Characterization by Synchrotron-Radiation X-Ray Photoelectron Spectroscopy of NO Adsorption on Rh

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Rhodium nanoparticles were deposited by the evaporation method on a silicon wafer. The process used He gas in a Rh evaporation chamber that was connected to the load-lock chamber of BL6N1 at Aichi Synchrotron Radiation Center (Aichi SR). NO gas was introduced into the evaporation chamber, and the deposited Rh nanoparticles were exposed to NO with and without an ambient atmosphere to study the effect of O$_2$ on the electronic properties of the Rh nanoparticles and the behavior of NO molecules using synchrotron-radiation X-ray photoelectron spectroscopy (SR-XPS). The diameter of the Rh nanoparticles was estimated by transmission electron microscopy to be 2.7±0.6 nm. The XPS analysis indicates that the deposited Rh nanoparticles before NO exposure were in the metallic state. After exposure to NO, a part of the outermost surface of the Rh nanoparticles changed into Rh oxide, and NO molecules, atomic N and O species, and NO$_2$ were detected. On the other hand, after exposure to NO in ambient air, the surface of the Rh nanoparticles was preferentially oxidized. In addition, a few NO molecules were adsorbed on the surface of Rh, and a small amount of the adsorbed NO that reacted with the surface oxygen turned into NO$_2$. [DOI: 10.1380/ejssnt.2018.36]

Keywords: Rhodium; Nanoparticle; Transmission electron microscopy; Synchrotron-radiation X-ray photoelectron spectroscopy; Nitrogen oxide; Oxidation

I. INTRODUCTION

Catalysts play an important role in purifying exhaust gases to meet the stringent regulations for automobile emissions. From the point of view of fuel efficiency, automobile engines are required to operate under lean condition (high air-to-fuel ratio) which means that maintaining the performance in NO reduction becomes a serious issue. Rhodium is a precious metal that is essential to cutting NO emission by reducing nitrogen oxides to nitrogen and oxygen [1–3], and one way to make Rh more effective in NO reduction is minimizing the Rh particle size to maximize the number of reaction sites. As the metal particle size decreases below 10 nm, electronic and geometric properties that are different from those of the bulk material can be observed [4–7]. Another way to boost NO reduction is exploiting the Rh surface, whose electronic properties are suitable for NO adsorption. The first concern regarding effective use of Rh is understanding the intrinsic properties of Rh nanoparticles. In-situ X-ray photoelectron spectroscopy (XPS) is a suitable analytical method for characterization of the electronic properties of Rh because it can exclude the effect of any adsorbed species. On the other hand, the catalysts for purification of exhaust gases are used in ambient air. Therefore, the second concern is understanding the properties of nanoparticles under practical application conditions. Ex-situ XPS, that is XPS analysis conducted after exposure to atmospheric air, clarifies this issue. In previous studies, a Rh oxide layer was observed on the surface of Rh particles after exposure to ambient air, and the thickness of this oxide layer was found to affect its performance [8–11]. In our previous work, using synchrotron radiation (SR) XPS, we revealed that Rh nanoparticles that were not exposed to ambient air were in the metallic state, but they were oxidized into Rh$_2$O$_3$ and RhO$_2$ on the outermost surface upon exposure to the atmosphere [12].

The purpose of this paper is to report effect of ambient O$_2$ on the electronic properties of Rh nanoparticles and...
the behavior of NO molecules using in-situ or ex-situ XPS with SR.

II. EXPERIMENTAL

A. Preparation of Rh nanoparticles

Rh nanoparticles were fabricated by the evaporation method [13] in a Rh evaporation chamber. The evaporation chamber was connected to the load-lock chamber of BL6N1 at the Aichi Synchrotron Radiation Center (Aichi SR) in Japan. A Rh wire (4N) was evaporated to release Rh atoms and the Rh nanoparticles were grown under 50 Torr of high-purity He gas (5N5). The nanoparticles were transferred to the deposition chamber through a stainless steel pipe and deposited on a grid and an n-type Si wafer with (100) orientation. The Si wafer had been cleaned by only ultrasonic waves with an ethanol solution. The grid and the Si wafer were set in the deposition chamber as the substrates of the transmission electron microscopy (TEM) and XPS samples, respectively.

B. Analysis of Rh nanoparticles under different conditions

TEM experiments were carried out using a transmission electron microscope (JEM-3000F, JEOL, Japan) at an accelerating voltage of 300 kV. To evaluate the size of the Rh nanoparticles, the dispersed Rh nanoparticles were deposited on the grid within a short period of time.

The chemical states of the Rh nanoparticles under different conditions were investigated by SR-XPS at BL6N1 in Aichi SR. The photon energy for XPS analysis was set at 2.0 keV. As the evaporation chamber for Rh nanoparticles was connected to the load-lock chamber, the Rh
nanoparticles could be analyzed without exposure to ambient air. A NO (2% in He) gas cylinder was connected to the evaporation chamber and the NO gas was introduced after deposition of the Rh nanoparticles. X-ray photoelectron spectra were collected for three different samples of Rh nanoparticles: (a) before exposure to NO; (b) after exposure to NO for 5 min; (c) after exposure to NO for 5 min in ambient air. The spectra were calibrated against the peak of Au 4f7/2 at 83.95 eV [14]. The binding energies of Rh 3d5/2 for metallic Rh, Rh2O3, and RhO2 are 307.2, 308.2, and 309.5 eV, respectively [15–17], and the difference between Rh 3d5/2 and Rh 3d3/2 is 4.74 eV. The deconvolution analysis of the Rh 3d5/2 peaks was performed by CASA XPS [18], and each area of the Rh species with a different oxidation state was estimated as the fraction of that species in the deposited Rh nanoparticles.

