Reactant-Induced Dynamic Stabilization of Highly Dispersed Pt Catalysts on Ceria Dictating the Reactivity of CO Oxidation

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ABSTRACT: The reactant-induced dynamics of catalysts under harsh conditions have a profound impact on their reactivity and stability, and identification of the underlying principle and active sites is vital for the rational design of catalysts. Based on a comprehensive first-principles investigation, we reveal here a reactant-induced dynamic stabilization of the highly dispersed Pt complexes that formed on ceria surfaces and their decisive role in CO oxidation. Compared to those of Pt nanoparticles, reactant-stabilized single-nuclear Pt₈(CO)₇ and/or multinuclear Pt₇(CO)₆ complexes prevail under CO-rich conditions on the defective CeO₂ (111), (110), and (100) surfaces considered. At lower temperatures, the Pt₇(CO) complexes emerge as active sites for CO oxidation, whereas at higher temperatures, the active sites transit dynamically to the Pt₈(CO)₉ complexes. We found that oxygen defects not only stabilize the complexes but also promote activity via the facile Mars–van Krevelen mechanism. These insights reveal the great impact of the reactant-interference structure–activity relationship under operando conditions.

KEYWORDS: catalyst-induced dynamics by reactants, platinum complexes, theoretical modeling, platinum on cerium oxide, CO oxidation, reaction mechanisms

INTRODUCTION

Heterogeneous catalysis drives a myriad of industrial processes, from energy production to environmental protection, and its success relies critically on the ability to transform raw materials into valuable products with high activity, selectivity, and stability. The activity and selectivity of catalysts are essentially determined by their composition and structure for the desired bond-breaking and making involved.1 Under elevated temperatures and pressures, the presence of reactants significantly changes the chemical state and structure of the catalyst during catalytic reactions.2 For supported metal nanocatalysts, the reactants can accelerate sintering and/or disintegrate into small metal complexes, eventually deactivating the catalysts.3 However, for fully exposed clusters and/or single-atom catalysts, reactants can fully populate highly coordinately unsaturated metal atoms with increased flexibility and distinct functionalities.4−6 Revealing the structural dynamics and impact on activity and stability among supported single atoms, clusters, and nanoparticle catalysts under operational conditions is of paramount importance for the rational design of catalysts.7

Ceria-supported platinum (Pt/CeO₂) is widely employed as a preeminent catalyst for mitigating exhaust gas emissions due to the exceptional oxygen storage capacities inherent in CeO₂ supports. For Pt/CeO₂-catalyzed CO oxidation, fully exposed Pt clusters and single-atom catalysts (denoted as Ptₓ/CeO₂ and Pt₁/CeO₂, respectively) were synthesized to maximize the atomic utilization efficiency of Pt₁−x.8−11 However, the evolution of the stability and structural dynamics of Ptₓ/CeO₂, Pt₁/CeO₂, and nanoparticles (PtₓNP/CeO₂) under operating conditions and their impacts on CO oxidation remain the subject of ongoing debate. Depending on the conditions, the dispersion or agglomeration of Pt varies in the form of single atoms and/or clusters, and the catalytic activities change accordingly.5,12 It was reported that atomically dispersed square Pt₁ exhibits low activity and/or acts as a spectator during CO oxidation,13 while others have demonstrated that highly dispersed Pt₁ sites are very active for CO oxidation.14 On the other hand, the as-prepared Pt₁ species was reported to be regenerated in situ as a highly active Ptₓ during CO oxidation.15 The formation of highly active sites at the Pt−CeO₂ interface was attributed to the high activity of Ptₓ/CeO₂.9,16,17 Nevertheless, the lack of uniformity in preparing
Pt/CeO₂ catalysts, often in a mixture of single atoms, clusters, and nanoparticles, which might change and transform dynamically depending on the reaction conditions, surface orientations, and defects,²⁷,²⁸ prevents the identification of the true active species responsible for the observed activity. Investigating the functions of Pt₁, Pt₈, and Pt NP catalysts under operating conditions, their restructuring, and the authentic active centers for CO oxidation is a formidable task from both experimental and theoretical points of view.

