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Stability of Pd_xO_y particles supported on strontium titanate perovskite under three-way catalyst operating conditions: Implications for sintering resistance

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Abstract

Self-regenerative materials are keys to the development of stable catalysts used under high temperature condition, e.g., three-way catalyst converters in automobiles. Among others, metal nanoparticles supported on perovskite oxides are promising ones. However, little is known about their atomistic details, which are crucial for understanding and development of thermally stable catalysts. Herein, we present a machinelearning enhanced density functional theory study of Pd_xO_y nanoparticles supported on a $Sr_3Ti_2O_7$ (001) surface and demonstrate that supported oxidized Pd particles fulfill the conditions for the self-regenerative catalysts. In the oxidative condition, solid-solution reaction of Pd with the support is found to be preferable, but is limited to the vicinity of the surface. Furthermore, formation of PdO-like clusters enhances their binding strength to the support, inhibiting the agglomeration (sintering) of the Pd_xO_y nanoparticles. We present detailed thermodynamic and electronic structure analyses and clarify the roles of the oxide support, cluster size of the oxidized metal nanoparticle, and the metal-support interaction. This work may provide a guideline for the rational design of the thermally stable catalyst against sintering.

Keywords: sintering; metal-support interaction; oxidative dispersion; global optimization; thermodynamics; machine learning; DFT.

Introduction

Thermal stability of heterogeneous catalysts, along with high activity and selectivity, plays a central role in the catalyst design for industrial applications,¹⁻⁴ e.g. three-way catalyst (TWC) converters to purify emission of exhaust gases⁵⁻⁸ or fuel cells. However, the thermal instability originated from the agglomeration (sintering) of metal NPs over time under operating condition is the major concern, especially for the catalyst with metal NPs in small sizes.⁹ Self-regenerable metal nanoparticles on the oxide surface show great potential to overcome this problem.¹⁰⁻¹⁹ Metal oxide NPs are highly anchored on the oxide support under oxidative conditions with strong metal-support interaction (MSI) leading to the sintering resistance, while they are subsequently reduced back to active metallic NPs under reductive conditions.¹⁰⁻¹⁹ This approach is often employed to prepare the ultrastable TWCs in which the platinum-group metal (PGM) NPs are exposed to the high-temperature reductionoxidation (redox) fluctuations of exhaust gas.^{10,20} PGM-O-*M* bonds (*M* is the metal of the support surface) formed in oxidative atmospheres can suppress sintering effectively.^{12,18,21-29}

However, a very strong PGM-O-M bonding can lead to another deactivation process, i.e., a solid-solution reaction (SSR) under oxidative condition,^{10–15} where the PGM ions are incorporated into the metal sites of oxide support. If the PGM cannot be reduced back to metallic NPs even under reductive conditions, the catalyst is deactivated.^{12–15} For example, strong Rh-O-Al bonds in Rh/ γ -Al₂O₃ effectively inhibit the sintering,^{12,13,15} but the SSR between Rh₂O₃ and γ -Al₂O₃ deactivates the catalyst under the TWC oxidative condition. Replacing γ -Al₂O₃ with LaMgAl₁₁O₁₉ can help mitigate SSR because the La-O layer of LaMgAl₁₁O₁₉^{12,13,15} suppresses the penetration of Rh³⁺ and preserves Rh³⁺ near the surfaces. Consequently, it is important to inhibit the direct PGM ions penetration from the support surface to the bulk region and to allow a smooth redox cycle of PGM NPs by TWC atmospheric fluctuation.^{12–17}

Among the numerous candidates for the TWC support materials, titanate perovskite $(ATiO_3)$ and the related materials have received considerable research attention because of their chemical stability, strong anchoring effect, and low SSR.^{14,16,17,25} Irvine et al. found that highly anchored Pt NPs on an A-site-deficient $A TiO_3$ exhibits better catalytic NO + CO reaction activity and superior thermal stability.¹⁴ Pt is incorporated into $A TiO_3$ in the synthesis process and stable Pt clusters are formed upon reductive condition. During the reaction condition, self-regenerable Pt NPs are observed with a low SSR of Pt. Beppu et al. found that Ti-rich $SrFe_xTi_{1-x}O_{3-\delta}$ -supported Pd catalysts (x = 0.0 and 0.2) have high catalytic activities for NO reduction and thermal stabilities under the stoichiometric condition because of the anchoring effect.²⁵ The catalysts was prepared by an impregnation method and PdO NPs are stable under the stoichiometric condition. However, the deactivation of $SrFe_x Ti_{1-x}O_{3-\delta}$ -supported Pd catalysts occurs under oxidative conditions. Very recently, well-dispersed and closely integrated Pd NPs supported on $Sr_3Ti_2O_7$ (STO-327) in a Ruddlesden–Popper phase have been synthesized. Here, the Sr₃Ti₂O₇-supported Pd catalyst shows the superior NO catalytic activity and thermal stability even after a long air-aging period.³⁰ Pd oxide (PdO) NPs with an average size of 2–5 nm are grown epitaxially on STO-327(001) surfaces with a strong metal-support interaction (MSI). The SSR of Pd with the STO-327 lattice is limited to the vicinity of the surface, presumably because of the presence of the rock-salt-type SrO layer that inhibits the diffusion of Pd atoms into bulk STO-327. However, the atomistic details of Pd (PdO) NPs, STO-327(001) surfaces,

and their interfaces under operating conditions, which are crucial for the development of sintering-resistant catalysts, are yet to be elucidated.

Herein, we use density functional theory (DFT), machine learning enhanced global optimization, and thermodynamics to investigate the structures, oxidation states, and binding strengths of small Pd clusters (Pd_xO_y) supported on STO-327(001) under those relevant to the TWC conditions. We demonstrate that supported $\mathrm{Pd}_x\mathrm{O}_y$ on STO-327 can be a selfregenerable catalyst with low SSR and strong MSI. First, we evaluate the possibility of the SSR of Pd and discuss the use of STO-327(001) to suppress SSR by constructing phase diagrams of Pd-doped bulk STO-327 and STO-327 surfaces. Next, we consider MSI by investigating the structures and binding strengths of several Pd_xO_y clusters on STO-327(001) and on non-hydroxyl-terminated γ -Al₂O₃(100). The PdO-like clusters supported on all surfaces are stabilized compared to the metallic Pd clusters, suggesting that the oxidative treatment can suppress the sintering and facilitate the metal redispersion effectively. Moreover, we find that Pd_xO_y clusters are more stabilized on STO compared with γ -Al₂O₃(100); and the origin for the stronger MSI at the Pd_xO_y/STO interface arises from charge-transfer interaction. The change in the atomic structure and stoichiometry of Pd clusters supported on STO surfaces under oxidative and reductive conditions is evaluated. Finally, we discuss the nucleation of PdO-like clusters under the oxidative condition: some clusters show peculiar stability against Ostward ripening. Strong interfacial bonding for these magic number clusters can explain the sintering resistance of Pd NPs supported on STO-327.

Methods

DFT+U calculations

All spin-polarized DFT calculations were performed using QUANTUM ESPRESSO package.³¹ The PBEsol exchange-correlation functional³² and ultrasoft pseudopotentials^{33,34} were adopted. Wave functions and charge density were expanded by a plane wave basis set with kinetic energy cutoffs of 40 Ry and 320 Ry, respectively. The Hubbard U correction³⁵ with the effective U of 4.45 eV was employed for the Ti 3d states.³⁶ To mitigate the overbinding of the O₂ molecule, a correction of 1.11 eV was added to the total energy of O₂ (Figure S4).³⁷ Dispersion correction by Grimme^{38,39} (PBEsol+U-D3) was used for the adsorption of (oxidized) Pd clusters on surfaces; whereas other calculations related to the bulk and surfaces of STO-327 were performed without dispersion correction (PBEsol+U). The Brillouin zone was sampled by the Monkhorst–Pack scheme⁴⁰ with a k-points distance of 0.20 Å⁻¹. The ionic relaxation was performed with a residual force threshold of 0.03 eV/Å (10⁻³ Ry/Bohr). The reaction path search was performed using the nudged elastic band (NEB) method.^{41,42} Atomic charges were obtained using Löwdin population analysis.⁴³

The crystal structures of STO-327 (Figure 1(a)) and SrTiO₃ (STO-113) considered herein have space groups of I4/mmm and $P\overline{m}3m$, respectively, where both STO-327 and STO-113 are assumed to retain their perovskite structures.^{14,25} For comparison, we employed γ -Al₂O₃ using a nonspinel model and its nonhydroxyl terminated (100) surface.⁴⁴ The optimized lattice constants of STO-327, STO-113, and γ -Al₂O₃ are listed in the Supporting Information (SI).

