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Theoretical Approach To Predict the Stability of Supported Single-Atom Catalysts

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Supporting Information

ABSTRACT: Heterogeneous single-atom catalysts involve isolated metal atoms anchored to a support, displaying high catalytic performance and stability in many important chemical reactions. We present a general theoretical framework to establish the thermodynamic stability of metal single atoms and metal nanoparticles on a support in the presence of adsorbates. As a case study, we establish for Pt–CeO₂ the CO partial pressure and temperature range within which Pt single atoms are more stable than Pt nanoparticles. Density functional theory and kinetic Monte Carlo simulations demonstrate that Pt atoms doped into the CeO₂ surface exhibit a very high CO oxidation activity and thermodynamic stability in comparison to models involving Pt single atoms on terraces and steps of CeO₂. An intermediate CO adsorption strength is important to explain a high activity. Our work provides a systematic strategy to evaluate the stability and reactivity of single atoms on a support.

KEYWORDS: theoretical chemistry, single-atom catalysis, stability, Pt/CeO₂, CO oxidation

INTRODUCTION

Supported metal catalysts are extensively used in exhaust gas cleanup because of their high catalytic activity for CO and hydrocarbon oxidation and NOx reduction.1–3 The size of the supported metal nanoparticles (NPs) is often decisive for the catalytic performance.4–6 Due to their highly undercoordinated nature, supported metal single-atom catalysts (SACs) can display a very high catalytic activity. SACs are rapidly becoming a new frontier in heterogeneous catalysis.7–9 Besides the low coordination number of the catalytic metal atom, the support usually plays an important role in the catalytic cycle, akin to noninnocent ligands in homogeneous catalysts.10,11

In environmental catalysis, ceria is one of the most used supports, because it can reversibly store oxygen atoms and also because it strongly interacts with transition metals, leading to a large metal–support interface.12,13 Generally, single atoms (SAs) are more mobile on a support than NPs and, thus, prone to agglomeration.14–16 SA stabilization on oxide supports is therefore of critical importance for the design of SACs. The preparation and performance of Pt SAs on ceria have recently been extensively studied.1,8,17–19 Experimental and theoretical data also emphasize the role of surface defects in ceria, such as steps and cation vacancies, for trapping of Pt SAs.1,6,18 Alternatively, Pt SAs can also strongly interact with the less stable CeO₂(100) surface by coordinating to four surface oxygen atoms in a square-planar configuration.8,19

Another aspect of highly dispersed supported metal systems is the strong adsorption of reactants that can lead to the breakup and dispersion of metal clusters and nanoparticles into SAs.20–25 For instance, Berko et al. observed by scanning tunneling microscopy a very rapid disintegration of TiO₂-supported Rh NPs of 1–2 nm to atomically dispersed Rh at 300 K and a pressure of 10⁻¹ mbar CO.22

On the basis of binding energies computed by density functional theory (DFT), we develop a theoretical framework that forms the basis for constructing condition-dependent stability diagrams of supported metal SAs with respect to supported metal NPs in the presence of CO. The influence of CO coverage and lateral interactions is also taken into account. This leads to predictions about the stability of NPs and a critical size below which the supported NPs will disperse into SAs in the presence of CO at given conditions. We employ this methodology to predict the stability of Pt SAs on stoichiometric CeO₂(111), stepped CeO₂(111), defective...
CeO$_2$(111), and CeO$_2$(100) surfaces. Finally, we compute potential energy diagrams for CO oxidation by Pt SAs for several of these cases. CO oxidation rates are predicted by graph-theoretical kinetic Monte Carlo (GT-kMC) simulations.  

## COMPUTATIONAL METHODS

### Density Functional Theory (DFT)

We carried out spin-polarized DFT calculations as implemented in the Vienna ab initio simulation package (VASP). The ion–electron interactions are represented by the projector-augmented wave (PAW) method and the electron-exchange-correlation by the generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE) exchange-correlation functional. The Kohn–Sham valence states were expanded in a plane-wave basis set with a cutoff energy of 400 eV. The Ce(5s,5p,6s,4f,5d), O(2s,2p), Pd(4d5s), and C(2s,2p) electrons were treated as valence states. The DFT-calculated energetics and vibrational frequencies were obtained using the linear response approach of Coccoccioni and de Gironcoli and is within the 3.0–6.0 eV range that results in the localization in Ce 4f orbitals of the electrons left upon oxygen removal from ceria.

