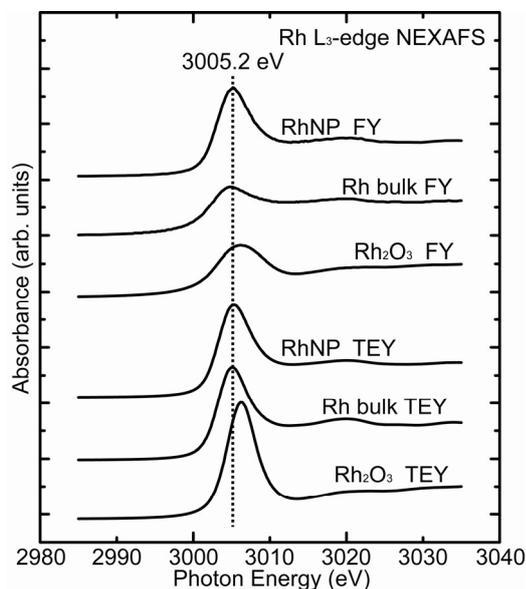
Fig. 3. The ex-situ Rh L_3-edge NEXAFS spectra for the Rh nanoparticle (RhNP) and standard samples (Rh bulk and Rh_2O_3) with FY and TEY methods.

Rh 3d XPS results

Fig. 4 shows the in-situ Rh 3d XPS spectra for the Rh(PVP) nanoparticle (Rh(PVP): gray line) and the Rh nanoparticle fabricated by the gas evaporation method (RhNP: black one) before the exposure to DMS. The Rh(PVP) nanoparticle was fabricated by the chemical reduction method with PVP as a surfactant, and the average diameter and standard deviation were estimated at 2.9±0.5 nm [5]. The measurement sample of Rh(PVP) nanoparticle was prepared by coating Ni substrate evenly with the colloidal solution of Rh(PVP) nanoparticles and heated up to 723 K in the air. This sample was subsequently set in the XPS measurement chamber and cleaned by Ar^+ sputtering (3 keV, 90 min) to remove the burned embers of PVP and impurities derived from the air on the surface of the Rh(PVP) nanoparticles [6]. The signal-to-noise ratio of the spectrum for the Rh(PVP) is worse than the one of the RhNP by remaining surface contamination. The both Rh $3d_{5/2}$ peak positions for the Rh(PVP) and RhNP are 307.2 eV that corresponds to a binding energy for the chemical state of Rh^0. Compared the spectra for the Rh(PVP) to the RhNP, the Rh $3d_{5/2}$ peak for the Rh(PVP) has a shoulder-like structure at about 308 eV which it for the RhNP does not

have. Considering that FWHM of a peak for a metal particle with smaller size is generally wider, a chemical state represented by this structure at higher energy position than 307.2 eV can be identified as oxidized Rh. These results show that the chemical state of Rh nanoparticle fabricated by the gas evaporation method is lower degree of oxidized than the Rh(PVP) nanoparticle. The difference in the chemical states causes the difference in the DMS adsorption reaction on their surface. We reveal the difference of that reaction through the following discussion of XPS and NEXAFS results.
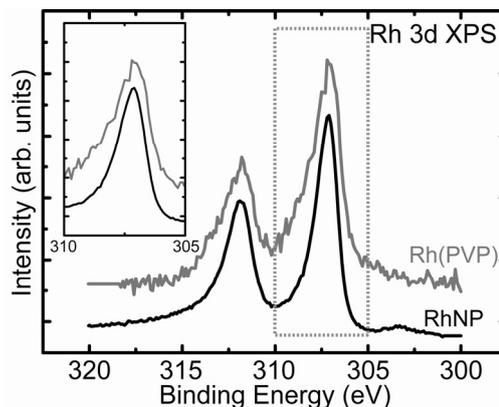
Fig. 4. Rh 3d XPS spectra for the Rh(PVP) nanoparticle (Rh(PVP): gray) and the Rh nanoparticle fabricated by the gas evaporation method (RhNP: black). The inset is the enlarged figure in the 305 to 310 eV region.

