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Electronic Supplementary Information for

Element Selective Oxidation on Rh−Pd Bimetallic Alloy Surfaces

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1. Surface segregation of Rh under the 10^{-5} Torr O_2 ambient

Fig. S1 shows Pd $3d_{5/2}$ and Rh $3d_{5/2}$ X-ray photoelectron (XP) spectra taken from Rh_1Pd_9(111) surface before and after oxidation under 10^{-5} Torr O_2 ambient at 300 ºC for 15 min. Before the oxidation, the clean surface is mainly composed of Pd, judged from total peak intensities of Pd$3d_{5/2}$ and Rh$3d_{5/2}$ levels. Rh exhibits a single peak assigned as the bulk Rh (Rh_b). After the oxidation, the Pd surface oxide is formed on the surface, as discussed in main text (Fig. 1). For the Rh$3d_{5/2}$ level, a new peak appears at the higher binding energy side, which is assigned as the oxygen bonding surface Rh (Rh_c). Since the total peak intensity of the Rh$3d_{5/2}$ level increases, the O_2 exposure at 10^{-5} Torr causes a segregation of Rh to the surface which forms an O-chemisorbed phase on the surface.

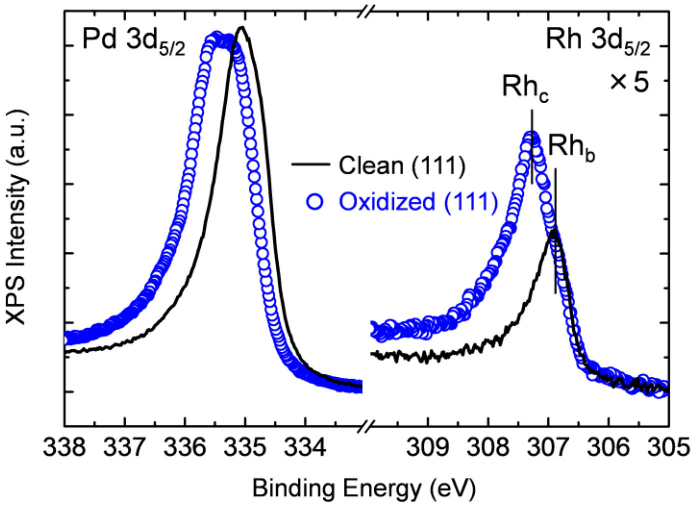

Fig. S1. Pd $3d_{5/2}$ and Rh $3d_{5/2}$ XP spectra taken from clean (black line) and oxidized (blue open circle) Rh_1Pd_9(111) surfaces. Here the Rh $3d_{5/2}$ level is indicated on a magnified scale by 5 times.

2. O 1s level for Rh_1Pd_9 alloy surfaces

The O 1s level provides additional information on the present oxygen/surface systems. The coverage and chemical state of oxygen on the surface are deduced from the O 1s XP spectra shown in Fig. S2. The chemical interactions with oxygen give rise to changes in the spectral shape of O 1s level. In Fig. S2, the black line is taken from a metallic Rh_1Pd_9(111) surface exposed to 10^{-7} Torr O_2 at room temperature which corresponds to a chemisorbed oxygen phase. It is noted that a prominent peak at 532 eV is attributed to Pd $3p_{3/2}$ level. The saturation coverage of chemisorbed oxygen is 0.25 monolayer (ML) on the Pd(111) surface[1], whereas 0.50 ML on the Rh(111) surface[2]. On the oxygen-chemisorbed Rh_1Pd_9(111) surface, the oxygen coverage is estimated to be ~0.25 ML, where the peak intensity of oxygen-saturated Pd(111) is used as the standard. It is consistent with the fact that the surface is mainly composed of Pd (Fig. S1).

The oxidation leads to enhancement of O 1s peak intensities for the both surfaces. For the (111) surface (blue open circle), the O 1s spectrum exhibits an asymmetric feature with a shift to the higher binding energy side. It is assumed that this feature is composed of two components with different chemical states. The Pd_5O_4 surface oxide formed on Pd(111) has an O−Pd−O tri-layer structure.[3] The surface and interface oxygen atoms give two peaks at different binding energies in O 1s level. The peak separation for the Pd_5O_4 phase on Pd(111) surface is too narrow to be resolved under the present energy resolution.