For Pt/ CeO$_2$(111), we use a periodic ceria slab with a (4 × 4) surface unit cell. For Brillouin zone integration, a 1 × 1 × 1 Monkhorst–Pack mesh was used. The bulk equilibrium lattice constant (5.49 Å) previously calculated at the PBE+U level (U = 4.5 eV) was used. The CeO$_2$(111) slab model consists of three Ce–O–Ce layers (48 Ce and 96 O atoms) and a vacuum gap of 15 Å. The atoms in the bottom layer were frozen to their bulk positions, and only the top two Ce–O–Ce layers were relaxed. The climbing image nudged-elastic band (CI-NEB) algorithm was used to identify the transition states in the elementary reaction steps of CO oxidation. A frequency analysis was performed to confirm that each transition state has only a single imaginary frequency in the direction of the reaction coordinate. The total energy difference was less than 10$^{-4}$ eV, and the relaxation convergence criterion was set at 0.05 eV/Å.

### Graph-Theoretical Kinetic Monte Carlo (GT-kMC)

The DFT-calculated energetics and vibrational frequencies were input in the GT-kMC framework as implemented in the software package Zacros. In this approach, participating species and elementary steps are represented as graphs.

For nonactivated adsorption as employed in this work, we assume an early 2D gas-like transition state. The rate constants of adsorption and desorption are calculated as 

$$k_{\text{ads}} = \frac{P_A e^\Delta E_{\text{ads}}}{2\pi rmh\kappa_bT}$$

$$k_{\text{des}} = \frac{q_{\text{eh},X\text{(gas)}} q_{\text{rot},X\text{(gas)}} q_{\text{trans2D},X\text{(gas)}} k_bT}{\hbar} \exp \left( \frac{\Delta E_{\text{ads}}}{k_bT} \right)$$

where $h$ is Planck’s constant, $k_b$ is Boltzmann’s constant, $T$ is the temperature, $P_A$ is the partial pressure of a species $x$, $A_x$ is the area of an adsorption site, $m$ is the molecular mass of the adsorbent, $\Delta E_{\text{ads}}$ is the gas adsorption energy, and $q$ is the partition function for gas-phase species and adsorbates (computed using statistical mechanical expressions). For each surface reaction, the rate constants were calculated by transition state theory in an Arrhenius form, yielding 

$$k_{\text{fwd}} = \frac{k_bT}{h} \frac{Q^f}{Q_R} \exp \left( -\frac{E_{\text{fwd}}(\sigma)}{k_bT} \right)$$

and

$$k_{\text{rev}} = \frac{k_bT}{h} \frac{Q^r}{Q_p} \exp \left( -\frac{E_{\text{rev}}(\sigma)}{k_bT} \right)$$

where $k_{\text{fwd}}$ ($k_{\text{rev}}$) is the rate constant of the forward (reverse) elementary reaction step, $k_b$ is the Boltzmann constant, $T$ is the temperature, and $h$ is Planck’s constant. $Q^f$, $Q_R$, and $Q_p$ are the quasi-partition functions of the transition, reactant, and product states, respectively. Finally, $E_{\text{fwd}}(\sigma)$ ($E_{\text{rev}}(\sigma)$) is the activation energy for configuration $\sigma$ in the forward (backward) direction. Other inputs to the software include the operating conditions (temperature, pressure, and gas-phase composition), a lattice structure, energetics of each surface species, and the reaction mechanism parametrized by eqs 1–4. We did not take into account lateral interactions, because we only consider dispersed single Pt atoms and their neighboring sites, as such interactions between adsorbates are irrelevant. The GT-kMC supports site-dependent chemistry. Three types of sites were considered in each unit cell including a Pt atom, to which CO can adsorb, and two oxygen vacancy sites, where O$_2$ can adsorb and dissociate (see Supporting Information).