Thermodynamics analysis

The formation of the Pd solid solution into the STO-327 bulk was evaluated by examining the stability of several Pd-doped STO-327 crystals (Pd@STO-327) in a $(2 \times 2 \times 1)$ supercell using the grand potential, which is defined as

$$\Omega_{\text{bulk}}(T, p_i) = G - \sum_i N_i \mu_i(T, p_i), \qquad (1)$$

where G, $\mu_i(T, p_i)$, and N_i are the Gibbs free energy of Pd@STO-327, chemical potential of the atomic species i (i = Sr, Ti, O, Pd) at temperature T and partial pressure p_i , and number of atoms, respectively. All neutral atomic vacancies (V_{Sr} , V_{Ti} , V_{O}) and complex vacancies (V_{SrO}, V_{TiO}, V_{TiO₂}, and V_{SrTiO₃}) were considered for STO-327. For Pd@STO-327, we considered the substitution of Pd for the cations (Pd@Sr and Pd@Ti) and the substitution of Pd for the atom in the associated complex vacancies (Pd@C-V_V where C = Sr and Ti; V = Sr,Ti, and O).

The relative stability of STO-327 surfaces under conditions relevant to the TWC operating ones was investigated by calculating the surface excess free energy $(\Omega_{\text{surf}}(T, p_i))$ and details are given in section SI.4 of SI.

We assumed that the structure is in equilibrium with bulk STO-327, which implies

$$3\mu_{\rm Sr} + 2\mu_{\rm Ti} + 7\mu_{\rm O} = \gamma_{\rm Sr_3Ti_2O_7}^{\rm bulk},\tag{2}$$

where $\gamma_{\text{Sr}_{3}\text{Ti}_{2}\text{O}_{7}}^{\text{bulk}}$ denotes the Gibbs free energy of the bulk STO-327 per formula unit.

Vibrational frequencies and entropy were calculated within the harmonic approximation using Phonopy package.⁴⁵ Phonon contributions to the grand potential were found to be small with the order of 0.2 eV for T < 1200 K, which is in line with previous works.^{46,47} As a result, thermodynamic stabilities of Pd@STO-327 and surface termination were evaluated without the phonon contribution. Then, we constructed phase diagrams of Pd@STO-327 and the STO-327 surfaces as a function of the chemical potentials of Sr ($\Delta\mu_{Sr}$) and O ($\Delta\mu_{O}$) relative to those of bulk Sr in the face-centered cubic (fcc) structure and gas-phase O₂, respectively. The ranges of $\Delta\mu_{Sr}$ and $\Delta\mu_{O}$ were restricted by the thermodynamical preference to form bulk STO-327 without the precipitation of constituent compounds,⁴⁸ namely SrO, TiO₂, Ti, Sr, and O₂ (See section SI.5 of SI). For the Pd chemical potential, we used bulk fcc Pd and tetragonal PdO as references, where $\mu_{Pd} = E(Pd)$ if $\Delta\mu_{O} \leq \Delta H_f(PdO)$, and $\mu_{Pd} = E(PdO) - \mu_O$ otherwise. Here, E(Pd), E(PdO), and $\Delta H_f(PdO)$ are the total energies per formula unit of bulk fcc-Pd, tetragonal PdO, and enthalpy of formation of PdO, respectively.

Considering the system is in equilibrium with the O₂ atmosphere, $^{46,49} \Delta \mu_{O}$ can be esti-

mated by

$$\Delta \mu_{\rm O}(T,p) = \frac{1}{2} [\mu_{\rm O_2}(T,p) - E({\rm O_2})] = \frac{1}{2} [H_{\rm O_2}(T,p^0) - H_{\rm O_2}(0 \ {\rm K},p^0)] - \frac{1}{2} T [S_{\rm O_2}(T,p^0) - S_{\rm O_2}(0 \ {\rm K},p^0)] + \frac{1}{2} k_B T \ln \frac{p}{p^0},$$
(3)

where $\mu_{O_2}(T, p)$ is the O₂ chemical potential at temperature T and partial pressure p, $E(O_2)$ is the DFT total energy of an isolated O₂, H is the enthalpy, S is the entropy, and p^0 is 1 atm. $H_{O_2}(T, p^0)$ and $S_{O_2}(T, p^0)$ are obtained from the NIST-JANAF thermochemical tables.⁵⁰

In TWC, the reaction environment is changed frequently by sequential switching between fuel-lean and fuel-rich conditions, and this results in the change in the O₂ partial pressure (p_{O_2}) . Moreover, thermal stability of TWC was tested by an air-aging experiment. The corresponding $\Delta \mu_O$ for fuel-rich, stoichiometric, fuel-lean, and air-aiging conditions are tabulated in Table 1.^{51,52}

Table 1: Relative chemical potential of an oxygen atom ($\Delta \mu_{\rm O}$) calculated using thermodynamics for the fuel-rich, stoichiometric, fuel-lean, and air-aging conditions. For the TWC operating conditions, the excess oxygen ratio (λ) and air-to-fuel weight ratio (A/F) are shown.^{51,52} λ is defined as the amount of oxygen atoms in a gas feed divided by the amount of oxygen atoms under stoichiometric conditions.

Conditions	λ	A/F	T (K)	p_{O_2} (atm)	$\Delta \mu_{\rm O} \ ({\rm eV})$
Fuel-rich	0.45	14.20	800	10^{-30}	-3.22
Stoichiometric	1.00	14.60	800	$10^{-11.3}$	-1.74
Fuel-lean	1.97	15.00	800	10^{-3}	-1.08
Air-aging			1200	0.20	-1.42

Global optimization of small supported Pd_xO_y

The structures of Pd_xO_y clusters supported on STO surfaces were investigated using the global optimization with first-principles energy expression (GOFEE) algorithm, ^{53–55} which is based on the evolutionary algorithm and Gaussian process regression. The GOFEE method has been successfully applied for finding stable structures of supported metal clusters, ^{56,57} ultrathin oxide overlayer, ⁵⁵ and aromatic hydrocarbons supported on graphene. ⁵⁸ DFT

calculations within GOFEE were performed using the grid-based projector augmented wave code⁵⁹ with the Perdew–Burke–Ernzerhof (PBE) functional,⁶⁰ double zeta-polarized basis, and a grid spacing of ≈ 0.20 Å. Only the Γ point was sampled. During global optimization, only atomic configurations of Pd_xO_y were optimized on a thin two-layer 1-unit-cell-thick STO-113 slab. To ensure the reliability, ten parallel GOFEE searches were performed and we considered the search is successful if a similar global minimum (GM) with a small distortion were found in 30% of the total GOFEE runs. Then, we reoptimized all non-equivalent structures within a 0.50 eV window from the set of the stable structures found by GOFEE using PBEsol+U-D3. The accuracy of this approach is discussed in SI SI.7. This approach is also applied to find stable Pt_xO_y on $Ce(111)^{56}$ and metal-embedded graphene.⁵⁷

The binding strength of the supported Pd_xO_y clusters, i.e., the formation energy with respect to bulk fcc-Pd and tetragonal PdO, is calculated as

$$E_{\rm f}(\mathrm{Pd}_x\mathrm{O}_y) = \frac{1}{x} [E(\mathrm{Pd}_x\mathrm{O}_y/\mathrm{S}) - E(\mathrm{S}) - y \times E(\mathrm{PdO}) - (x - y) \times E(\mathrm{Pd})], \tag{4}$$

where $E(Pd_xO_y/S)$, E(S), E(PdO), and E(Pd) are the total energies of the supported Pd_xO_y , clean surface, bulk tetragonal PdO, and bulk fcc-Pd per formula unit, respectively. A lower E_f indicates that Pd_xO_y is more stable on the support surface.