For the (100) surface (red open circle), it is obvious that the surface oxygen species appear as two different chemical states. The two oxygen-induced peaks separated by 0.95 eV are attributed to the surface and interface oxygen atoms of the RhO_2 surface oxide.[4]

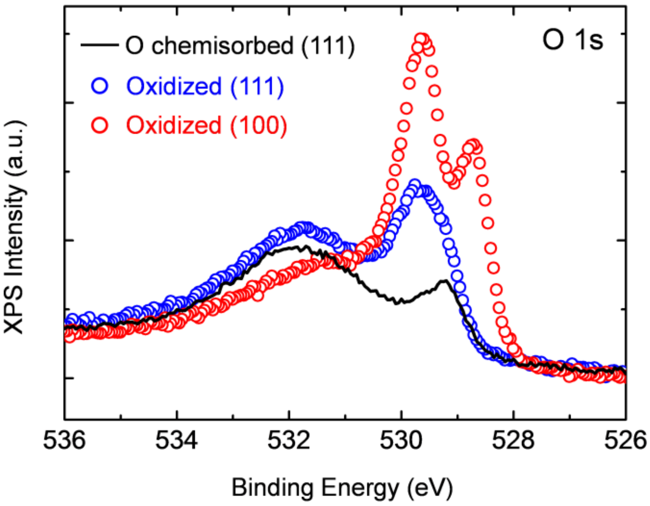

Fig. S2. O 1s XP spectra taken from oxygen-chemisorbed and oxidized Rh_1Pd_9(111) and (100) surfaces. The oxygen-chemisorbed (111) surface was prepared by exposing to 10^{-7} Torr O_2 at room temperature. While the oxidized surfaces were prepared by exposing to the 10^{-5} Torr O_2 ambient at 300 ºC for 15 min. Here the incident photon energy was tuned to be 630 eV.

3. Model structures of surface oxides

The surface oxides formed on Rh and Pd single-crystal surfaces have been extensively investigated and their geometric structures are well characterized; (9 × 9)-RhO_2 on Rh(111)[5], c(8 × 2)-RhO_2 on Rh(100)[4], Pd_5O_4 on Pd(111)[3] and (√5 × √5)-PdO on Pd(100)[6] (Fig. S3).

Based on these results, the surface oxides formed on the Rh−Pd alloy surfaces are modeled as the same structures as those on the monometallic surfaces shown in Fig. S3. Experimental results indicate that the amounts of Pd in the near surface regions of the alloy surfaces are fairly larger than those of Rh. Therefore the element composition of the second layer underneath the surface oxide is assumed as the bulk composition; Pd : Rh = 9 : 1 in DFT calculations.

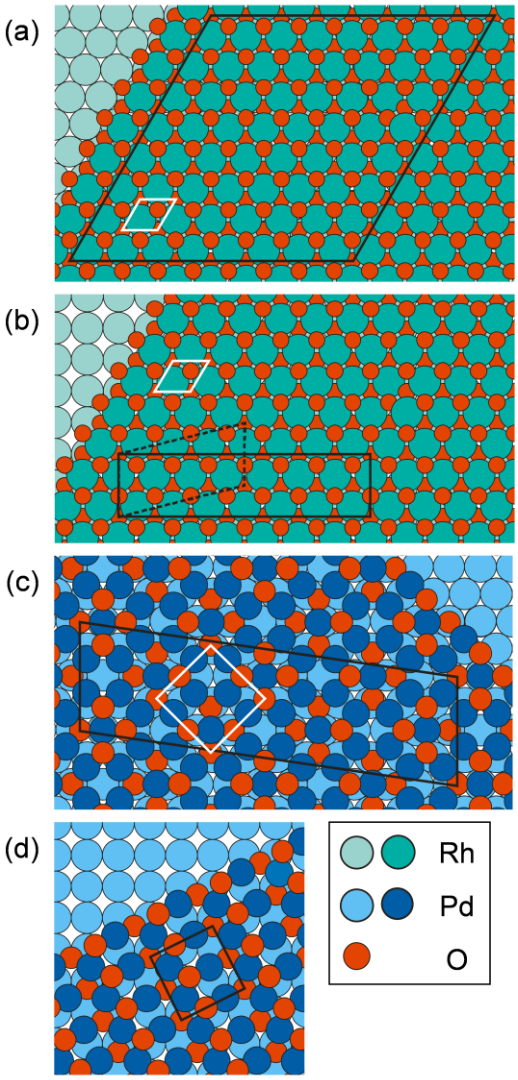

Fig. S3. Schematic models of surface oxides formed on the Rh and Pd surfaces, Rh(111), (a); Rh(100), (b); Pd(111), (c); Pd(100), (d). The unit cells of surface oxide layers are shown by white tetragons, whereas the commensurate unit cells are shown by black tetragons.