The chemical master equation describes the time evolution of the probability $p_i(t)$ of finding the system in a particular state $i$

$$\frac{dp_i(t)}{dt} = \sum _{j \neq i} [w_{i \rightarrow j}p_j(t) - w_{j \rightarrow i}p_i(t)]$$

where $w_{i \rightarrow j}$ denotes the propensity of the system going from state $i$ to $j$, which is related to the rate constants of the microscopic events. Solving the chemical master equation numerically is often impractical due to the large number of possible states. Instead, the kMC framework solves the chemical master equation stochastically. At each instant, the possible next events on the lattice are identified by solving subgraph isomorphism problems given the current lattice configurations. The probability of a queue of events is generated, and one event is chosen proportional to its probability.

$$p_i(\tau) = k_i \exp \left[ -\int_0^\tau k_i dt' \right]$$

where $t$ is the current time and $\tau$ is the time increment between the current time $t$ and the next event $i$. The time increment is generated stochastically for all possible events at time $t$ following an exponential distribution

$$\tau_i = \frac{1}{k_i} \ln(1 - u)$$

where $u$ is a random number sampled from the uniform distribution between 0 and 1. These times are stored in a priority queue in the form of a binary heap structure. The event $i$ with the smallest occurrence time occurs next. Next, the
lattice and simulation time are updated. The procedure is repeated until the stopping criteria are reached. In practice, to reduce stochastic noise, multiple independent trajectories generated using different random seeds are run in parallel and averaged. Given a long enough simulation time, steady-state properties such as average surface species coverages, turnover frequency (TOF), and reaction orders can be obtained.

# RESULTS AND DISCUSSION

Stability of Supported NPs and SAs. The driving force for sintering of supported metal catalysts is the reduction in surface free energy of the active metal phase. Metals usually cannot be kept in atomic dispersion on a support, because a metal adatom usually does not bind strong enough to the support. The cohesive energy is typically used to account for the strength of metallic bonds in NPs. Its absolute value decreases when particles become smaller, indicative of the weaker metallic bonds in NPs compared to bulk metal. When a nanoparticle is placed on a support, the total energy is lowered by the interactions with a part of the metal atoms that form the interface. However, the influence of the support on the total energy is minor for particles with more than 20 atoms, and we can use the cohesive energy of the corresponding free NP in vacuum as a first approximation as demonstrated for Pd NPs on CeO$_2$(111). In order to compare stabilities, this cohesive (or binding) energy per metal atom for the supported NP or supported SAs system can be compared to the binding energy of a single metal adatom placed on a support. We develop our approach for Pt on the most stable CeO$_2$(111) surface. The resulting expressions for the binding energies of ceria-supported Pt NPs and a ceria-supported single Pt atom, Pt$_x$/CeO$_2$(111), are

$$E_{\text{bind}}^{\text{Pt}x/\text{CeO}_2(111)} = \frac{(nE_{\text{Pt}x} - E_{\text{Pt}x/\text{CeO}_2(111)})}{n} \quad (8)$$

and

$$E_{\text{Pt}x/\text{CeO}_2(111)} = E_{\text{Pt}x} + E_{\text{CeO}_2(111)} - E_{\text{Pt}x/\text{CeO}_2(111)} \quad (9)$$

where $E_{\text{Pt}x}$, $E_{\text{Pt}x/\text{CeO}_2(111)}$ and $E_{\text{Pt}x/\text{CeO}_2(111)}$ are the energies of a free single Pt atom, a free Pt NP, the CeO$_2$(111) slab, and the Pt$_x$/CeO$_2$(111) model, respectively, and $n$ is the number of Pt atoms in a NP. The binding energy for a free metal NP of $n$ atoms scales with $n^{-1/3}$ (Figure S1). We compute a binding energy of 3.21 eV for a single Pt atom on the most stable CeO$_2$(111) termination, which is close to the earlier reported value of 3.30 eV. Adsorbates like CO stabilize a supported single Pt adatom more than a Pt NP because of the stronger adsorption of CO to a single metal atom and also because only a fraction of the Pt atoms in a NP is covered by CO, shown in Figure 1. The binding energy of a single Pt atom with adsorbed CO as a function of temperature ($T$) and pressure ($P$) is given by

$$E_{\text{bind}}^{\text{Pt}x/\text{CeO}_2(111)}(T, P) = E_{\text{Pt}x/\text{CeO}_2(111)}^{\text{bind}} - [E_{\text{CO}}^{\text{ads}} - \mu_{\text{CO}}(T, P)]$$