To investigate the composition of the supported Pd_xO_y clusters, we calculated the free energy of formation as

$$\Delta G_{\rm f}(\mathrm{Pd}_x \mathrm{O}_y) = G(\mathrm{Pd}_x \mathrm{O}_y/\mathrm{S}) - G(\mathrm{STO}) - x \times \mu_{\mathrm{Pd}} - (y - N_{\mathrm{Vo}}) \times \mu_{\mathrm{O}}(T, p), \tag{5}$$

where $G(Pd_xO_y/S)$, G(STO), and N_{V_O} are the Gibbs free energies of Pd_xO_y/STO , pristine STO, and the number of oxygen vacancies (V_O's), respectively. The vibrational contribution of Pd_xO_y to $\Delta G_f(Pd_xO_y)$ was not considered because it plays a minor role⁶¹.

The effective charge q of supported Pd_xO_y is defined as $q = Z - q_L$, where Z is the sum of the valencies of constituent atoms and q_L is the sum of the number of valence electrons estimated by the Löwdin population analysis.

Results and Discussion

Solid solution reaction of Pd with STO-327

The Pd solid solution is studied by elucidating the stability of Pd@STO-327 in equilibrium with gas-phase O_2 . The kinetic of the Pd dissolution is beyond the scope of the present study and we encourage others to employ molecular dynamics or NEB methods to explore this problem. 62,63 The crystal structure of STO-327 with five different surface terminations of the (001) facet is shown in Figure 1 (a). The stable phases in the $(\Delta \mu_O, \Delta \mu_{Sr})$ space are shown in Figure 1 (b), and the crystal structures of Pd@STO-327 are shown in Figure S6. The hatched region represents the stable region of bulk STO-327 without the precipitation of the associated compounds (SrO, TiO₂, Ti, Sr, and O₂) and typical TWC operating conditions are located in a region limited by two white dotted lines, i.e $-3.22 \text{ eV} < \Delta \mu_{\rm O} < -1.08 \text{ eV}$. As shown in Figure 1 (b), pristine STO-327 is the most stable phase under the reductive conditions ($\Delta \mu_{\rm O} < \text{ca.} -1.8 \text{ eV}$); while the Pd solid solution is preferably formed, where the Pd atoms occupy the Ti sites (Pd@Ti, 3Pd@Ti, and 4Pd@Ti) without any defects, under the oxidative conditions ($\Delta \mu_{\rm O} > \text{ca.} -1.8 \text{ eV}$). We found that the PdO₆ octahedra is distorted and tilted from the ideal TiO_6 octahedra because of the strain effect of the STO-327 lattice (Figure S6). The Pd@Ti structure with the a distorted PdO_6 octahedron is more stable than that with an undistorted PdO_6 octahedron by 14 meV. On the other hand, the 4Pd@Ti structure with the distorted PdO_6 octahedra in the PdO_2 layer is more stable than that with the undistorted PdO_6 octahedra by 0.55 eV, showing that the distortion of PdO_6 plays a more crucial role in the high Pd doping concentration. We find that the planar PdO_4 coordination that formed in bulk PdO cannot be formed in Pd@STO-327. To form a PdO_4 configuration in bulk STO-327, two V_O formations are required. In the case of Pd@Ti, this occurs under a rather reductive condition, i.e. $\Delta \mu_{\rm O} < -7.1$ eV, showing that planar PdO₄ coordination



Figure 1: (a) Crystal structure of STO-327 with various terminating (001) planes. (b) Phase diagram of STO-327 with several defects and Pd@STO-327 in the ($\Delta\mu_{\rm O}$, $\Delta\mu_{\rm Sr}$) space. (c) Grand potentials of a single Pd substituted for Ti (Pd@Ti) and for Sr at the perovskite (Pd@Sr_C) and rock-salt (Pd@Sr_B) layers under the fuel-lean condition. The grand potentials at the SrO and TiO₂ precipitation boundaries are shown in red and blue, respectively. The phonon contributions to grand potentials of Pd@Ti, Pd@Ti-V_O, and Pd@Sr are elucidated. (d) Phase diagrams of the (001) and (100) surfaces of STO-327 in the ($\Delta\mu_{\rm O}$, $\Delta\mu_{\rm Sr}$) space and (e) atomic models of STO-327(001). For the phase diagrams, the hatched region corresponds to the region where STO-327 is thermodynamically stable without the deposition of associated compounds, which is defined by (1) SrO, (2) TiO₂, (3) Ti, and O₂ ($\Delta\mu_{\rm O} \leq 0$) precipitation lines. The area between two white dotted lines corresponds to typical O₂ conditions in TWC. The blue line represents the bulk PdO/Pd thermodynamic phase equilibrium at $\Delta\mu_{\rm O} = -1.59$ eV.

is hardly formed in Pd@STO-327. When the environment is changed from the TiO₂-rich condition [the region near line (2)] to the SrO- rich [the region near line (1)] condition, the Pd solid-solution becomes favorable at a lower $\Delta \mu_{\rm O}$ (-0.8 eV to -1.7 eV), indicating that the SSR of Pd proceeds more easily under the SrO-rich conditions. Consequently, the Pd solid solution is thermodynamically preferable under oxidative SrO-rich conditions, where Pd is incorporated into the Ti site. The appearance of SSR highlights the strong MSI of Pd NPs with STO-327.

The above analysis indicates that Pd can be dissolved into the STO-327 bulk region in oxidative conditions, confirming that SSR is highly probable and may cause catalyst degradation. However, we discuss that the SrO rock-salt layer of STO-327 plays an important role to inhibit the Pd penetration deep into the STO-327 bulk region. To this end, we compare the stability of Pd substituted for the Ti (Pd@Ti) and Sr sites (Pd@Sr_C and Pd@Sr_B) under the fuel-lean condition ($\Delta \mu_{\rm O} = -1.08 \text{ eV}$). In Figure 1 (c), the stability of the substituted Pd at the SrO precipitation [line (1)] and TiO₂ precipitation [line (2)] boundaries are shown by red and blue lines, respectively. Under the SrO-rich condition, Pd@Ti is preferable, whereas Pd@Sr's are significantly less stable than Pd@Ti by at least 3.78 eV. To diffuse along the [001] direction, Pd should cross the SrO rock-salt layer; however, to cross the SrO rock-salt layer, Pd must be substituted for Sr. Therefore, thermodynamic barrier for the Pd dissolution from STO-327(001) to the bulk region is approximately the grand potential difference between Pd@Ti and Pd@Sr. The instability of Pd substitution for the Sr site suggests that the diffusion of Pd is suppressed along the [001] direction. Under the TiO₂-rich condition, Pd@Sr structures are stabilized compared with that under the SrO-rich condition. However, Pd@Sr's are less stable than Pd@Ti by at least 1.37 eV. Furthermore, the Pd dissolution becomes less stable than pristine STO-327. Hence, under both SrO-rich and TiO₂-rich conditions, the Pd diffusion along the [001] direction should be suppressed by the SrO rock-salt layer, which is parallel to the STO-327(001) surface. Thus, the Pd penetration from the STO-327(001), which is found to be the most stable (Figure 1 (d)), to the bulk region is mitigated. Consequently, the SSR between Pd and STO-327 is rather limited near the subsurface,¹³ suggesting that STO-327(001) can suppress the undesired SSR in the oxidative atmosphere.