Here, through a comprehensive first-principles-based multi-scale investigation, we reveal the dynamic formation of active Pt₁ and Pt₈ carbonyl complexes from Pt NPs under CO-rich conditions and their decisive role as active sites in catalyzing the oxidation of CO on various defective ceria surfaces. Ab initio thermodynamic calculations showed that the presence of CO tends to disintegrate small Pt NPs on defective CeO₂(111) into Pt carbonyl complexes. Using basin-hopping-driven grand canonical Monte Carlo (GCMC) simulation, two disintegrated prototype complexes, namely, single-nuclear complexes (Pt₁(CO),₂) and cluster complexes (here as a showcase, Pt₈(CO),₉), were identified under CO-rich conditions,²¹ and ab initio molecular dynamics (AIMD) further confirmed that these complexes transform dynamically at elevated temperatures. For CO oxidation, first-principles kinetics simulations revealed that the number of active sites changes from the Pt₁(CO) complexes to the Pt₈(CO),₉ complexes with...
increasing temperature. Here, oxygen defects play a central role not only by stabilizing Pt carbonyl complexes but also by increasing activity via the facile Mars van Krevelen (MvK) mechanism. To investigate the influence of redox properties and the local coordination of oxide supports, stepped CeO$_2$ (111), (110), and (100) surfaces were considered. These findings highlight the impact of reactants on the dynamic formation of highly active single-atom and cluster catalysts, dictating catalytic reactivity under reaction conditions.

### RESULTS AND DISCUSSION

**Structures of the Pt/CeO$_2$ Catalyst under a CO Atmosphere.** To establish a structure–function relationship, it is necessary to determine the stability of the structure under realistic operational conditions. Here, we reveal the chemical stability of Pt/CeO$_2$ catalysts across single atoms, clusters, and NPs in the presence of CO, revealing the strong interplay between metals, reactants, and supports during CO oxidation. Two prototype Pt$_x$ species were studied, namely, Pt$_1$ adsorbed on the surface and trapped in the Ce lattice vacancy, noted as Pt$_1$/Ce$_{1−x}$O$_x$. A representative yet computationally fortable magic-numbered Pt$_8$ cluster on CeO$_2$(111) was used to simulate a Pt$_8$/CeO$_2$ catalyst. GCMC simulations were employed to determine the composition and structure of the Pt$_1$/CeO$_2$ and Pt$_x$/CeO$_2$ catalysts under typical CO-rich conditions (T = 373 K, P$_{CO}$ = 0.01 atm), corresponding to the CO oxidation reaction. For comparison, the low-index Pt(111), (110), and (100) surfaces were employed to present the large Pt NPs on support, given their maximized surface area—an assertion supported by surface energy calculations and the Wulff construction method, and corresponding CO coverage was identified through kinetic Monte Carlo (KMC) simulations and GCMC simulations.

Compared to that of bare Pt$_1$ on CeO$_2$(111), the formation of Pt$_1$(CO) carbonyl complexes can be thermodynamically exothermic due to the strong interaction between Pt and CO, although the adsorption of another CO to form dicarbonyls becomes endothermic (Figures 1a,c and S1−S3). Namely, in the presence of CO, Pt$_1$, alone cannot exist but can exist in the form of the Pt$_1$(CO) complex on CeO$_2$(111). In fact, its free energy is even lower than the chemical potential of supported 3 nm Pt NPs as determined by the Gibbs–Thomson equation (Figure S2) below 350 K and with P$_{CO}$ = 0.01 atm. This implies that the corresponding Pt NPs are unstable and tend to disintegrate from CO. The presence of CO can reduce the ceria surface area and generate additional oxygen vacancies, as determined by our thermodynamic calculations (Figures S4 and S5), in agreement with the experimental results$^{11,24}$ In turn, the oxygen vacancies (V$_O$) further stabilize the Pt$_1$(CO) complexes, and the CO-induced disintegration of the Pt NPs can be maintained at an even higher temperature of 400 K (Figure 1b). These results indicate that neither the supported Pt NPs nor the bare Pt$_1$ are stable on CeO$_2$(111); instead, the Pt$_1$(CO) complexes are thermodynamically more favorable under typical CO conditions (T < 400 K and P$_{CO}$ = 0.01 atm). Note that Pt$_1$ could be trapped at the Ce$^{4+}$ vacancies, and it is very stable and free from agglomeration due to its strong exothermic formation energy of −3.91 eV with respect to the Pt bulk metal (Figure S6). Generally, the Ce vacancy (V$_{Ce}$) is more difficult to generate than the V$_{O}$.$^{25}$ Like the Pt/TiO$_2$ system, while Ce vacancies (V$_{Ce}$) can form under oxygen treatment, enabling Pt to be trapped within these vacancies. However, the formation of Ce vacancies under low-temper-