(10)

in which $\mu$ is the chemical potential of CO in the gas phase at temperature $T$ and a CO partial pressure $P$ with respect to a reference state of CO in the gas phase at standard conditions. Here, we ignored the contribution of vibrational entropy of the adsorbed CO to the binding energy of a single Pt atom or Pt

NPs. The vibrational entropy contribution to the free energy is less than 0.03 eV for CO adsorption on the metal surface. The computed adsorption energy of CO on Pt$_x$/CeO$_2$(111), $E_{\text{Pt}x/\text{CeO}_2(111)}^{\text{CO}}$ is $-3.45$ eV. Accordingly, we can rewrite eq 10 as

$$E_{\text{Pt}x/\text{CeO}_2(111)}^{\text{bind}}(T, P) = 6.66 + \mu_{\text{CO}}(T, P) \quad (11)$$

CO adsorption also stabilizes a supported Pt NP. The stabilization will depend on the number of available surface Pt atoms and the CO coverage at a certain $T$ and $P$. Therefore, we evaluate the binding energy per Pt atom for such a system by taking into account that $m$ Pt adsors to a NP containing $n$ Pt atoms at a given temperature and pressure

$$E_{\text{Pt}x/\text{CeO}_2(111)}^{\text{bind}}(nE_{\text{Pt}x} + mE_{\text{CO}} - E_{\text{Pt}x/\text{CeO}_2(111)}) = E_{\text{Pt}x} - \frac{mE_{\text{CO}}^{\text{ads}}}{n}$$

(12)

here, $E_{\text{CO}}^{\text{ads}}$ is the average CO adsorption energy obtained from the DFT-computed data

$$E_{\text{Pt}x/\text{CeO}_2(111)}^{\text{bind}}(nE_{\text{Pt}x} + mE_{\text{CO}} - E_{\text{Pt}x/\text{CeO}_2(111)}) = \frac{mE_{\text{CO}}^{\text{ads}}}{n}$$

(13)

Thus, the binding energy of a CO-covered Pt NP can be expressed in terms of the binding energy of the free Pt NP and a correction for the adsorption of CO. This correction term can be computed in the following manner by taking the chemical potential of CO molecules into account

$$\Delta E(n, P, T) = \frac{m[E_{\text{Pt}x/\text{CeO}_2(111)}^{\text{CO}}(T, P) - \mu_{\text{CO}}(T, P)]}{n}$$

(14)

where $\omega(n) = N/n$, i.e., the ratio between the number of surface Pt sites to which CO can adsorb ($N$) and the total number of Pt atoms ($n$) and $\theta = m/N$, i.e., the surface coverage at given temperature and pressure. As we will show below, $\omega(n)$ depends strongly on the particle size

$$\omega(n) = \frac{E_{\text{Pt}x/\text{CeO}_2(111)}^{\text{bind}} - E_{\text{Pt}x/\text{CeO}_2(111)}^{\text{bind}}}{2f_{\text{Pt}x/\text{CeO}_2(111)}} = 5.529n^{-1/3}$$

(15)

Figure 1. Schematic illustration of the relative stability of Pt SAs and NPs on CeO$_2$ in the presence of adsorbed CO molecules.
in which $E_{\text{bind}}^{\text{bulk}}$ is the binding energy of Pt bulk (6.40 eV) extrapolated from Figure S1, $E_{\gamma}^{\text{Pt}}$ is the surface energy of Pt NPs, and $A_{\text{atom}} = A/N$ is the area of a surface atom of Pt. The detailed derivation of eq 15 is in the Supporting Information. To compute the surface energy of Pt NPs, we use the Wulff construction to estimate that sufficiently large NPs consist of 65% (111) and 35% (100) facets. The explicitly calculated binding energy of Pt bulk is 6.37 eV, in accordance with the extrapolated value of 6.40 eV. Accordingly, we neglect the more reactive atoms at the edges and corners. The surface free energy is then the weighted surface energy based on DFT-computed values.