We here discuss the phonon contributions to the grand potential of Pd@STO-327. Details on the phonon analysis and free energy estimation are in section SII of SI. The Ω_{bulk} 's of Pd@Ti, Pd@Ti-V_O, and Pd@Sr_B remain almost unchanged regardless of the phonon contribution under TWC oxidative condition at T = 800K and the SrO precipitation condition (Figure 1 (c)). The phonon contribution plays a minor role in the thermodynamic stability of Pd@STO-327 (Figure S8), and thus our conclusions regarding Pd solid solution and the role of the SrO layer are not altered.

The stable phases of the STO-327(001) and (100) surfaces in the $(\Delta \mu_{\rm O}, \Delta \mu_{\rm Sr})$ space are shown in Figure 1 (d), and the corresponding atomic structures are depicted in Figure 1 (e). The SrO-terminated (001) surface generated by cleaving at the rock-salt layer (SrO-B)⁶⁴ is stable under reductive conditions, whereas SrO-C is formed preferably only at $\Delta \mu_{\rm O} \leq -1.8$ eV under the SrO-rich condition. Under oxidative SrO-rich conditions ($-1.8 < \Delta \mu_{\rm O} < -1.0$ eV), Ti of the subsurface TiO₂ layer is substituted with Pd (SrO-B-Pd and SrO-B-PdO₂), whereas under the TiO₂-rich condition, the stable surface is SrO-B. The surface stabilities of STO-327(001) and (100) at the SrO and TiO₂ precipitation lines are shown in Figure S9.

Metal-support interaction of the supported Pd_xO_y

Enhanced bonding by the cluster oxidation

To elucidate the MSI of supported Pd clusters, we evaluate the binding strengths of several Pd_xO_y clusters to STO-327(001) and to γ -Al₂O₃(100). The most stable STO-327(001) surfaces are composed of simple SrTiO₃ pevroskite layers with a SrO termination. Therefore, we simplify our support models to study the MSI of the supported Pd_xO_y by using both SrO- and TiO₂- terminated STO-113(001) surfaces (SrO-STO-113 and TiO₂-STO-113). The detailed GOFEE sampling is given in SI.6.



Figure 2: The atomic geometries of the stable Pd_9O_y supported on (a) SrO- and (b) TiO₂-STO-113. Large spheres represent the cluster and surface atoms involved in the interfacial bonds. The glowed spheres indicate O atoms involved in the anchoring PdO_4 bonding configuration at the interface.

We begin by discussing the structural change of the supported Pd cluster upon cluster oxidation. The atomic geometries of the stable Pd_9O_y clusters on SrO- and TiO₂-STO-113's are shown in Figures 2 (a) and (b), respectively, and those of Pd_9O_y on γ -Al₂O₃(100) are shown in Figure S10. Furthermore, the atomic geometries of Pd_xO_y with different cluster sizes on three supports are depicted in Figures S11 - S15. On three supports, the structural transition of Pd_xO_y (x > 4) takes place from compact fcc-like shapes for the metallic clusters (y = 0) to almost planar structures for the PdO-like clusters $(y/x \ge 1)$. Figure 2 shows that the supported metallic Pd₉ clusters have bulk fcc-Pd shapes and bind to the STO-113 surfaces via Pd- surface O bonds. In contrast, the PdO-like clusters have raft-like shapes and bind to the STO-113 surfaces via both Pd- surface O and cluster O - Sr/Ti bonds, which results in the shape transition. The interfacial bonds in PdO-like clusters create anchoring PdO₄ bonding configurations with the substrate, which is observed in CeO₂-supported Pd and Pt NPs.^{27,65,66} For the supported Pd_xO_y in the low oxidation state (y = x/2 or (x+1)/2), most oxygen atoms occupy the perimeter sites of Pd clusters to create Pd-O-Sr/Ti bonds (Figure 2); some O atoms are adsorbed on Pd clusters at hollow sites. A similar structural transition of the Pd_xO_y clusters on γ -Al₂O₃(100) upon cluster oxidation is observed.

Figure 3(a) shows the calculated $E_{\rm f}$'s of ${\rm Pd}_x {\rm O}_y$ on SrO-, ${\rm TiO}_2$ -STO-113's and γ -Al₂O₃. Overall, $E_{\rm f}$'s decrease monotonically with increasing oxygen content up to $y/x \simeq 1$ and they increase above $y/x \ge 1$, implying that the MSI between ${\rm Pd}_x {\rm O}_y$ and support is enhanced upon the oxidation of the cluster and the interaction of the PdO-like clusters with the support is the strongest. Therefore, the agglomeration of oxidized Pd clusters is mitigated in the oxidative atmospheres via the anchoring effect^{21,24,67} and highly dispersed PdO NPs with a small size may be retained. Moreover, the cluster oxidation can regulate the catalytic activity⁶⁸ and the binding strength of adsorbate.⁶¹

In the experiments, the sintering resistance is significantly improved in the oxidative atmosphere, where PGM NPs are in the oxide state rather than in the reductive atmosphere, where PGM NPs are in the metallic state.^{9,21,22,56,69–76} Nagai *et al.* found that the sintering



Figure 3: (a) Formation energy $(E_{\rm f})$ of ${\rm Pd}_x {\rm O}_y$ on SrO- and TiO₂-STO-113's and γ -Al₂O₃(100). (b) Energy decomposition analysis of ${\rm Pd}_9 {\rm O}_y$ supported on SrO-, TiO₂-STO-113's, and γ -Al₂O₃(100). (c) Effective charge (q) of supported ${\rm Pd}_x {\rm O}_y$. The figure legend is similar with that of (a).

inhibition of Pt NPs supported on CeO₂ under the air-aging condition originates from the formation of PtO₂ NPs, where Pt-O-Ce bonds stabilize PtO₂ NPs at T = 1073 K.^{21,22} Cuenya *et al.*^{70,72,73} found the enhanced stabilization of γ -Al₂O₃- and SnO₂- supported Pt NPs after oxidative pretreatment, which is supposedly attributed to the formation of PtO_x species with Pt-O interfacial bonds (or Pt-OH in H₂O pretreatment) at T = 673 K. Our results are in line with recent DFT reports on Pt₁₃O_x on γ -Al₂O₃(100)⁷⁶ and Pt₆O_x on CeO₂(111).⁵⁶

We note that metal NP often undergoes a partial oxidation with a thin metal oxide layer formation in the strong metal-support interaction.⁷⁷ The size of metal NPs has a strong influence in its oxidation state, in which the larger NP is more difficult to oxidize,⁷⁸ hence the partially oxidized state may be observed experimentally in the oxidative treatment. As will be shown later, in the small size regime (Pd_9O_y) considered herein, the full oxidized state is stable under normal oxidative conditions and the partially-oxidized state is stable under rather reductive condition.

The sintering resistance of STO-327 is further highlighted by comparing the binding strengths of Pd_xO_y supported on STO-113 with those on γ -Al₂O₃. Figure 3 (a) shows that the E_f 's of Pd_xO_y on both SrO- and TiO₂-STO-113's are smaller than those on the γ -Al₂O₃ surface, indicating the stronger binding strength of Pd_xO_y clusters to the STO surfaces. The average E_f 's of small metallic Pd_x clusters ($x \ge 4$) on SrO- and TiO₂-STO-113 are 1.45 and 1.52 eV, respectively, while that of γ -Al₂O₃ (100) is 1.85 eV. Moreover, the average E_f 's of stoichiometric Pd_xO_x ($x \ge 4$) on SrO- and TiO₂-STO-113's (0.65 and 0.57 eV) are significantly smaller than that of γ -Al₂O₃ (100) (1.12 eV). These results highlight that the Pd_xO_y clusters are further stabilized on the STO support compared with those on γ -Al₂O₃.

