A Density Functional Theory Study of Self-Regenerating Catalysts LaFe$_{1-x}$M$_x$O$_{3-y}$ (M = Pd, Rh, Pt)

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S *Supporting Information*

ABSTRACT: Periodic density functional theory was used to investigate the stability and electronic structures of precious-metal atoms in the vicinity of LaFe$_{1-x}$M$_x$O$_3$ (M = Pd, Rh, Pt) perovskite catalyst surfaces. It was found that the surface segregation of Pd and Pt is significantly stabilized by the introduction of O vacancies, whereas the solid-solution phase is favorable for Rh, suggesting an important role of O vacancies in the self-regeneration of Pd and Pt. On the basis of the results, we propose a possible scenario for the self-regeneration of the precious metal in the perovskite catalyst.

The growth of metal particles is one of main causes of catalyst degradation in three-way catalysts. Pd-containing perovskite catalysts such as LaFe$_{0.95}$Pd$_{0.05}$O$_3$ exhibit excellent durability by suppression of the sintering effect, resulting in dramatic reduction of precious metals by 70−90%.[1−4] The perovskite catalysts display quite peculiar behavior. Pd nanoparticles are self-regenerated during catalytic reactions by reversibly moving into and out of the perovskite lattice depending on the fluctuations between the oxidative and reductive atmospheres in emission. It has been concluded that Pd forms a solid solution with the LaFeO$_3$ perovskite crystal and partially occupies the Fe site under an oxidative atmosphere, while Pd segregates to form metal particles under a reductive atmosphere. A recent experiment using energy-dispersive X-ray absorption fine-structure spectroscopy showed two important properties for the self-regeneration of the perovskite catalysts:[4] (I) The structural change of Pd is rapid enough to respond to the control frequency (1−4 Hz) of actual gasoline engines. If Pd diffuses through the perovskite lattice during the self-regeneration, the Pd diffusion seems to be extremely fast. (II) The growth of the size of metal particles segregated on perovskite catalysts is limited at about 1 nm, while Pd metal particles supported on Al$_2$O$_3$ continuously grow under a reductive atmosphere. It is desirable to clarify the mechanism of the self-regeneration of the perovskite catalysts in order to design new ageless catalysts.

Recently, Kizaki et al.[5] proposed a nanoscale spinodal decomposition mechanism to explain the rapid switch between reduced and oxidized states. However, this model still encounters a difficulty in explaining the rapid redox cycle of Pd atoms embedded deeply in the host perovskite lattice. Since the surface plays an important role in catalysis and segregation of the precious metal, a microscopic understanding of the catalyst surface is of critical importance in clarifying the self-regeneration in the perovskite catalyst.

In this work, we investigated the effect of the surface on the segregation process by means of periodic density functional theory (DFT) calculations and propose a possible scenario for the self-regeneration of the precious-metal-containing perovskite catalysts LaFe$_{1-x}$M$_x$O$_3$ (M = Pd, Rh, Pt). We found that the surface segregation of Pd and Pt is significantly stabilized by the introduction of O vacancies (V_O), whereas the solid-solution phase is favorable for Rh, suggesting an important role of V_O in the self-regeneration process in the perovskite catalyst.[6] On the basis of the results, we propose a possible self-regeneration mechanism for LaFe$_{1-x}$Pd$_x$O$_3$ in which V_O promotes surface segregation of Pd atoms, hence forming LaPdO$_{3-y}$ in the vicinity of the LaFe$_{1-x}$Pd$_x$O$_3$ surface. The surface LaPdO$_{3-y}$ layer thus formed enables Pd atoms to move into and out of the host perovskite lattice without diffusing over long distances in the bulk during redox cycles.

We carried out DFT calculations within the spin-polarized generalized gradient approximation (GGA) of Perdew, Burke, and Ernzerhof (PBE)[7] as implemented in the STATE[8] code. Electron−ion interactions were described by ultrasoft pseudo-potentials (USPPs),[9] and the wave functions and augmentation charge density were expanded using a plane-wave basis set. It has been shown that our USPP approach is able to reproduce the electronic structure obtained with the full-potential linearized augmented plane-wave method.[10] We also carried out the calculations with the on-site Coulomb repulsion (DFT+U) and verified that the electronic structures with DFT+U are qualitatively the same and that our conclusion is unchanged. We considered LaFeO$_3$ with a GdFeO$_3$-type orthorhombic unit cell with local magnetic moments of Fe aligned in the G-type antiferromagnetic order. The optimized lattice constants a = 0.5591 nm, b = 0.5563 nm, and c = 0.7917 nm are in good agreement with experiment.[11,12] To represent LaFeO$_3$ surfaces, an FeO$_2$-terminated LaFeO$_3$ (001) slab with five FeO$_2$ layers was constructed using theoretical lattice constants. A (1 × 1) surface