![Figure 2](https://doi.org/10.1021/acscatal.3c05590)

**Figure 2.** Identification of the dynamic structural evolution between Pt$_x$(CO)$_y$/CeO$_{2−x}$(111) and Pt$_1$(CO)/CeO$_{2−x}$(111). (a) Constrained AIMD simulations unveil the dynamic structural evolution between Pt$_x$(CO)$_y$/CeO$_{2−x}$(111) and Pt$_1$(CO)/CeO$_{2−x}$(111). Representative snapshot structures from AIMD simulations conducted at T = 373 K are depicted. (b) PES diagram illustrates the dynamic structural evolution between Pt$_x$(CO)$_y$/CeO$_{2−x}$(111) and Pt$_1$(CO)/CeO$_{2−x}$(111) at T = 373 K.
underscoring the dynamic changes between Pt$_8$(CO)$_9$ and Pt$_1$(CO) under elevated temperatures. This complicates the identification of the active sites and reaction mechanisms, but it has not been addressed before.

Compared to the Pt$_8$(CO)$_9$ and Pt$_1$(CO) complexes on supports, Pt NPs remain stable when their size is larger than $\sim$6 nm (Figure 1c); moreover, the low-index Pt(111), (110), and (100) surfaces are used as representative models for extended Pt nanoparticle catalysts. To identify the corresponding structure and coverage under reaction conditions, we employed KMC simulations\textsuperscript{23} to explore CO adsorption on Pt(111) at different coverages (Figure 1e,f). Through atomistic thermodynamic analysis, we found that under the specified conditions of $T = 373$ K and $P_{CO} = 0.01$ atm, the saturation coverage of CO is 0.50 ML (half at the top sites and half at the bridge sites), herein termed CO/Pt(111), which is used in the following control investigation. GCMC simulations were further carried out to ascertain the surface coverage of CO on the Pt(110) and Pt(100) surfaces under reaction conditions (T = 373 K and $P_{CO} = 0.01$ bar). These simulations revealed that the CO surface coverage is 11/16 ML for Pt(100) and 15/16 ML for Pt(110).

**CO Oxidation Mechanism.** To identify the active sites and catalytic role of Pt$_1$/CeO$_{2-x}$, Pt$_1$(CO), and Pt$_8$(CO)$_9$ supported on CeO$_{2-x}$(111), and CO/Pt(111) considered thus far, we calculated the potential energy surfaces (PESs) for CO oxidation. The elementary activation barriers are indicated in eV. (g–i) Geometric structures of key transition states involved in CO oxidation over different types of Pt/CeO$_2$ catalysts. The distances between the two reacting fragments at the transition state are indicated in Å. The green spheres are O atoms involved in CO oxidation.

**Figure 3.** CO oxidation mechanism study across various Pt/CeO$_2$ catalyst structures. (a–c) Schemes for CO oxidation cycles over the Pt$_1$/CeO$_{2-x},$ Pt$_8$/CeO$_{2-x},$ and CO/Pt(111) structures. * and # represent the Pt sites and oxygen vacancies on the CeO$_2$ support, respectively. (d–f) Gibbs free energy diagrams for CO oxidation. The elementary activation barriers are indicated in eV. (g–i) Geometric structures of key transition states involved in CO oxidation over different types of Pt/CeO$_2$ catalysts. The distances between the two reacting fragments at the transition state are indicated in Å.
reaction. In this case, when an incoming CO molecule adsorbs at a single Pt atom, it can react with lattice oxygen in a thermodynamically exothermic manner, resulting in a more energetically favorable process (Figures 3a and S10). As a result, Pt\(_1\)(CO)/CeO\(_2\)\(_{\sim x}\) (111) is highly active for CO oxidation, following an MvK with elementary reaction barriers consistently lower than 0.67 eV (Figure 3d). The migration of lattice oxygen to the neighboring Pt site emerges as the step with the highest elementary barrier of 0.67 eV (Figures 3d,g, and S10), potentially acting as the rate-determining step (RDS) governing the activity. Notably, Pt\(_1\)(CO) complexes on oxygen vacancy-rich surfaces can lead to a reduction in activity, as evidenced by an increase in the barrier of at least 0.15 eV associated with oxygen migration (Figures S10−S12). For Pt\(_8\)(CO)/Ce\(_{1−y}\)O\(_2\) (111), the optimized PES is plotted in Figure S13, where a high barrier of 1.57 eV for O\(_2\) dissociation alone limits its overall activity, particularly compared to Pt\(_1\)(CO)/CeO\(_2\)\(_{\sim x}\) (111).