Equation 15 can be generally used for the prediction of the dispersion of free metal NPs. For the supported NPs considered in our study, we assume that one of the surface facets of the cuboctahedra NPs (predicted by the Wulff theorem) forms an interface with the CeO$_2$(111) support. In this way, we can determine $\omega(n)$ as a function of $n$ for the nonwetting case. The deviation between $\omega(n)$ for free and supported NPs is relatively small. We also considered the case of partial wetting in which one-half of the Wulff shape is visible in a Winterbottom approach. This partial wetting case results

![Figure 2](image.png)

Figure 2. (a) Computed CO adsorption energy on Pt(111) and Pt(100) facets as a function of the CO coverage and (b) CO coverage at given temperature and CO partial pressure for Pt(111).

![Figure 3](image.png)

Figure 3. Critical size diagrams of the supported Pt NPs with respect to the thermodynamic stability as a function of temperature and CO partial pressure relative to isolated Pt SAs (a) on the terrace of CeO$_2$(111) with nonwetting and (b) wetting, (c) on the step-edges of CeO$_2$(111), and (d) on the terrace of CeO$_2$(100). Gray area relates to Pt NPs with less than 38 atoms, which were not considered in this study.
in a lower \( \omega(n) \) for given \( n \) (Figure S3). Nevertheless, \( \omega(n) \) depends much less on the wetting degree than on \( n \).

On the basis of these assumptions for the surface energy and \( \omega(n) \) we can write the correction term as

\[
\Delta E(n, T, P) = \omega(n) \sum_i f_i \theta_{i,\text{CO}} E_{\text{Pt}i}^{\text{CO-ads}}(T, P) - \mu_{\text{CO}}(T, P)
\]

in which \( f_i \) and \( f_2 \) are the fractions of the NP surface occupied by \( (111) \) and \( (100) \) facets. The binding energy per Pt atom for our \( \text{Pt}_{n}/\text{CeO}_2(111) \) system at a given temperature and pressure is then given by

\[
E_{\text{Pt}(\text{CO})}^{\text{bind}}(n, T, P) = E_{\text{Pt}(\text{CO})}^{\text{bind}} - \omega(n) \sum_i f_i \theta_{i,\text{CO}} E_{\text{Pt}i}^{\text{CO-ads}}(T, P) - \mu_{\text{CO}}(T, P)
\]

The coverage dependence of the CO adsorption energy for the \( \text{Pt}(111) \) and \( \text{Pt}(100) \) surface facets was evaluated by DFT calculations of CO adsorption in a \((3 \times 3)\) surface unit cell and fitted with polynomial functions (Figure 2a). At a given \( T \) and \( P \), the corresponding coverage of CO can be determined by

\[
dE_{\text{Pt}(\text{CO})}^{\text{CO}}(\theta) = \frac{\partial \left[ \theta_i \theta_{i,\text{CO}} E_{\text{Pt}i}^{\text{CO-ads}}(T, P) \right]}{\partial \theta} = \mu_{\text{CO}}(T, P)
\]

where \( dE_{\text{Pt}(\text{CO})}^{\text{CO}}(\theta) \) is the differential adsorption energy of CO molecules on a particular facet (here, either the \( (111) \) or the \( (100) \) facet). As an example, Figure 2b shows the CO coverage on \( \text{Pt}(111) \) facets as a function of \( T \) and \( P \). These predictions compare well with available experimental data for single-crystal \( \text{Pt}(111) \) data.\(^{21-34}\)

We can now determine \( n, T, \) and \( P \) for which a Pt NP with \( n \) Pt atoms covered with \( m \) CO is equally or less stable than a CO-covered single Pt atom located on \( \text{CeO}_2(111) \)

\[
E_{\text{Pt}(\text{CO})}/\text{CeO}_2(111)(T, P) \geq E_{\text{Pt}(\text{CO})}^{\text{bind}}(n, T, P)
\]