### III. RESULTS AND DISCUSSIONS

#### A. TEM study

The TEM image of the Rh particles in Fig. 1 shows that particles with spherical shape were deposited. Using Fig. 1, the size of the Rh particles was evaluated, and the size distribution of the Rh particles is shown in Fig. 2. The diameter of the Rh particles varied from 1.7 to 4.8 nm, and the estimated average size was 2.7±0.6 nm, where the standard deviation (S.D.) was used for the uncertainty.

#### B. XPS analysis

The peaks of Rh 3d and Rh 3p, and the valence band can be found in the in-situ XPS survey spectrum of Rh nanoparticles for sample (a), which is not shown here.
The peaks of O 1s and C 1s are absent, which means that the nanoparticles that were not exposed to ambient air were in the metallic state and there was no contamination. The peaks of the silicon substrate are also absent. These XPS results and the TEM images indicate that the Rh nanoparticles were deposited like a thin film on the substrate. Hereafter, the deposited film is referred to as the “Rh nanoparticles”.

Figures 3 and 4 show the Rh 3d and N 1s spectra of sample (a), and the components corresponding to the Rh 3d\textsubscript{5/2} spectrum are summarized in Table 1. The peak in the Rh 3d\textsubscript{5/2} spectrum of sample (a) is located at 307.3 eV. The deconvolution analysis indicates that the Rh nanoparticles in sample (a) were in the metallic state. In the N 1s spectrum, the small peak at 397.5 eV corresponds to atomic N, which might be related to contaminants [19, 20].

Next, NO gas was introduced to the deposited Rh nanoparticles without exposing the sample to ambient air. The electronic properties of sample (b) were measured, and Figs. 5 and 6 show the Rh 3d and N 1s spectra of the sample. The peak top in the Rh 3d\textsubscript{5/2} spectrum of sample (b) is located at 307.4 eV, and it is wider than the same peak in the Rh 3d\textsubscript{5/2} spectrum of sample (a). When the Rh 3d\textsubscript{5/2} spectrum for sample (b) was deconvolved, the resolved peaks of sample (a) fit those of sample (b), which means that the Rh nanoparticles of sample (b) were also in the metallic state, including 7% of Rh\textsubscript{2}O\textsubscript{3}. These results indicate that part of the Rh surface changed to the Rh\textsuperscript{2+} state upon exposure to NO. In the N 1s spectrum of sample (b), three peaks appear at 397.5, 400, and 403.5 eV, which correspond to atomic N, chemisorbed NO, and chemisorbed NO\textsubscript{2}, respectively, according to the results of previous works [19, 20]. These results suggest that some NO molecules were directly chemisorbed on Rh metal, while others dissociated into atomic N and O, where the O atoms reacted with incoming NO molecules to form NO\textsubscript{2}. Since NO\textsubscript{2} had the electron-withdrawing effect of oxygen at the surface, the surface of Rh nanoparticles could have had a different oxidation state [19, 20].

Finally, the effect of ambient air on NO adsorption was examined. Figures 7 and 8 show the Rh 3d and N 1s spectra of the Rh nanoparticles, and the components corresponding to the Rh 3d\textsubscript{5/2} spectrum are summarized in Table 3. The peak in the Rh 3d\textsubscript{5/2} spectrum of sample (c) is located at 307.5 eV, with a peak at 308.6 eV. The deconvolution analysis indicates that the Rh nanoparticles in sample (c) were in the metallic state, including 13% of Rh\textsubscript{2}O\textsubscript{3}. In the N 1s spectrum, only a small peak corresponding to NO\textsubscript{2} appears at 403.0 eV possibly because the surface of the Rh nanoparticles was preferentially oxidized by O\textsubscript{2} from the ambient air, and a small amount of adsorbed NO reacted with the surface oxygen to form NO\textsubscript{2}.

### IV. CONCLUSIONS

Adsorption of NO occurred when the surface of Rh nanoparticles remained in the metallic state. The in-situ SR-XPS analysis showed that chemisorbed NO, atomic N, and NO\textsubscript{2} were present on the Rh nanoparticles, and part of the Rh surface changed to the Rh\textsuperscript{2+} state. The presence of ambient O\textsubscript{2} led to a difference in the adsorption of NO on the Rh nanoparticles because O\textsubscript{2} preferentially oxidized the surface of the Rh nanoparticles and inhibited NO adsorption. Ex-situ XPS analysis showed that only a small amount of adsorbed NO reacted with the surface oxygen to form NO\textsubscript{2}.

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**TABLE I.** Result of deconvolution analysis of Rh 3d\textsubscript{5/2} spectrum of sample (a) before exposure to NO.

| Rh species | Position (eV) | Fraction of species (%) |
|------------|--------------|-------------------------|
| Rh metal   | 307.3        | 100                     |

**TABLE II.** Result of deconvolution analysis of Rh 3d\textsubscript{5/2} spectrum of sample (b) after exposure to NO without ambient air.

| Rh species | Position (eV) | Fraction of species (%) |
|------------|--------------|-------------------------|
| Rh metal   | 307.4        | 93                      |
| Rh\textsubscript{2}O\textsubscript{3} | 308.4        | 7                       |

**TABLE III.** Result of deconvolution analysis of Rh 3d\textsubscript{5/2} of spectrum (c) after exposure to NO in ambient air.

| Rh species | Position (eV) | Fraction of species (%) |
|------------|--------------|-------------------------|
| Rh metal   | 307.5        | 87                      |
| Rh\textsubscript{2}O\textsubscript{3} | 308.6        | 13                      |

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