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Study of the Electronic States and Adsorption Characteristics of Pd-Rh Alloy Surfaces using Micro X-ray Photoelectron Spectroscopy

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1 Introduction

Pd-Rh alloys consisting of Rh and Pd, which are neighbours in the periodic table, exhibit high catalytic activity and are excellent heterogeneous catalysts such as CO oxidation [1]. It is known that the properties of these bimetallic alloys vary greatly depending on the composition ratio [2]. In this study, we investigated the electronic structure and molecular adsorption properties of composition-gradient Pd-Rh alloy surfaces by micro-X-ray photoelectron spectroscopy (μ-XPS) using synchrotron radiation to verify the effect of compositional differences on the catalytic activity.

2 Experiment

An alloy sample was synthesized by melting pellets of Pd and Rh with the compositional ratio of 85 : 15 by the arc melting method. The obtained ingot was cut into a disc of ca. 5 mm in diameter and 1 mm in thickness, and the surface was mirror polished. The compositional gradient of Pd and Rh was confirmed by electron probe microanalysis measurements. μ-XPS experiments were performed using a micro-focused beam at the beamline 13B of the Photon Factory

3 Results and Discussion

Figure 1 (top) shows a two-dimensional (2D) map of Rh $3d_{5/2}$/Pd $3d_{5/2}$ peak intensity ratios of a 1 mm x 1 mm region on a clean surface. There is an elliptical region of 200 μm width × 600 μm length with a high Rh density (maximum Rh/Pd atomic ratio is about 2). A compositional gradient is observed from the high Rh region to the surrounding Pd-rich region. Figure 1 (bottom) shows a 2D map of the C 1s intensity. This corresponds to the same region as Fig. 1 (top), but was measured after acetic acid was saturated the alloy surface. Although acetic acid was adsorbed over the entire surface, it was found to be adsorbed more on the Rh-rich regions. This indicates that Rh has a higher adsorption activity for acetic acid than Pd. This result is consistent with the fact that Rh, which has one less electron, is more reactive than Pd, which has a d^{10} closed shell structure.

Focusing on the binding energies of the Pd and Rh 3d core levels, interesting differences were observed between the clean surface and the acetic acid adsorbed surface. The binding energy of the Pd $3d_{5/2}$ core level is independent on the Rh/Pd composition ratio on the clean surface, while it showed a shift toward the higher binding energy with increasing the Rh concentration on the acetic acid adsorbed surface. On the other hand, the Rh $3d_{5/2}$ core level shows a shift toward higher binding energy with the Rh concentration on both clean and adsorbed surfaces. This result indicates that when acetic acid is adsorbed, valence electrons are transferred from the metal atoms to the adsorbed acetic acid, regardless of the difference between Pd and Rh.

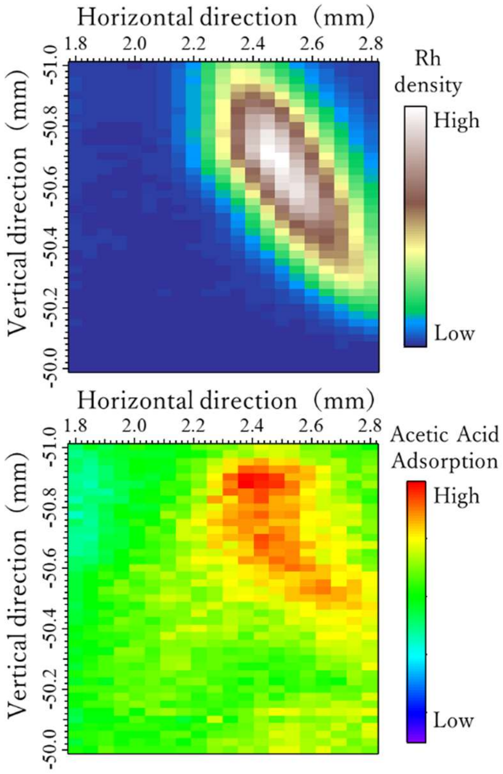

Fig. 1 : 2D maps of the Rh $3d_{5/2}$/Pd $3d_{5/2}$ peak intensity ratio on the clean surface (top) and the C 1s peak intensity on the acetic-acid saturated surface (bottom). The photon energy was 460 eV.

References

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