We depict the results in Figure 3a in which the isolines represent this condition for a given \( n \). Figure 3a predicts that, at a typical condition of low-temperature CO oxidation (\( P_{\text{CO}} = 10^{-3} \text{ atm}, T = 100 ^\circ \text{C} \)), Pt(CO) can be dislodged from Pt NPs of up to \( \sim 150 \) atoms on the \( \text{CeO}_2(111) \) surface. Particles larger than this critical size will not break up to form Pt SAs. With increasing CO partial pressure, Pt SAs can compete with larger Pt NP. The reason is that the higher coverage of CO on the Pt NPs means that the larger number of Pt–CO bonds can increasingly outweigh the Pt–Pt interactions in the Pt NP. If, on the other hand, the temperature is raised, the CO coverage will decrease and Pt NP will become increasingly favored over single Pt(CO) species (e.g., \( T > 300 ^\circ \text{C} \)). It can explain some experimental observations that CO induces sintering of metal adatoms on oxide supports at extremely low CO pressure and/or high temperature.\(^{35-37}\)

Figure 3b and Figure S4 show how these predictions are affected by the wetting of the \( \text{CeO}_2(111) \) surface by the Pt NPs. Clearly, the main trends remain very similar, while increasing wetting leads to a lower dispersion and a lower stability of Pt NPs.

It is important to emphasize that these predictions refer to the thermodynamic stability of an isolated Pt–carbonyl species in comparison to CO-covered Pt NPs. In experiment, the size of the NPs is determined by many factors including the preparation and activation (reduction) method.\(^{56}\) The dislodgement of a Pt–carbonyl species from a supported Pt NP will involve overcoming a kinetic barrier. For instance, the activation barrier for dislodging a Pt atom from CeO\(_2\)-supported Pt is 2.46 eV. This barrier decreases to 0.45 eV when a CO is adsorbed to the dislodging Pt atom when the Pt\(_n\) cluster is covered by 4 CO, the cluster will spontaneously break up into 4 Pt(CO) SA species (Figure S5). The activation barrier for dislodging a Pt atom from a Pt\(_n\) cluster amounts to 2.14 and 0.61 eV in the absence and presence of CO, respectively (Figure S6). Therefore, these results demonstrate that dislodgement of Pt atoms in the presence of CO is feasible at typical reaction conditions.

The computed frequency of the CO stretching vibration for the Pt(CO) SA on CeO\(_2(111)\) is 2047 cm\(^{-1}\). Notably, this value is significantly different from the typical frequencies of linearly adsorbed CO on Pt(111) and Pt(100), which are 2090 and 2080 cm\(^{-1}\), respectively.\(^{57-60}\) Bazin et al. observed a CO feature at 2046 cm\(^{-1}\) and attributed this to linear CO adsorption on a Pt atom at the Pt–CeO\(_2\) interface in Pt/CeO\(_2\).\(^{61}\) Teschner and co-workers also reported that linear CO adsorption leads to the strongest adsorption at the Pt–CeO\(_2\) boundary and a vibrational frequency of 2054 cm\(^{-1}\).\(^{62}\) Therefore, we speculate that these signals should be attributed to dislodged Pt(CO). We also refer to related IR studies of CO adsorption on oxide-supported Pt catalysts.\(^{63,64}\)

The binding energy of a Pt atom at the ceria step edge is much higher (5.54 eV) than that on CeO\(_2(111)\) (3.21 eV). This leads to a higher propensity of ceria step-edge sites to break up Pt NP, as shown in Figure 3c. These results show that atomically dispersed Pt can be stabilized on a ceria step edge over a much wider range of conditions than on the CeO\(_2(111)\) surface.\(^{18}\) The finding that this stability extends to high temperature and low CO coverage can explain why ceria-supported small Pt NPs are atomically dispersed at high temperatures, where kinetic barriers for atom dislodgement from Pt NPs can be easily overcome.\(^{31,18}\) On the basis of the similar stability of Pt(CO) complexes on the CeO\(_2(111)\) step and CeO\(_2(100)\), we predict that Pt SAs can also be stabilized over a wide range of conditions on the more open CeO\(_2(100)\) surface (Figure 3d), in agreement with experimental observations.\(^{55}\)