S K-edge NEXAFS results

Fig. 5 shows the ex-situ S K-edge NEXAFS spectrum for the DMS adsorbing on the RhNP. To compare with the DMS adsorption reaction on the Rh(PVP) nanoparticle which was fabricated by the chemical reduction method, the spectra for the DMS adsorbing on the Rh(PVP) nanoparticle (Rh(PVP)) and PVP are also shown in the figure [6]. In addition, the spectra for standard samples are inserted as a marker for each chemical state [9]. The spectra for the three samples are normalized with the edge-jump to compare the difference of chemical states per S atom. Judging from the spectra for these samples, a peak of the chemical state corresponding to the SO_4 is the largest peak for all the spectra. Furthermore, the spectrum for the RhNP has a shoulder-like shape at lower photon energy than the peak of the SO_4. It is thought that this shape is derived from the chemical state of SO_X (X=between 3 and 4). The difference between RhNP and Rh(PVP) in the degree of this oxidation reaction of atomic S

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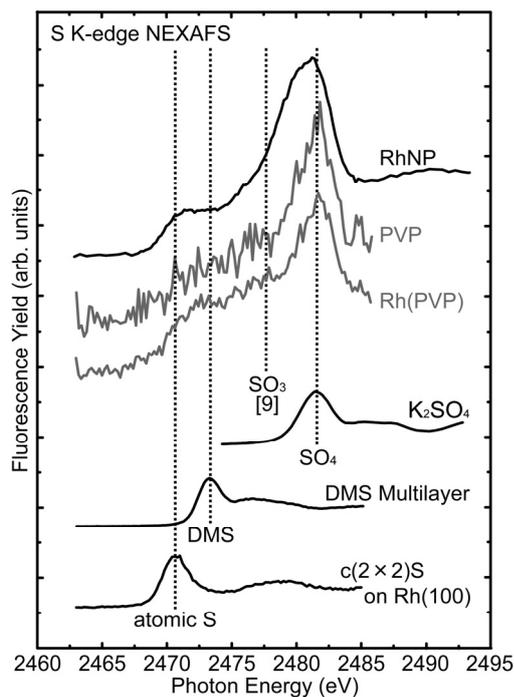
Fig. 5. The S K-edge NEXAFS spectra for the DMS adsorbing on the Rh nanoparticle (RhNP), Rh(PVP) nanoparticle (Rh(PVP)) and PVP. They are normalized with the edge-jump.

indicates that they have a different strength in the chemical bonding with atomic S. It is considered that the RhNP has a lot of electrons contributing the chemical bonding with atomic S since the RhNP has the lower degree of oxidized state than the Rh(PVP) nanoparticle as indicated in the XPS result. Therefore, the lower degree of oxidized RhNP has the stronger bonding with atomic S than the more oxidized one.

4. Conclusion

We have investigated the adsorption reaction of DMS on the RhNPs fabricated by the gas evaporation method using the Rh wire as evaporation source. The size and chemical states of the Rh nanoparticle are estimated by using AFM, XPS and NEXAFS. The AFM result shows that we can fabricate the Rh nanoparticle which has a small diameter with a narrow distribution and high dispersion of it by the gas evaporation method with the Rh wire as an evaporation source. The ex-situ Rh L_3-edge NEXAFS results show that the surface and bulk of Rh nanoparticle

fabricated by the gas evaporation method is stable in the chemical state of Rh^0 despite exposure to air. The in-situ Rh 3d XPS results indicate that the chemical state of RhNP fabricated by the gas evaporation method is lower degree of oxidized than the Rh(PVP) nanoparticle. The ex-situ S K-edge NEXAFS results show that the lower degree of oxidized RhNP has the stronger bonding with atomic S than the more oxidized one.

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