Energy decomposition analysis and charge state of Pd_xO_y

Using Pd_9O_y as a representative cluster, the energy decomposition analysis is performed to provide insight into MSI of the supported Pd_xO_y and the increase in MSI upon cluster oxidation, as shown in Figure 3 (b). The formation energy of Pd_9O_y , $E_f(Pd_9O_y)$, is decomposed into the cluster-substrate interaction energy $E_{int}(Pd_9O_y-S)$, isolated (intrinsic) cluster formation energy $E_{\rm f}^{\rm i}({\rm Pd}_9{\rm O}_y)$, deformation energy of the cluster $E_{\rm def}({\rm Pd}_9{\rm O}_y)$, and deformation energy of the substrate $E_{\rm def}({\rm S})$ (SI SI.8). From Figure 3(b), we find that interactions between Pd₉O_y and the substrates are greatly strengthened upon cluster oxidation as indicated by a decrease in $E_{\rm int}({\rm Pd}_9{\rm O}_y{\rm -S})$ from y = 0 to 11 by 0.9 eV. The intrinsic formation energy of the Pd₉O_y cluster, as characterized by $E_{\rm f}^{\rm i}({\rm Pd}_9{\rm O}_y)$, is moderately decreased from the fully reduced Pd₉ (2.26 eV) to Pd₉O₆ (1.68 eV); and it is then slightly increased to the PdO-like Pd₉O₉ cluster (1.77 eV). The energies required to deform the substrate ($E_{\rm def}({\rm S})$) and isolated Pd₉O₉ clusters ($E_{\rm def}({\rm Pd}_9{\rm O}_y)$) to their adsorbed geometries are moderately increased by 0.3 eV. As the result, the isolated cluster formation energy and deformation energies compensate each other and MSI of the supported cluster mainly governs by cluster-substrate interaction. Therefore, we conclude that the stronger MSI of the PdO-like clusters arises solely from the electronic interactions between PdO-like clusters and support surfaces.

The energy decomposition analysis in Figure 3 (b) also reveals that the stronger MSI of Pd/STO-327 than Pd/ γ -Al₂O₃ mainly arises from electronic interactions between Pd NPs and substrate. The lower $E_{\rm f}$ of Pd₉O_y on STO-113's compared with that on γ -Al₂O₃ originates from the interaction of Pd₉O_y with the substrate. $E_{\rm int}({\rm Pd}_x{\rm O}_y-{\rm S})$ of Pd₉/SrO-STO-113 and Pd₉/TiO₂-STO-113 are -1.04 and -1.05 eV, respectively, which are considerably more stable than that of Pd₉/ γ -Al₂O₃ (-0.69 eV).

The effective charges (q's) of the supported Pd_xO_y clusters by the Löwdin population are shown in Figure 3 (c). All q's are negative, showing that CT takes place from the substrate to the Pd_xO_y clusters in all cases, leading to the Pd_xO_y clusters are negatively-charged upon adsorption.⁷⁹ We find that the magnitude of CT from the support surface to the Pd_xO_y clusters are in order SrO-STO-113 > TiO₂-STO-113 > γ -Al₂O₃(100). On STO substrates, the PdO-like clusters at y/x = 1 are further negatively charged compared with the metallic clusters (y = 0). It indicates that CT plays an important role in the stronger MSI of the PdO-like cluster on the STO support.⁸⁰ In contrast, the CT magnitude and CT change upon cluster oxidation for Pd_xO_y/γ -Al₂O₃ (100) are considerably small. Our results imply that a strong MSI of Pd NPs with the STO support via the electronic interactions, in which the CT interaction^{81–83} plays a crucial role, inhibits the sintering of Pd NPs on STO as observed by Tanaka *et al.*²⁵ at T > 1100 K. In contrast, the MSI between Pd NPs and γ -Al₂O₃ is weak, and thus, γ -Al₂O₃-supported Pd NPs would sinter quickly at this temperature.



Electronic structure analysis

Figure 4: (a) Plane-averaged $\Delta \rho$ along the z direction of Pd₉ and Pd₉O₁₁ on SrO-STO-113; Pd₉ and Pd₉O₉ on γ -Al₂O₃(100). Red, blue, green, and orange circle markers denote the average heights of the interfacial cluster Pd atoms in Pd₉/SrO-STO-113, Pd₉/ γ -Al₂O₃(100), Pd₉O₁₁/SrO-STO-113, and Pd₉O₉/ γ -Al₂O₃(100) respectively; while green and orange x markers denote the average heights of the interfacial O atoms in Pd₉O₁₁/SrO-STO-113 and Pd₉O₉/ γ -Al₂O₃(100), respectively. The gray dashed line indicates the z position of the substrate topmost layer. Top views and projections of the calculated $\Delta \rho$'s onto the plane containing the interfacial bonds of (b) Pd₉/SrO-STO-113 and (c) Pd₉O₁₁/SrO-STO-113. Isosurfaces are plotted at 0.013 $e^-/\text{Å}^3$ with yellow and cyan color represent charge accumulation and charge depletion, respectively. The projections (2) and (5) indicate the electrostatic attractions driven by Pd 4d orbitals polarization in Pd₉ and Pd₉O₁₁ on SrO-STO-113.

We first analyze the CT interaction between Pd_xO_y with oxide supports. We inspect the charge density difference $(\Delta \rho)$ of Pd_xO_y on SrO-STO-113 and γ -Al₂O₃(100) to provide the

Table 2: Average change in Löwdin population ($\Delta q_{\rm L}$) of the interface Pd 4d, Pd 5sp, and O 2p upon adsorption on the substrates. The unit is electrons (e⁻). A negative value of $\Delta q_{\rm L}$ indicates the decrease in the electron population upon the adsorption of Pd₉O_y on the substrate and vice versa.

Structure	$4d_{3z^2-r^2}$	$4d_{x^2-y^2}$	$4d_{xz}$	$4d_{yz}$	$4d_{xy}$	e_g	t_{2g}	sp	O $2p$
$Pd_9/SrO-STO-113$	-0.12	0.07	-0.01	-0.11	0.01	-0.04	-0.10	0.39	
$Pd_9O_{11}/SrO-STO-113$	-0.18	0.01	0.02	0.00	0.12	-0.17	0.14	0.21	0.17
Pd_{9}/γ -Al ₂ O ₃ (100)	-0.03	0.04	-0.09	0.00	0.03	0.01	-0.06	0.18	
$\mathrm{Pd_9O_9}/\gamma$ -Al ₂ O ₃ (100)	-0.20	0.04	0.05	0.06	0.01	-0.16	0.11	0.14	0.11

insights into the CT mechanism. $\Delta \rho$ is defined as $\Delta \rho(\text{Pd}_9/S) = \rho(\text{Pd}_9/S) - \rho(\text{Pd}_9) - \rho(S)$. The plane-averaged $\Delta \rho$ for Pd₉, Pd₉O₁₁ on SrO-STO-113 and Pd₉, Pd₉O₉ on γ -Al₂O₃(100) along the z direction are shown in Figure 4 (a); while the $\Delta \rho$ maps for Pd₉ and Pd₉O₁₁ on SrO-STO-113 are shown in Figure 4 (b) and (c), respectively. Average change in Löwdin population (Δq_L) of the interface Pd 4d, Pd 5sp, and O 2p upon adsorption on the substrates are tabulated in Table 2.