Pd doping in the CeO\(_2(111)\) surface has recently been explored in the context of stable CO and CH\(_4\) oxidation catalysis.\(^{66}\) Figure 4c–f shows similar structures for a Pt atom doped in the CeO\(_2(111)\) surface. Pd-dop-I contains an octahedral Pt atom obtained by placing a Pt atom on a Ce vacancy (\( \Delta E = -4.04 \text{ eV} \) with respect to bulk Pt).\(^{67}\) Pd-dop-II represents a slightly less stable structure (\( \Delta E = +0.36 \text{ eV} \)) in which Pt is located in a square-planar coordination between 4 lattice oxygens. Whereas removal of a surface oxygen from Pt-dop-I is endothermic (\( \Delta E = 1.75 \text{ eV} \)), forming an O vacancy (\( V_0 \)) on Pt-dop-II is exothermic (Pt-dop-II-\( V_0 \), \( \Delta E = -0.35 \text{ eV} \)). Removing a further oxygen from Pt-dop-II-\( V_0 \) is unfavorable (\( \Delta E = 1.23 \text{ eV} \)), however. Notably, Figure 4d–f shows that the local geometry around Pt in Pt-dop-II is very similar to that of a Pt atom at a step edge to which two excess O atoms are bound (Figure 4b).\(^{68}\) A phase diagram of these doped structures depicted in Figure 4g predicts that, under typical CO oxidation conditions, Pt-dop–II–\( V_0 \) is a thermodynamically stable structure.
Having established the conditions under which isolated Pt(CO) complexes are stable on the CeO$_2$(111) terrace and step edges, we will now compare the rate of CO oxidation on different isolated Pt species. We also explored alternative locations of a Pt SA doped into the CeO$_2$(111) surface. Co-adsorption of O$_2$ on isolated Pt(CO) is unfavorable ($E_{\text{ads}} = 0.08$ eV). This implies that CO oxidation via a conventional Langmuir–Hinshelwood (LH) mechanism is unlikely. Therefore, we explored a Mars–van Krevelen (MvK) mechanism involving lattice O atoms of the ceria support.\textsuperscript{1,17,68} Figure 5 shows the potential energy surface for CO oxidation. It is shown that the rate-limiting step on Pt$_1$/CeO$_2$(111) and Pt$_1$O$_2$/step is CO$_2$ desorption, which costs energy of 2.38 and 1.31 eV to produce an oxygen vacancy, respectively, while for CO oxidation by Pt-dop-II-VO, the CO$_2$ desorption is much easier and requires an energy barrier of 0.97 eV for CO$_2$ formation. Notably, CO adsorption can cause dynamic hopping of Pt dopants from subsurface to surface as well as Pd.\textsuperscript{66}

Next, we employed the GT-kMC simulations to determine the catalytic performance of these candidate sites in CO oxidation. The lattice for these kinetic Monte Carlo simulations consists of 100 Pt SA on ceria lattice consisting of 10 $\times$ 10 unit cells. Each cell contains 1 Pt atom and 2 empty sites accommodating O atoms. The steady-state turnover frequencies (TOF) and occupation of the states along the potential energy surface expressed in terms of fractional coverages are reported in Figure 6. The total pressure is set to 0.1 atm and the CO-to-O$_2$ ratio to 2.

Figure 6a shows the CO oxidation rates of the different Pt SAs supported on ceria as a function of the temperature. The Pt-dop-II-V$_0$ site is much more reactive than the Pt$_1$O$_2$/step model, while the Pt$_1$/CeO$_2$(111) is nearly inactive for CO oxidation under practical conditions. Recently, Datye and co-workers also suggested that atomically dispersed Pt on step edges of CeO$_2$ exhibits low low-temperature CO oxidation activity.\textsuperscript{18} Our study alternatively suggests that Pt atoms doped into the surface can be very active for CO oxidation.

Further insight can be obtained by inspecting the dominant surface states (also known as MARI, most abundant reaction intermediate) during CO oxidation in Figure 6b–d. For Pt$_1$O$_2$/step, the dominant state is CO adsorbed on Pt$_1$O$_2$/step model, while the Pt$_1$/CeO$_2$(111) is nearly inactive for CO oxidation under practical conditions. Besides, Datye and co-workers also suggested that atomically dispersed Pt on step edges of CeO$_2$ exhibits low low-temperature CO oxidation activity.\textsuperscript{18} Our study alternatively suggests that Pt atoms doped into the surface can be very active for CO oxidation.