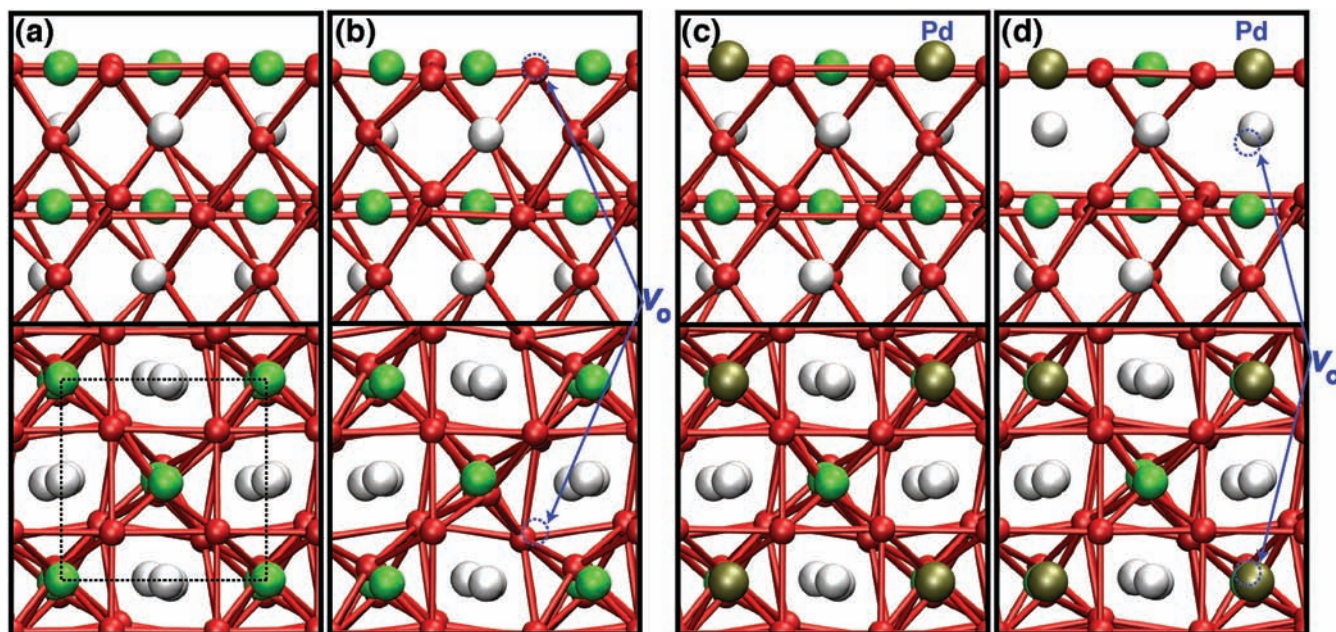**Figure 1.** Side views (upper) and top views (lower) of (a) clean LaFeO$_3$, (b) LaFeO$_{3-y}$, (c) LaFe$_{1-x}$Pd$_x$O$_3$, and (d) LaFe$_{1-x}$Pd$_x$O$_{3-y}$ (001) surfaces. White, green, tan, and red balls indicate La, Fe, Pd, and O atoms, respectively. The surface unit cell used is indicated by the dotted square in the lower panel of (a). Positions of O vacancies (V_O) are indicated by blue dotted circles.

unit cell was used, which is equivalent to a (001) ($\sqrt{2} \times \sqrt{2}$) $R45°$ unit cell of a cubic perovskite (001) surface (Figure 1a). We did not consider a LaO-terminated surface because it was found to be unstable over a wide range of O chemical potentials. We introduced one precious-metal atom and one V_O in a supercell. Further details of our calculations are described in the Supporting Information (SI).

To investigate the influence of the environmental conditions on the stability of a precious-metal atom M (M = Pd, Rh, Pt) near the LaFeO$_3$ surface, we calculated the total energy of the LaFe$_{1-x}$M$_x$O$_3$ slab with and without V_O as a function of the position of M. The most stable site for V_O was determined by examining all of the nonequivalent O sites for each position of M. It should be noted that the interstitial precious-metal atom was found to be energetically unfavorable and thus is not considered here.