The plane-averaged $\Delta \rho$ along z direction in Figures 4 (a) and S22 show that the charge is accumulated beneath Pd clusters (1.0 < z < 2.0 Å), while the charge is depleted above the substrate topmost layer (0.1 < z < 0.9 Å) for both metallic and oxidized Pd₉O_y clusters on SrO-STO-113, TiO₂-STO-113, and γ -Al₂O₃(100). It confirms that the CT interactions occur from those substrates to Pd clusters as indicated by q in Figure 3 (c). The negativelycharged states of Pd_xO_y are consistent with previous reports on Pt/STO-113,⁸⁴ Au/STO-113,⁸⁵ Rh₂/ γ -Al₂O₃(100),⁸⁰ and Pd₉O_y/ γ -Al₂O₃(100).⁷⁹

The energy positions relative to vacuum level (E_{vac}) of the conduction band minimum (CBM) and valence band maximum (VBM) of the support surfaces and that of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the Pd₉O_y are crucial for the CT interaction. Those energy positions for clean substrates, i.e. SrO-STO-113, TiO₂-STO-113, and γ -Al₂O₃(100) and isolated Pd₉O_y are shown in Figure 5 (a). The VBM and CBM of the deformed substrate and HOMO and LUMO of the deformed Pd₉O_y (denoted with superscript ^a), where atomic geometries are fixed at their adsorption



Figure 5: (a)Energy positions of the conduction band minimum (CBM) and valence band maximum (VBM) of the clean support surfaces, i.e. SrO-STO-113, TiO₂-STO-113, and γ -Al₂O₃(100); and energy position of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the isolated Pd₉O_y (y = 0, 6 and 9). $E_{\rm vac}$ is the vacuum level, which is defined as the average electrostatic potential at the center of the vacuum region. Energy positions of CBM and VBM of the deformed substrate; HOMO and LUMO of the deformed Pd_xO_y for (b) Pd₉ and Pd₉O₁₁ on SrO-STO-113, (c) Pd₉ and Pd₉O₉ on TiO₂-STO-113, and (d) Pd₉ and Pd₉O₉ on γ -Al₂O₃(100). The deformed substrate (S^a) and cluster (Pd₉O_y^a) have geometries fixed at Pd₉O_y/S.

geometries, for Pd_9O_y on SrO-STO-113, TiO₂-STO-113, and γ -Al₂O₃(100) are shown in Figure 5 (b), (c), and (d), respectively. From Figure 5 (a), the energy of VBM, which plays a role of the donor orbital, of clean SrO-STO-113, TiO₂-STO-113, and γ -Al₂O₃(100), are -4.27, -5.18, and -5.95 eV, respectively; showing that both STO-113's are better electroninjection substrates than γ -Al₂O₃(100). Moreover, the VBM positions of three clean supports generally explain the CT order in Figure 3 (c), where the magnitudes of $q(Pd_xO_y)$ are in order SrO-STO-113 > TiO₂-STO-113 > γ -Al₂O₃(100).

Cluster oxidation lowers the energy levels of Pd_xO_y LUMO, which plays a role of acceptor orbital, in both isolated and deformed geometries (Figure 5), thus the electron injection from the substrates to Pd_xO_y is more preferable upon cluster oxidation. This decrease in the LUMO level generally explains the increase in CT interaction and MSI upon cluster oxidation for Pd_xO_y supported on SrO- and TiO₂-STO-113 substrates as indicated by Figure 3 (b) and (c).

We then inspect the energy levels of deformed substrates and clusters in Figures 5 (b-d). The deformed Pd_xO_y 's become metallic in all cases. The Fermi levels (E_F) of Pd_xO_y are lower than SrO- and TiO₂-STO-113 VBM's, indicating that interunit CT interactions from STO-327 to Pd_xO_y occur easily. On the other hand, for Pd_9/γ -Al₂O₃(100), E_F of Pd_9^a is -4.49 eV, while the VBM and CBM of γ -Al₂O₃(100)^a are -5.46 and -3.10 eV, respectively (Figure 5 (d)). The pushback effect, in which charge flows from more contracted orbitals of closed shell system (γ -Al₂O₃(100)) to more diffuse orbitals of open shell system (Pd₉), is crucial to enable the CT from γ -Al₂O₃(100) to metallic Pd cluster.⁸⁶ The cluster oxidation brings E_F of Pd₉O₉^a to -5.47 eV, but it is still slightly higher than VBM of γ -Al₂O₃(100)^a (-5.67 eV). The VBM at a rather low energy relative to the vacuum level of γ -Al₂O₃(100) hinders the charge exchange with Pd_xO_y, leading to weaker MSI of Pd_xO_y on γ -Al₂O₃.

Having analyzed the CT interaction, we now reveal the binding mechanism of the Pd clusters to SrO-STO-113. The interactions between Pd₉ and SrO-STO-113 are governed by inter-unit CT and further stabilized by intra-unit polarization. The $\Delta \rho$ map in Figure 4 (b)



Figure 6: (a) Projected density of states (PDOS) onto the interfacial cluster Pd 4d states and surface O 2p states in the first layer of the substrate of Pd₉/SrO-STO-113. (b) PDOS onto interfacial cluster Pd 4d, surface O 2p states in the first layer of the substrate, and interfacial cluster O 2p states of Pd₉O₁₁/SrO-STO-113.

reveals that the charge depletion locates along the z direction of the interfacial Pd atoms, while the charge accumulation locates in the xy plane of the interfacial Pd atoms toward Sr sites. It indicates the electrons of Pd atoms are polarized by the interactions with support. Table 2 shows that interfacial Pd 5sp orbitals are further populated, while Pd 4d orbital are less populated upon adsorption on SrO-STO-113. The projected density of state (PDOS) of the interfacial cluster Pd 4d and surface O 2p in the first layer of SrO-STO-113 are shown in Figure 6 (a). Upon the binding, the 4d orbital of the interfacial Pd and the 2p orbital of O in the first layer of the substrate hybridize; the antibonding Pd $4d_{3z^2-r^2}$ and $4d_{yz}$ orbitals are lifted up to become partially empty; while the Pd $4d_{x^2-y^2}$ orbital is stabilized because of the attractive electrostatic interactions with Sr²⁺ ions of the substrate (Figures 4 (b) and S19 as well as $\Delta q_{\rm L}$ in Table 2). This intra-unit polarization of Pd atoms makes two contributions to enhance the cluster-substrate binding. The first is to reduce the repulsion originating from the antibonding counterparts of the (Pd 4d) - (O 2p) hybridized states. The second involves the fact that this polarization generates electrostatic attractions with the substrate Sr cations, which further strengthens the cluster-substrate interactions.

Upon cluster oxidation, Pd_9O_{11} binds to SrO-STO-113 via both Pd - surface O and O -

surface Sr bonds. Both inter-unit CT and intra-unit polarization are significantly enhanced when Pd_9O_{11} is formed. Table 2 shows that increase in population of interfacial Pd 5*sp* orbitals in Pd_9O_{11} is less than that in Pd_9 , while O 2*p* orbitals are further populated by bonding with surface Sr. PDOS in Figure 6(b) illustrates that Pd forms strongly hybridized states with surface O, as shown by the large splitting in the PDOS of 4*d* states compared with the PDOS of the metallic cluster. The antibonding Pd $4d_{3z^2-r^2}$ orbital of Pd₉O₁₁ is more empty than that of Pd₉ (Table 2), and thus, the Pauli repulsion derived from the those orbitals hybridization is diminished upon cluster oxidation. Moreover, the polarization of interfacial Pd 4*d* electrons in Pd₉O₁₁ stabilizes Pd 4*d*_{xz} and 4*d*_{xy} orbitals via electrostatic interactions with surface Sr cations (see the projection of $\Delta \rho$ (5) in Figure 4 (c)). This polarization stabilizes the Pd t_{2g} states of Pd₉O₁₁ compared with that of Pd₉. Together with the Pd-O bond, cluster O atoms strongly bind to the surface Sr cations underneath and a considerable electron donation occurs from Sr to O as seen by the downshift of cluster O 2*p*_z below the Fermi level (Figure 6 (b)). Overall, the enhanced Pd-O bonds and newly formed O-Sr bonds explain why MSI increases upon the cluster oxidation on STO supports.

It is important to clarify the difference in the binding strength of Pd_xO_y to γ -Al₂O₃ and STO. We find that the greater CT interaction is the main origin for stronger binding of Pd_xO_y to SrO-STO-113 than that to γ -Al₂O₃. Moreover, the Pd 4*d* polarization, which occurs to a greater extent due to electrostatic attractions with surface Sr cations in Pd_xO_y/SrO -STO-113, also enhances the cluster binding strength. This can be seen clearly in $\Delta\rho$ maps of Pd₉/SrO-STO-113 (Figure 4 (b)) and Pd₉/ γ -Al₂O₃(100) (Figure S22), where the charge accumulation in *xy* plane of Pd atom in Pd₉/ γ -Al₂O₃(100) is absent.