4. Details of DFT calculations for thermodynamics of surface oxides

In this section, details of our computational setup and a thermodynamic calculation are described. Vienna ab initio simulation package (VASP) was used for the calculations. The projector-augmented wave (PAW) method was applied to represent the core-levels with the revised Perdew−Burke−Ernzerhof (RPBE) exchange−correlation functional. The bulk lattice constants of Rh_1Pd_9 alloy, Rh and Pd were 3.97 Å, 3.86 Å and 3.98 Å, respectively. The surface structures are constructed by the slab model. The (4 × 4) Monkhorst−Pack k-point sampling was carried out on the (2 × 2) supercell. Similar k-point meshes were applied for other sized supercells.

The surface free energy (γ) under the gas ambient is described using the atomistic thermodynamics framework based on DFT calculations.[7] In this case, the oxide layer which has the lowest energy at a given condition is preferentially formed on the surface. Here the surface free energy is defined as follows;

$$\gamma = \frac{1}{A}\left[G_{\mathrm{slab}}(T, p_{\mathrm{O2}}, N_{\mathrm{O}}, N_{\mathrm{Rh}}, N_{\mathrm{Pd}}) - N_{\mathrm{Rh}}\mu_{\mathrm{Rh}} - N_{\mathrm{Pd}}\mu_{\mathrm{Pd}} - N_{\mathrm{O}}\mu_{\mathrm{O}}(T, p_{\mathrm{O2}})\right].$$

A is the surface area. G is the Gibbs free energy of a system at certain temperature (T) and pressure (p). N and μ are the number and chemical potential of atoms included in the system. G_{slab} can be represented by the total electron energy of the slab (E_{slab}), because the entropic contribution (vibrational free energy and configuration entropy) to the solid system can be considered negligibly small.[7]

The chemical potential of oxygen on the surface under equilibrium with the background gas is expressed as follows;

$$\mu_{\mathrm{O}}(T, p_{\mathrm{O2}}) = \frac{1}{2}\mu_{\mathrm{O2}}(T, p_{\mathrm{O2}}) = \frac{1}{2}\left[E_{\mathrm{O2}}^{\mathrm{total}} + \Delta\mu_{\mathrm{O2}}(T, p_{\mathrm{O2}})\right],$$

$$\Delta\mu_{\mathrm{O}}(T, p_{\mathrm{O2}}) = \frac{1}{2}\Delta\mu_{\mathrm{O2}}(T, p_{\mathrm{O2}}) = \frac{1}{2}\left[\Delta\mu_{\mathrm{O2}}(T, p^0) + k_{\mathrm{B}}T\ln\left(\frac{p_{\mathrm{O2}}}{p^0}\right)\right].$$

The oxygen chemical potential is decomposed into the total electron energy ($E_{\mathrm{O2}}^{\mathrm{total}}$) and the other part $\Delta\mu_{\mathrm{O2}}(T, p_{\mathrm{O2}})$. $\Delta\mu_{\mathrm{O2}}(T, p^0)$ is obtained from tabulated enthalpy and entropy values at the standard pressure $p^0(= 1\ \mathrm{atm})$.[8] k_{B} is the Boltzmann constant. These equations mean that the surface free energy of the system is expressed as a function of oxygen chemical potential. Taking into accounts of above considerations, the surface free energy is rewritten as follows;

$$\gamma = \frac{1}{A}\left[E_{\mathrm{slab}}(N_{\mathrm{O}}, N_{\mathrm{Rh}}, N_{\mathrm{Pd}}) - N_{\mathrm{Rh}}\mu_{\mathrm{Rh}} - N_{\mathrm{Pd}}\mu_{\mathrm{Pd}} - \frac{1}{2}N_{\mathrm{O}}E_{\mathrm{O2}}^{\mathrm{total}} - N_{\mathrm{O}}\Delta\mu_{\mathrm{O}}(T, p_{\mathrm{O2}})\right].$$

Based on above equations, we calculated the surface free energies for clean and surface-oxide-covered surfaces of Rh_1Pd_9(111) and (100) at 323 °C under equilibrium with gaseous oxygen. Resultant surface free energies are plotted as a function of O_2 pressure as shown in Fig. 4. The element composition of the second layer was assumed as the bulk composition; Pd : Rh = 9 : 1.

5. References

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