Figure 2 displays the calculated total energies of the LaFe$_{1-x}$M$_x$O$_3$ slabs relative to those with M in the bulk. We define the surface-segregated state as a state wherein M is in the substitutional surface Fe site and the solid-solution state as the state wherein M is in the bulk state. In the case of Pd, the surface-segregated state is slightly more stable than the solid-solution state by 0.06 eV, whereas the former is less stable than the latter by 0.34 and 0.23 eV for Rh and Pt, respectively. Introduction of V_O drastically changes the stabilities of the precious-metal atoms near the surface: segregated states are significantly stabilized by 0.88 and 1.06 eV for Pd and Pt, respectively, in comparison with the solid-solution state, suggesting an important role of V_O in the surface segregation of the precious metal. In the case of Rh, however, the solid-solution state is still favorable upon inclusion of V_O, although the surface-segregated state becomes less stable by 0.18 eV.

To relate these calculated energies to the relevant working conditions, we calculated the surface-segregation energy as a function of temperature T and O chemical potential μ_O as

$$E_{seg}(T, \mu_O) = \Omega_{M, surf}(T, \mu_O) - \Omega_{M, bulk}(T, \mu_O)$$

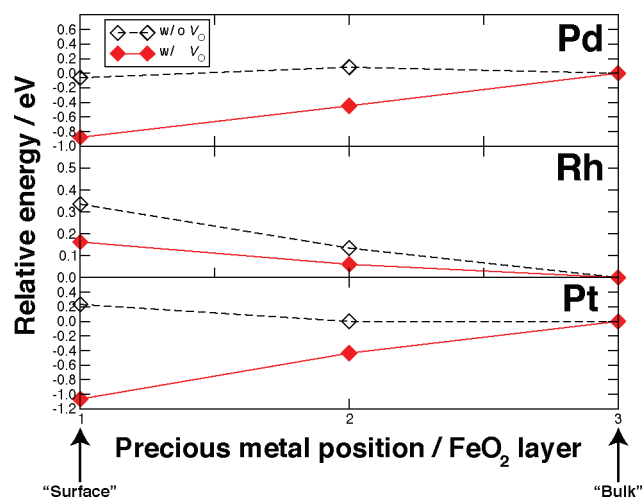**Figure 2.** Relative energy of the LaFe$_{1-x}$M$_x$O$_3$ slab as a function of position of the precious-metal atom M with (solid line) and without (dashed line) V_O for M = Pd (top), Rh (middle), and Pt (bottom). The zero of energy is the energy of the LaFe$_{1-x}$M$_x$O$_3$ slab with M in the "bulk", which was approximated by the total energy of the slab with M in the third FeO$_2$ layer.

where $\Omega_{M,surf/bulk}$ is the grand potential of the slab with an M atom in a surface/bulk Fe site, given by

$$\Omega_{M, surf/bulk}(T, \mu_O) = F_{M, surf/bulk}(T, N_{V_O}) + N_{V_O}\mu_O(T, p)$$

in which

$$\mu_O(T, p) = \mu_O(T, p°) - \frac{1}{2}k_B T \ln(p/p°)$$

$F_{M,surf/bulk}(T, N_{V_O})$ is Gibbs free energy of the slab with M atoms in surface/bulk Fe sites, and N_{V_O} is the number of V_O in the system. The temperature dependence of μ_O at $p° = 1$ atm was
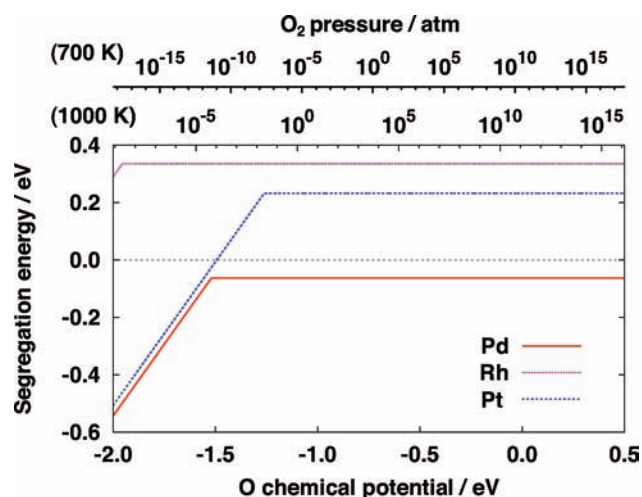
Figure 3. Surface-segregation energy as a function of O chemical potential for Pd, Rh, and Pt. The zero of the O chemical potential is half of the total energy of an O_2 molecule in the gas phase (O-rich limit). The O partial pressures at 700 and 1000 K are shown.
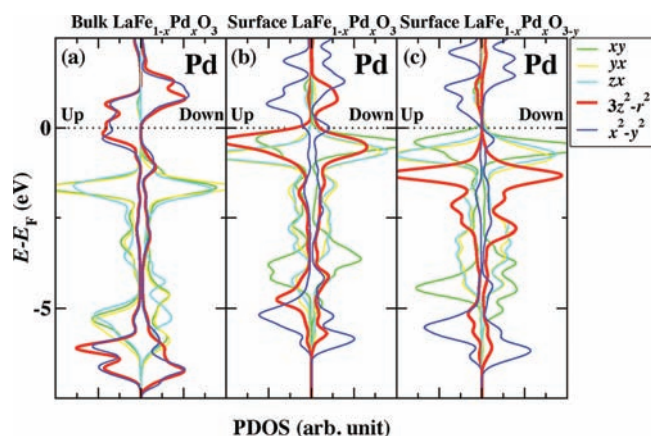