Roles of defects and different facets

The current insights into MSI of Pd cluster pertain to the most stable STO-327(001) surface. The surface defects⁸⁷ or different surface facet^{88,89} may stabilize Pd clusters. We explore the surface defects ($V_{\rm O}$, $V_{\rm Sr}$, and $V_{\rm Ti}$), the STO-327 facets, and Pd solid solution on the binding



Figure 7: (a) Formation energies $(E_{\rm f})$ of ${\rm Pd}_4{\rm O}_y$ on SrO-STO-113 with the surface $V_{\rm Sr}$ (SrO-STO-113 + $V_{\rm Sr}$), TiO₂-STO-113 with the surface $V_{\rm Ti}$ (TiO₂-STO-113 + $V_{\rm Ti}$), STO-327(100), and stoichiometric O-terminated STO-113 (110) [O₂-STO-113(110)]. (b) Atomic geometries of stable Pd₄O_y supported on TiO₂-STO-113 + $V_{\rm Ti}$, STO-327(100), and O₂-STO-113(110).

strengths of the Pd clusters. From Figure 3, $E_{\rm f}$'s of Pd₉O_y with y > 4 (3) for SrO-STO-113 (TiO₂-STO-113) surpass that of Pd₉ and O-deficient STO-113 surfaces (Pd₉+V_O, star symbols). Therefore, the oxidation of the Pd cluster has a more pronounced role in improving the binding strength of Pd clusters compared with formation of $V_{\rm O}$. From Figure 7, $E_{\rm f}$'s of Pd₄O_y is slightly increased upon the formation of surface $V_{\rm Sr}$ for SrO-STO-113 (Pd₄O_y + V_{Sr}), indicating that formation of V_{Sr} decreases the binding strengths of the Pd clusters. In contrast, $E_{\rm f}$'s of Pd₄O₂ and Pd₄O₄ on TiO₂-STO-113 + $V_{\rm Ti}$ are -0.08 and -0.13 eV, respectively, showing that Pd clusters prefer to bind to Ti vacancy of TiO₂-STO-113. Our results show that Pd clusters might be (partially) embedded in the TiO₂-STO-113 substrate to enhance the sintering resistance.¹⁴

The binding strengths of Pd_4O_y to different STO facets, namely STO-327(001) and stoichiometric O-terminated STO-113(110) $[O_2$ -STO-113(110)],⁸⁹ are shown in Figure 7. Comparing with the results on SrO- and TiO₂-STO-113, the binding strengths of Pd_4O_y are slightly increased on STO-327(001), where the Pd_4O_y clusters prefer to bind to STO-327(001) at the SrO rock salt layer position. On the other hand, Pd_4O_y clusters strongly bind to O_2 -STO-113(110), and E_f of Pd_4O_4 is negative. It indicates that the Pd clusters can be trapped effectively on STO-113(110).

We study the stability of oxidized Pd_9O_y (y = 9, 11) on the surface of the solid solution (SrO-B-PdO₂), which is realized under oxidative SrO rich conditions. The stability of those oxidized Pd clusters slightly decreases upon Pd solid solution for the TiO₂ subsurface of SrO-STO-113 (See section SVI of SI).

Finally, we note that the effect of migration of the support onto the Pd NPs to form thin overlayers is not considered herein because the metal NP with small size is difficult to be encapsulated by the substrate immigration.⁹⁰



Phase diagram of Pd_9O_y clusters on the STO supports

Figure 8: Free energy of formation $\Delta G_{\rm f}$ as a function of relative O chemical potential $\Delta \mu_{\rm O}$ for Pd₉O_y supported on (a) SrO- and (b) TiO₂-STO-113. The most stable compositions are indicated by the corresponding colors (see the legend) at the bottom of the box. The black, red, and blue vertical lines denote the typical $\Delta \mu_{\rm O}$ under TWC operating, air-aging, and bulk Pd/PdO phase equilibrium conditions, respectively.

We discuss how TWC operating conditions change the stoichiometry of the Pd_9O_y clusters. We choose Pd_9O_y clusters because they resemble Pd NPs.⁶⁸ Stable Pd_9O_y clusters are indicated by phase diagrams in Figures 8 (a) and (b) for Pd_9O_y on SrO- and TiO₂- STO-113, respectively.

In the TWC fuel-rich atmosphere, metallic Pd₉ clusters with V₀ formation at the support surfaces (Pd₉+V₀) are stable on both SrO- and TiO₂-STO-113 (Figures 8 (a) and (b)). On clean surfaces, the V₀ formation requires an extremely reductive condition ($\Delta \mu_0 \leq$ -4.45[-5.54] eV for TiO₂- [SrO-] terminated surfaces). The metallic Pd clusters catalyze the V₀ formation at a higher $\Delta \mu_0$ of -3.0 eV for both surfaces, which can occur spontaneously under the TWC reductive condition. Binding strengths (E_f 's) of Pd₉'s on the O-deficient STO surfaces are enhanced and those clusters are further negatively charged when V₀'s are formed (Figure 3). These indicate that the V₀ acts like the anchoring site to stabilize the supported Pd NPs in reductive conditions⁹¹ and enhances the CT from the support.⁹²

Partially oxidized Pd₉ clusters, where O atoms are adsorbed on them, are stable under rather reductive conditions ($-2.8 < \Delta \mu_{\rm O} < -2.1 \text{ eV}$). From Figure 8, Pd₉O₃ and Pd₉O₅ are stable on SrO-STO-113 with $-2.80 < \Delta \mu_{\rm O} < -2.20 \text{ eV}$; while Pd₉O₅ and Pd₉O₆ are stable on TiO₂-STO-113 with $-2.84 < \Delta \mu_{\rm O} < -2.08 \text{ eV}$.

Under TWC stoichiometric ($\Delta \mu_{\rm O} = -1.74 \text{ eV}$), air-aging ($\Delta \mu_{\rm O} = -1.42 \text{ eV}$), and fuellean ($\Delta \mu_{\rm O} = -1.08 \text{ eV}$) conditions, PdO-like clusters are stable, in line with experimental observation.²⁵ The supported PdO-like clusters are stable when $\Delta \mu_{\rm O} \geq -2.00 \text{ eV}$, while the isolated PdO-like Pd₉O_y ($y \geq 9$) clusters and bulk PdO are stable when $\Delta \mu_{\rm O} \geq -1.30$ eV (Figure S24) and -1.59 eV, respectively. Thus, the STO support stabilizes the high oxidation state of Pd, which arises from the strong interaction between PdO-like clusters and supports.^{21,56,78} The stability of PdO-like clusters on the STO support in the fuel-lean and air-aging atmospheres indicates that the sintering resistance is governed by those clusters. Our results highlight the importance of the support materials in regulating the oxidation state of metal catalysts.^{21,56,78}



Growth of supported PdO-like clusters

Figure 9: Reaction free energy (ΔG) of the first step of a monodisperse system sintering via the Ostwald ripening of Pd_xO_y as a function of the number of Pd atoms under (a) the airaging condition (T = 1200 K and $p_{O_2} = 0.2$ atm) and (b) the fuel-lean condition (T = 800 K and $p_{O_2} = 10^{-3}$ atm). The ΔG with the vibrational contribution of Pd_xO_y clusters (Pd_4O_5 and Pd_5O_6) are shown in the open blue circle. (c) The effective charge (q) of the most stable Pd_xO_y under air-aging condition. The number near each point shows y of the most stable Pd_xO_y . Atomic structures of (d) $Pd_4O_5/SrO-STO-113$, (e) $Pd_4O_4/TiO_2-STO-113$, and (f) $Pd_6O_6/TiO_2-STO-113$, which are stable against the sintering via the Otsward ripening.