For Pt\(_8\)(CO)\(_m\)/CeO\(_2\)\(_{\sim x}\) (111), a new reaction pathway emerges, where CO reacts with oxygen atoms from O\(_2\) dissociation to form CO\(_2\) at the perimeter sites between Pt\(_8\)(CO)\(_m\) and CeO\(_2\)\(_{\sim x}\) (111) (Figure 3b), with no longer migration of the lattice oxygen. In fact, O\(_2\) dissociation could occur either on the CeO\(_2\)\(_{\sim x}\) (111) surface exclusively to heal the oxygen vacancies (Figure S14) or at the perimeter sites between Pt\(_8\)(CO)\(_m\) and CeO\(_2\)\(_{\sim x}\) (111) to heal one oxygen vacancy but retain another oxygen atom coordinating to the Pt atoms of the complexes (Figures 3e,h, and S15). For the former pathway, only one Pt atom is involved, but two atoms are involved in the latter pathway, although lattice oxygen is involved in both pathways. For Pt\(_8\)(CO)\(_m\)/CeO\(_2\)\(_{\sim x}\) (111), the maximum elementary barriers for these two pathways are comparable at 0.79 and 0.86 eV, respectively, and are slightly higher than those of Pt\(_1\)(CO)/CeO\(_2\)\(_{\sim x}\) (111) by at least 0.12 eV (Figure 3d,e). This indicates that Pt\(_1\)(CO) might be more active than less-populated Pt\(_8\)(CO)\(_m\), particularly at low temperatures. However, at elevated temperatures, Pt\(_8\)(CO)\(_m\) might be more active than Pt\(_1\)(CO) due to the relatively weak CO bonding on the latter (\(E_{CO} = −0.36\) eV).

For comparison, we note that CO oxidation on CO/Pt(111) follows a well-established Langmuir−Hinshelwood mechanism via the so-called peroxide-like OCOO intermediate. This mechanism is found to be energetically more favorable than the O\(_2\) dissociation pathway by 0.36 eV (Figures 3c,f,i and, S16 and S17). Compared to Pt\(_1\)(CO) and Pt\(_8\)(CO)\(_m\) supported on CeO\(_2\)\(_{\sim x}\) (111), the limiting barrier through the OCOO intermediate on the CO/Pt(111) bond is 0.19 eV lower. However, the highly endothermic adsorption of O\(_2\) (\(\Delta G_{O_2} = 1.49, 0.87,\) and 1.58 eV) on the CO/Pt(111), CO/Pt(110), and CO/Pt(100) surfaces significantly suppresses its overall activity, as shown below.
Microkinetic simulations\textsuperscript{29} were used to quantitatively assess the intrinsic activity of the Pt/CeO\textsubscript{2} catalysts considered thus far (Tables S1–S4). Note that the CO/Pt(111), CO/Pt(110), and CO/Pt(100) surfaces exhibit the highest apparent activation barrier \( E_{\text{app}} \) (2.13–2.70 eV) for CO oxidation, resulting in the lowest oxidation rate over the whole range of temperatures considered (Figure 4a) due to CO poisoning, in agreement with the observed diminished activity on Pt NPs at relatively lower \( T \).\textsuperscript{30} The \( E_{\text{app}} \) of Pt\((CO)/\text{CeO}_{2−x}(111)\) is only 0.55 eV, which is notably lower than those of Pt\((CO)/\text{CeO}_{2−x}(111)\) (1.22 eV) and Pt/\text{Ce}_{3+}\text{O}_{x}(111) (1.07 eV) at \( T \) values less than 318 K (Figure 4a). Consequently, the Pt\((CO)/\text{CeO}_{2−x}(111)\) structure exhibits the highest reaction rate within the temperature range below 318 K. Compared to Pt\(/\text{Ce}_{3+}\text{O}_{x}\), although Pt\((CO)/\text{CeO}_{2−x}(111)\) has a higher \( E_{\text{app}} \), it has a relatively higher rate because less CO\textsuperscript{*} can adsorb at the Pt site over the former surface during CO oxidation (Figure S28). We note that when \( T \) > 318 K, the activity of Pt\((CO)/\text{CeO}_{2−x}(111)\) decreases dramatically due to the strong tendency for desorption of another weakly bound CO (Figure S28). As a result, Pt\((CO)/\text{CeO}_{2−x}(111)\) became the most active catalyst. The Pt\(/\text{Ce}_{3+}\text{O}_{x}\) surface, often employed as a model for single-atom catalysts, consistently exhibits a lower activity than those of Pt\((CO)/\text{CeO}_{2−x}(111)\) and Pt\((CO)/\text{CeO}_{2−x}(111)\).

