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Micro-XPS Study of Palladium-Rhodium Alloy Surface

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1 Introduction

Pd is a useful metal as a catalyst for various chemical reactions. Alloys of Pd and metals have been extensively investigated because of the tailoring of their catalytic function. For example, an alloy with Rh promotes the CO oxidation reaction [1]. When verifying and comparing functional properties of alloys of different compositions, one need to prepare several samples and repeat the same measurements. This is time and cost consuming. In contrast, if we prepare an alloy sample with compositional gradient, a single measurement with a microscopic technique is enough to assess the compositional dependence of physicochemical surface properties. Such a research style should accelerate the research and development of materials.

The beamline (BL) 13B is dedicated for material research using micro-X-ray photoelectron spectroscopy (μ-XPS) [2]. Here, we investigated a Pd-Rh alloy surface with a compositional gradient to understand the roles of Pd and Rh in surface chemical reactions.

2 Experiment

The Pd-Rh alloy sample was prepared from Pd and Rh metal pieces using an arc melting method. A disk of about ϕ4 mm × ^{t}1 mm was cut from the alloy ingot, and its surface was polished to a mirror finish. The surface was cleaned under an ultrahigh vacuum condition by cycles of annealing and Ar^+ sputtering until no carbon contaminants.

The μ-XPS measurements were conducted at BL-13B using soft X-rays. The synchrotron radiation beam was focused by a toroidal mirror to 15 μm (vertical) × 80 μm (horizontal). The sample surface was faced to the electron energy analyzer (SES200), and the sample was scanned to acquire two-dimensional (2D) distribution maps of the Pd/Rh composition and chemical activity. Acetic acid was used to assess the surface chemical activity. The acetic acid vapor was introduced into the chamber and the Pd-Rh alloy sample was exposed to the gas at room temperature.

3 Results and Discussion

Fig. 1 shows a compositional distribution of the clean Pd-Rh alloy surface. A high Rh concentration area with a size of about 400 μm × 200 μm (white) is surrounded by a high Pd concentration region (blue), and a gradient is formed between these two regions (brown−yellow−green).

As the surface is exposed to acetic acid, acetic acid adsorbs more on the Rh-rich region than the Pd-rich region. Rh has approximately 1.4 times higher adsorption activity than Pd for acetic acid. A fraction of the adsorbed molecules undergoes decomposition, forming acetate (CH_3COO^-) and other C-containing species. Interestingly, the adsorbed amount of the C-containing species is higher on the Pd-rich region, suggesting that Pd is more active than Rh for the decomposition reaction. The Pd-Rh alloy exhibits a dual function of adsorption and decomposition brought about by Rh and Pd, respectively.

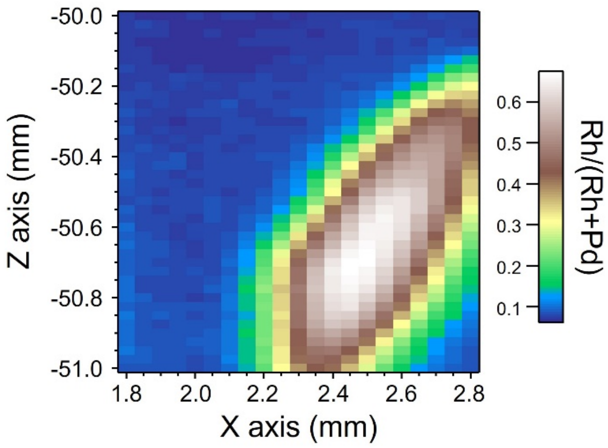

Fig. 1: Distribution of the compositional ratio, Rh/(Rh+Rd), verified from the Rh $3d_{5/2}$ and Pd $3d_{5/2}$ XPS peak intensities. The *Z* and *X* axes are vertical and horizontal directions, respectively.

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References

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