Finally, we discuss the growth mechanism of small PdO-like Pd_xO_y clusters supported on STO surfaces in oxidative atmospheres. Small NPs with the size of ≤ 2 nm sinter more easily,^{2,93,94} and thus understanding the growth mechanism of NP at the sub-nano regime is beneficial to design an acquisition strategy that prevents the rapid loss of subnanometer NPs. The most stable cluster at each cluster size of the PdO-like clusters is evaluated by comparing ΔG_f (Pd_xO_{x, x+1, x+2}). First, we evaluate the detachment free energy (G_{det}) of Pd_xO_y in SrO-STO-113 under TWC fuel-lean condition, i.e. the free energy change of the reaction: $Pd_xO_y + 1/2(y_1 + 2 - y) O_2 \rightarrow Pd_{x-1}O_{y1} + PdO_2$. Moreover, we investigate activation energies for diffusion of PdO_2 , Pd_2O_2 , Pd_3O_3 , and Pd_4O_5 on SrO-STO-113. Those results are shown in Figure S33. We find that the detachment of PdO_2 from Pd_xO_y , which is relevant to the Ostward ripening, is more preferable than the particle diffusion, which is relevant to coalescence.⁸⁷ An analogous observation is made for TiO₂-STO-113. The growth of PdO-like clusters thus may follow the Ostward ripening, i.e., the migration of atomic species from smaller to larger NPs at the sub-nano regime.⁸⁷ The activation energies for diffusion of the small clusters (x < 4) are less than 2 eV (Figure S33). Using a lattice-hop model,⁹⁵ the diffusion of a particle with an activation energy of 2.0 eV occurs at T > 700K. Thus, the coalescence mechanism is still possible for those small Pd_xO_y clusters (x < 4).

At a fixed chemical potential, the stability of Pd_xO_y can be estimated by considering the first step of a monodisperse system sintering via Ostward ripening^{96,97} as

$$2\mathrm{Pd}_{x}\mathrm{O}_{y} + \frac{1}{2}(y_{1} + y_{2} - y)\mathrm{O}_{2} \to \mathrm{Pd}_{x-1}\mathrm{O}_{y_{1}} + \mathrm{Pd}_{x+1}\mathrm{O}_{y_{2}},\tag{6}$$

and the reaction free energy is calculated by

$$\Delta G(x) = E(\mathrm{Pd}_{x-1}\mathrm{O}_{y_1}/S) + E(\mathrm{Pd}_{x+1}\mathrm{O}_{y_2}/S) - 2E(\mathrm{Pd}_x\mathrm{O}_y/S) - (y_1 + y_2 - y)\mu_{\mathrm{O}},$$
(7)

where $E(\operatorname{Pd}_{x-1}\operatorname{O}_{y_1}/S)$, $E(\operatorname{Pd}_{x+1}\operatorname{O}_{y_2}/S)$, and $E(\operatorname{Pd}_x\operatorname{O}_y/S)$ are the total energies of the supported $\operatorname{Pd}_{x-1}\operatorname{O}_{y_1}$, $\operatorname{Pd}_{x+1}\operatorname{O}_{y_2}$, and $\operatorname{Pd}_x\operatorname{O}_y$, respectively. $\Delta G(x)$ is estimated using only the global minimum for each $\operatorname{Pd}_x\operatorname{O}_y$ cluster, which provides a reasonable explanation for size dependence.⁹⁶ A positive $\Delta G(x)$ indicates that $\operatorname{Pd}_x\operatorname{O}_y$ is stable and its growth is less preferable. The contribution of cluster vibrational entropy in $\Delta G(x)$ is negligible because it plays a minor role (Figure 9 (a) and (b)).

Figures 9 (a) and (b) shows the calculated ΔG 's for air-aging and fuel-lean conditions at $\Delta \mu_{\rm O} = -1.42$ and -1.08 eV, respectively, as a function of the number of Pd atoms in the

cluster. The effective charges (q's) of the most stable Pd_xO_y 's under the air-aging condition are shown in Figure 9 (c). The corresponding atomic structures for SrO- and TiO₂-STO-113 are shown in Figures S35 and S36, respectively. The ΔG 's for certain cluster sizes are positive, which indicate that they are stable against Ostwald ripening and the cluster growth may be diminished.^{96,97} The largest ΔG 's are found for Pd₄O₅ on SrO-STO-113, and Pd₄O₄ and Pd₆O₆ on TiO₂-STO-113 under the air-aging condition. Similarly, the largest ΔG 's are found for Pd₄O₅ on SrO-STO-113 and Pd₆O₆ on TiO₂-STO-113 under the oxidative condition. Thus, Pd₄O₅ on SrO-STO-113, and Pd₄O₄ and Pd₆O₆ on TiO₂-STO-113 are called magic number clusters.^{96,97}

The stability of the magic number clusters can be understood from their geometries (Figures S35 and S36). The Pd_4O_5 (Pd_4O_4) cluster on SrO-STO-113 (TiO_2 -STO-113) has a monolayer geometry with all Pd atoms bonding to the substrate O atoms, as shown in Figure 9 (d) (Figure 9 (e)). The growth of Pd_4O_5 (Pd_4O_4) may be realized by adding PdO (PdO_2) to form Pd_5O_6 in a bilayer geometry with the same number of the interfacial Pd-O bonds. The charge transfer to the additional PdO (PdO_2) is negligibly small and does not contribute to the stabilization of the larger Pd_5O_6 (Figure 9 (c)). In the case of Pd_6O_6 on TiO_2 -STO-113, the cluster can be considered as Pd_5O_6 plus a Pd atom residing next to the cluster. The additional Pd atom creates an additional interfacial Pd-O bond, which results in a significant CT (Figure 9 (c)) and stabilizes the cluster.

Overall, our results indicate that oxidation of the Pd clusters strengthens the interfacial bonds of the Pd_xO_y cluster. This lowers the mobility of Pd_xO_y by increasing the activation energy for diffusion and triggers the Ostward ripening by lowering the free energy of detachment. The activation energies for diffusion of Pd_4O_5 and PdO_2 on SrO-STO-113 are 3.13 and 0.82 eV, respectively, which are higher than that of Pd_4 and a Pd adatom (1.52 and 0.50 eV, respectively). On the other hand, free energies of detachment of PdO-like clusters are slightly lower than that of metallic Pd_x (Figure S33). Our finding is consistent with the Sabatier principle proposed by Li et al.⁸³ where a stronger MSI lowers the mobility and stimulates the Ostward ripening.

Chemical potentials of the PdO-like NPs in the hemispherical shape supported on SrO-STO-113 and γ -Al₂O₃(100) are elucidated based on Campbell-Mao equation⁹⁸ to highlight the role of MSI in the NP size. We find that the growth of the PdO-like NP is almost diminished on SrO-STO-113 with the size of 4 nm, while the sintering trend on γ -Al₂O₃(100) is still rapid with the size of 4 nm (See section SXII of SI).

Conclusion

In summary, we demonstrated that supported oxidized Pd_xO_y particles on STO-327 fulfill the conditions for the self-regenerative catalyst by elucidating their MSI under the TWC operating conditions by using DFT calculations combined with GOFEE and thermodynamics. First, the Pd solid solution is found to be preferable in the oxidative atmosphere. But the rock-salt SrO layer was predicted to have ability to mitigate the penetration of Pd from STO-327(001) to bulk region, leading to SSR suppression. Second, we showed that PdOlike clusters strongly bind to support surfaces, which implies that the cluster oxidation can improve the thermal stability against sintering. The effects of the oxide support and cluster size on cluster stability were revealed where the CT interactions play an important role. Our findings provide unique insights into the role of the metal oxidation state and support interactions in the stability of supported metal clusters, which may be useful for the development of sintering resistant TWC's.

Supporting Information Available

Preliminaries and calculation details; Crystal structures of Pd@STO-327 and and phonon analysis; Surface stability of STO-327 (001) at SrO and TiO₂ precipitation lines; Atomic geometries of supported Pd_xO_y ; Slab thickness dependence on the formation energy of the supported Pd_9O_y ; Role of solid solution of Pd in stabilization of small Pd clusters; Bonding nature of Pd clusters with SrO-STO-113 surface; Stability of gas-phased Pd_9O_y ; Diffusion and detachment of supported oxidized clusters; Atomic structures of the most stable Pd_xO_y under the air-aging conditions; Size dependence of PdO-like nanoparticle

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TOC Graphic