Further insight can be obtained by inspecting the dominant surface states (also known as MARI, most abundant reaction intermediate) during CO oxidation in Figure 6b–d. For Pt$_1$O$_2$/step, the dominant state is CO adsorbed on Pt$_1$O$_2$/step at all temperatures tested, indicating strong CO adsorption. In the Pt$_2$/CeO$_2$(111) model, strong CO adsorption results in the CO-adsorbed state on Pt$_2$/CeO$_2$(111) being the MARI at high temperatures and adsorbed CO$_2$ at low temperatures. On Pt-dop-II-V$_0$ at high temperatures ($T > 600$ K), the system is in the initial state Int0 (Pt-dop-II-V$_0$), where CO oxidation becomes rate limiting. Reaction orders were also computed and emphasize that CO reaction orders are zero when the MARI is a CO-adsorbed state and unity for an empty surface (Figure S16). This discussion is further supported by a degree of rate control analysis (Figure S18). Overall, we find that strong CO adsorption leads to higher barriers for CO oxidation. Moderate CO bonding of a Pt atom embedded in the CeO$_2$(111) surface is therefore preferred to achieve high CO oxidation activity.

FIGURE 4. Pt SAs located at a CeO$_2$(111) step before (a) and after (b) O$_2$ dissociation, and (c–f) doped into the CeO$_2$(111) surface (color code: white, Ce; gray, irrelevant O; red, relevant O; black, C; blue, Pt). (g) Ab initio-determined phase diagram of the Pt-doped CeO$_2$(111) surface.

FIGURE 5. CO oxidation pathways by Pt SAs on CeO$_2$(111), on stepped CeO$_2$(111), and doped in the CeO$_2$(111) surface.

CO oxidation. It is shown that the rate-limiting step on Pt$_1$/CeO$_2$(111) and Pt$_1$O$_2$/step is CO$_2$ desorption, which costs energy of 2.38 and 1.31 eV to produce an oxygen vacancy, respectively, while for CO oxidation by Pt-dop-II-V$_0$, the CO$_2$ desorption is much easier and requires an energy barrier of 0.97 eV for CO$_2$ formation. Notably, CO adsorption can cause dynamic hopping of Pt dopants from subsurface to surface as well as Pd.\textsuperscript{68}

Next, we employed the GT-kMC simulations to determine the catalytic performance of these candidate sites in CO oxidation. The lattice for these kinetic Monte Carlo simulations consists of 100 Pt SA on ceria lattice consisting of 10 $\times$ 10 unit cells. Each cell contains 1 Pt atom and 2 empty sites accommodating O atoms. The steady-state turnover frequencies (TOF) and occupation of the states along the potential energy surface expressed in terms of fractional coverages are reported in Figure 6. The total pressure is set to 0.1 atm and the CO-to-O$_2$ ratio to 2.
(partially) CO-covered Pt NPs on CeO₂ surface. The constructed stability diagrams show that isolated Pt(CO) may be expected to form on the terrace and step and doping sites of CeO₂(111). In general, the thermodynamic propensity for dislodgement increases with lower temperature and higher CO coverage. Kinetically, CO coverage facilitates the disruption of Pt–Pt bonds. Further investigation of CO oxidation reactivity demonstrates that doping of Pt in the CeO₂(111) surface presents the highest CO oxidation turnover rate among the SA models. This is mainly because CO strongly binds to a Pt SA located on the stoichiometric CeO₂ surface or PtO on a ceria step-edge site, resulting in low activity. The moderate CO binding suggests the importance of a Sabatier optimum for CO oxidation for Pt SAs on CeO₂. The herein developed single-atom thermodynamic concept can be generally applied for supported metal catalysts. This study provides deeper insight into the stability and activity of SACs and establishes a useful concept facilitating the rational design of SACs with high stability and catalytic activity.

■ ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.9b00252.

Derivation of the dispersion formula; critical size diagrams of supported Pt NPs and frequency analyses of CO bound to Pt facets; kinetic data of Pt atom dislodging from Pt₄ and Pt₆ supported on CeO₂(111); DFT-determined catalytic cycles of CO oxidation and GT-kMC data (PDF)

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Notes
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