Figure 4. Density of states projected onto Pd d states (PDOS) for (a) bulk $LaFe_{1-x}Pd_xO_3$, (b) surface $LaFe_{1-x}Pd_xO_3$ without V_O, and (c) $LaFe_{1-x}Pd_xO_{3-y}$ with V_O.
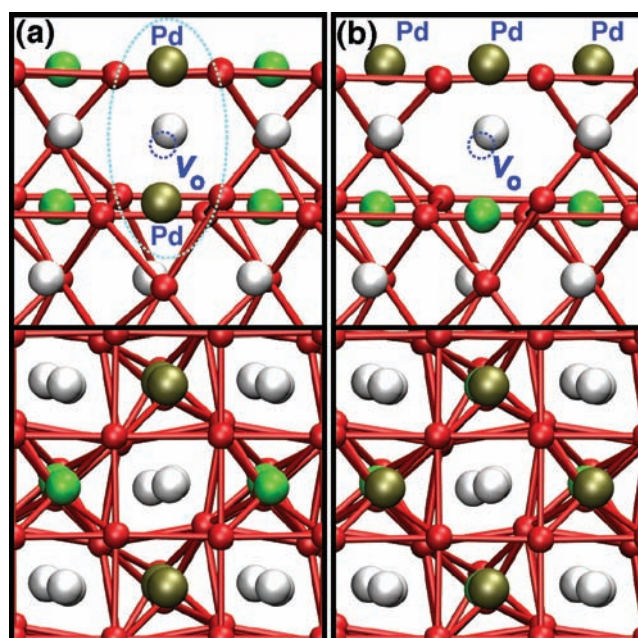

Figure 5. Side views (upper) and top views (lower) of $LaFe_{1-x}Pd_xO_{3-y}$ with two Pd atoms and one V_O: (a) the most stable configuration, in which Pd atoms agglomerate in the vicinity of subsurface V_O; (b) the second stable configuration with the topmost PdO_2 layer and subsurface V_O. The former is more stable than the latter by 0.317 eV. Introduction of one more subsurface V_O (which is the most stable position for the second V_O) in the unit cell results in the stabilization of the latter structure.

calculated using thermochemical tables.[13,14] The calculated E_{seg} values are shown in Figure 3. It turns out that surface segregation is favorable for Pd over a wide range of O partial pressures, while surface segregation of Pt becomes stable only below 1.0×10^{-4} atm at 1000 K (1.0×10^{-11} atm at 700 K). On the other hand, the solid-solution phase is favorable for Rh over the entire region considered here. Our results are in qualitative agreement with the experiment by Tanaka et al.,[2] who found that the segregation of precious metals from $LaFeO_3$ to form nanoparticles is facilitated in the order Pd > Pt > Rh.

The most stable position for V_O is the topmost surface O site in the cases of pristine $LaFeO_3$ and the solid-solution phase of $LaFe_{1-x}M_xO_3$ slabs, as shown in Figure 1b. On the other hand, in the surface-segregation state of $LaFe_{1-x}M_xO_3$, V_O forms at a subsurface site beneath the surface M metal (Figure 1d). The subsurface V_O has significantly lower formation energy of 1.52 eV relative to an isolated O_2 molecule (as compared with the value of 2.13 eV for the clean $LaFeO_3$ slab) and stabilizes the surface segregation of the precious metal.

