Hindrance to the Oxidation of Pd–Au Alloy Surfaces Depending on the Atomic Configuration: An AP-XPS Study

The oxidation behavior of $Pd_{3}Au$ (100) and (111) alloy surfaces was observed by a combination of *in situ* ambient-pressure X-ray photoelectron spectroscopy (AP-XPS) at elevated pressure (100 mTorr O_{2} ambient) and density functional theory calculations. It was found that alloying with Au hinders the surface oxidation of $Pd_{3}Au$ surfaces compared with pure Pd surfaces. Remarkably, the oxidation behavior is largely different between $Pd_{3}Au(111)$ and (100) surfaces. The (100) surface forms a surface oxide, whereas oxidation of the (111) surface is inhibited. It was revealed that the atomic configuration of the Pd-Au surfaces is a key factor determining the oxidation behavior.

Palladium (Pd) is widely used as a heterogeneous catalyst for various chemical syntheses and pollution control. For example, Pd-Au alloy shows excellent activities for highly efficient vinyl-acetate synthesis [1] and low-temperature carbon monoxide (CO) oxidation [2, 3]. Alloying with a second element changes the chemical and electronic structures, which are key factors for catalytic activity. Recent in situ measurements have found that elemental compositions and chemical states at alloy surfaces dynamically change depending on temperature, pressure, and chemical environment. For the CO oxidation reaction, oxygen-rich Pd surface states (e.g. oxides and dense chemisorbed phases) accelerate the catalytic activity on pure Pd surfaces [4, 5]. However, it is still unclear how the presence of chemically inert Au influences the formation of O-rich Pd surface states. To understand the alloying effects of Au on oxidation of Pd surfaces, O/Pd-Au alloy systems were investigated both from experimental and theoretical points of view [6].

AP-XPS experiments were carried out at a soft X-ray beamline, BL-13B. The AP-XPS apparatus consists of three vacuum chambers: a high-pressure chamber, a preparation chamber and a load-lock chamber. The high-pressure chamber is equipped with an electron energy analyzer with a differential-pumping system, which enables XPS measurements under *in situ* conditions.

On clean surfaces, Au-rich surface compositions are preferred due to their higher chemical stability. XPS data shows that the (near) surface Au fractions are 48% for the (100) surface, compared with 64% for the (111) surface, indicating that these surface compositions are more Au-rich than those of the bulk composition. Corresponding model surface structures of Pd_3Au alloy are shown in Fig. 1.

The oxidation behavior of the Pd₃Au alloy and pure Pd surfaces was traced by *in situ* AP-XPS as a function of temperature (**Fig. 2**). The O₂ gas was introduced to the chamber up to 100 mTorr, and the surfaces were heated to 563 K. **Figure 2(a)** shows an example of the Pd 3d_{5/2} XP spectrum of an oxidized Pd₃Au(100) alloy surface taken under oxidizing conditions. Judging from the spectral shape, the Pd₃Au(100) surface is covered by a surface oxide. A uniform ultra-thin surface oxide overlayer has been identified with a ($\sqrt{5} \times \sqrt{5}$)*R*27° periodicity (**Fig. 2(a)**, inset). The oxidized surface Pd atoms are coordinated by two or four O atoms, which are la-



Figure 1: A photograph of Pd₃Au alloy single-crystal and model structures of Pd₃Au(100) and (111) surfaces.



Figure 2: (a) Pd $3d_{5/2}$ XP spectrum taken from an oxidized Pd₃Au(100) surface. Each peak component is labeled as follows: B, Pd in the bulk; SS, Pd in the sub-surface layer; 2f and 4f, oxidized Pd bonding with two and four O atoms. (b) Evolution of Pd oxide on Pd₃Au and Pd surfaces as a function of temperature. The fraction of Pd oxide is deduced from the intensity of the 4f Pd oxide peak.

beled as two-fold Pd (2f) and four-fold Pd (4f). The corresponding O 1s XP spectrum also indicates the formation of the surface oxide (not shown). **Figure 2(b)** shows the oxide growth on Pd₃Au alloy and pure Pd surfaces during oxidation. The fraction of oxide is deduced from the 4f peak intensity of Pd $3d_{5/2}$ XPS. The oxide formation on Pd₃Au alloy surfaces starts at around 490 K, which is higher than that on pure Pd surfaces, showing that surface oxidation is hindered by alloying with Au. Remarkably, the growth curves exhibit different profiles between Pd₃Au(100) and (111) surfaces; the oxidation of the Pd₃Au(111) surface is rather suppressed compared with that of the (100) surface.

The adsorption of oxygen on Pd_3Au and pure Pd surfaces was simulated by density functional theory (DFT) calculations. It was found that the adsorption energy of oxygen at the four-fold-hollow site of the Pd_4 local configuration in the first layer of $Pd_3Au(100)$ is almost the same as that of Pd(100), while the adsorption energy of oxygen at the three-fold-hollow site of the Pd_3 local configuration in the first layer of $Pd_3Au(111)$ is significantly smaller than that of Pd(111). This suggests that the oxygen adsorption is substantially suppressed on $Pd_3Au(111)$, leading to hindrance of further oxidation. These theoretical results are consistent with the experimental results.

In summary, *in situ* monitoring of the surface oxidation of Pd₃Au alloy and pure Pd surfaces was conducted



by using AP-XPS. Comparative analysis of the surface oxidation revealed that alloying with Au suppresses oxide formation. The surface oxide is formed on the Pd₃Au(100) surface at a higher temperature, but not on the (111) surface even at the same temperature. DFT calculations suggest that the oxide formation is controlled by the adsorption energies of oxygen atoms on the alloy surfaces with different atomic configurations.

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