To investigate why the surface segregation is promoted by the introduction of V_O, we inspected the density of states for $LaFe_{1-x}M_xO_3$ projected onto the M atoms in the solid-solution and surface-segregated states, and the results are shown in Figure 4 for $LaFe_{1-x}Pd_xO_3$ (see the SI for other cases). In the solid-solution state, the degenerate e_g states of Pd and Pt are singly occupied (Figure 4a), and they are formally trivalent [the actual charge state is $(3-\delta)^+$, since the e_g states with opposite spin are partially occupied], suggesting that the solid-solution state is unstable. It should be noted that Jahn–Teller-type distortion does not take place in these cases and that Pd and Pt favor divalent or tetravalent states, with trivalent forms being rarely observed. However, in the previous theoretical calculation, it was shown that Pd in $LaPd_{0.5}Co_{0.5}O_3$ perovskite is trivalent,[1] providing justification for the present result. On the other hand, because the number of valence electrons of Rh is one less than for Pd and Pt, the e_g states of Rh are completely empty, forming a stable closed shell. This explains why Rh prefers the solid-solution phase.

Because of the symmetry lowering, the degeneracy of the Pd e_g state is lifted at the surface (Figure 4b). Pd forms strongly hybridized states with surface O via its $d_{x^2-y^2}$ state, as suggested by the large bonding–antibonding splitting in the density of states. The Pd $d_{3z^2-r^2}$ state also forms weakly hybridized states with the p state of O underneath, which appears close to the Fermi level. Introduction of subsurface V_O beneath the surface Pd leads to the formation of a nonbonding $d_{3z^2-r^2}$ state (Figure 4c). Because the antibonding counterpart of the $(Pd\ e_g)-(O\ p)$ hybridized state is occupied in the absence of subsurface V_O, the formation of a nonbonding $d_{3z^2-r^2}$ state results in a gain in the band energy, leading to great stabilization of the surface-segregation states. The charge state of the surface Pd is therefore close to 2+.

On the basis of our calculations, we propose that V_O and its stabilization of the surface-segregated precious metal are the keys to the self-regeneration in perovskite oxides. Precious-metal-containing perovskite catalysts were prepared by calcination of the precious metal containing precursor at 1073 K for 2 h in air.[2,3] Although experimentally it was concluded that the precious metal forms a uniform solid solution with the perovskite crystal, we speculate that considerable amounts of V_O are introduced during the sample preparation process and promote the surface segregation, hence forming a $LaPdO_{3-y}$ layer in the vicinity of the surface. The surface $LaPdO_{3-y}$ layer thus formed enables Pd atoms to move into and out of the host perovskite lattice without diffusing over long distances in the bulk during redox cycles and thus plays a vital role in the self-regeneration. Indeed, our preliminary calculations with two Pd atoms in a supercell showed that the additional Pd atom favors the substitutional Fe site closest to the subsurface V_O (Figure 5a), suggesting the agglomeration of precious-metal atoms around the subsurface V_O. Futhermore, introduction of one more V_O into the unit cell results in stabilization of the topmost PdO_2 layer (see Figure 5b), demonstrating the decisive role of V_O in the formation of the $LaPdO_{3-y}$ layer. Very recently, the existence of Pd^{2+} with square-planar coordination was reported experimentally in the case of highly reactive Pd-doped $LaFeO_3$.[15] From an X-ray photoelectron spectroscopy analysis of $Pt/LaFeO_3$ catalysts, Dacquin et al.[16] suggested the stabilization of a PtO and/or PtO_2 layer at the surface, providing strong support for our scenario of the self-regeneration mechanism.

To summarize, on the basis of DFT calculations we have proposed a possible mechanism for the self-regeneration of perovskite catalysts wherein O vacancies promote the surface segregation of precious-metal atoms and thus play a central role in the self-regeneration. We found that the Pd exists in the vicinity of the $LaFeO_3$ surface as a $LaPdO_{3-y}$ layer, which facilitates the segregation of Pd metal particles on the surface without diffusion over long distances in the bulk. We think that the surface segregation of Pd occurs in the sample preparation process rather than in the redox cycle. The formation of the surface $LaPdO_{3-y}$ layer in an as-prepared sample allows the facile formation of Pd nanoparticles on the surface, as observed in experiments. We believe that our finding is a step toward a detailed understanding and prediction of new self-regenerating catalysts. Our finding may also be the key to understanding the very high turnover frequency of Pd-containing perovskites for Suzuki—Miyaura couplings.[17]

ASSOCIATED CONTENT

S Supporting Information. Details of the computational methods and optimized geometries, segregation energies, and electronic structures of $LaFe_{1-x}M_xO_{3-y}$. This material is available free of charge via the Internet at http://pubs.acs.org.

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(6) We discriminate "segregation" and "surface segregation" in this manuscript as follows: (i) "segregation" is defined as the formation of metallic nanoparticles on the supported surface, and (ii) "surface segregation" is defined as a state wherein precious-metal atoms are in the substitutional surface Fe sites, as shown in Figures 1c,d and 5b.

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