We further studied the CO oxidation mechanism over two metastable isomers, namely, Pt\((CO)\)\textsuperscript{y8} and Pt\((CO)\)\textsuperscript{m8}, which are less stable than Pt\((CO)\)\textsuperscript{y9} and Pt\((CO)\)\textsuperscript{m9}, respectively. This indicates that these metastable isomers can exist as the most stable isomers under CO oxidation conditions but are distinguished by the varying local environments surrounding the Pt atoms. The calculated structures, PES diagram, and microkinetic simulation results for CO oxidation over the metastable Pt\((CO)\)\textsuperscript{y8} and Pt\((CO)\)\textsuperscript{m8} isomers are shown in Figures 4a, S22, S30, S31, S37, and Table S3. Although both the most stable Pt\((CO)\)\textsuperscript{y9} and metastable Pt\((CO)\)\textsuperscript{m9} exhibit similar high activation barriers for CO oxidation, the latter isomer demonstrates greater activity due to its stronger O\textsuperscript{2−} adsorption by 0.79 eV (Figure S30 and Table S3). We found the metastable Pt\((CO)\)\textsuperscript{y8} structure has a low \( E_{\text{app}} \) of 0.87 eV and exhibits the highest CO oxidation activity at 0.14 s\textsuperscript{−1}, surpassing the most stable Pt\((CO)\)\textsuperscript{y8}/\text{CeO}_{2−x}(111) structure. However, the Pt\((CO)\)\textsuperscript{m8} isomer has the lowest CO oxidation activity due to its highest CO oxidation barrier of 1.27 eV (Figure S31 and Table S3). Although the activity of the metastable isomer Pt\((CO)\)\textsuperscript{y8} is greater than that of the most stable Pt\((CO)\)\textsuperscript{y9}, the predominant catalyst for CO oxidation at low temperatures is the Pt single atom, while at higher temperatures, the metastable Pt cluster takes precedence (Figures 4a and S22). Therefore, Pt\((CO)/\text{CeO}_{2−x}(111)\) emerges as the active site for CO oxidation in the low-\( T \) regime, while Pt\((CO)\)\textsuperscript{y8}/\text{CeO}_{2−x}(111) takes precedence in CO oxidation in the high-\( T \) regime. Notably, variations in the choice of exchange–correlation functional, including the PBE, RPBE, and PBE + vDW functional, in DFT calculations only induced a marginal change in barriers (less than 0.12 eV, Table S6 and Figure S18) and did not change the trend found above.

**Surface Structure Sensitivity of the CeO\textsubscript{2} Support.**

Stepped and open CeO\textsubscript{2−x} surfaces, which expose lower coordinated surface Ce\textsuperscript{3+/Ce\textsuperscript{4+} and/or O atoms, may interact distinctively with Pt and influence the results above (Figures S23–S31). Accordingly, we investigated the polar and reconstructed CeO\textsubscript{2}(100) surface, where half of the oxygen atoms on the top surface were eliminated. Moreover, we considered the stepped CeO\textsubscript{2}(111) surface, which was represented by a \( p(4 \times 4) \) CeO\textsubscript{2}(111) surface model with two columns of topmost O–Ce–O layers removed. Although previous investigations have highlighted the formation of carbonate on ceria support and its substantial impact on support reconstruction\textsuperscript{11}, this topic is beyond the focus of this specific study. On oxygen-defective CeO\textsubscript{2}(110), (100), and stepped (111) surfaces, GCMC simulations reveal that Pt\textsubscript{x} clusters can stably adsorb eight or nine CO molecules at 373 K and \( P_{\text{CO}} \) = 0.01 atm, denoted as Pt\((CO)\)\textsuperscript{n}/CeO\textsubscript{2−x}(110), Pt\((CO)\)\textsuperscript{n}/CeO\textsubscript{2−x}(100), and Pt\((CO)\)\textsuperscript{n}/CeO\textsubscript{2−x}(step) (Figure S21), respectively, indicating little influence of the support on the formation of large Pt\textsubscript{x} carbonyl complexes. However, these surfaces considerably stabilize the Pt\textsubscript{1} carbonyl complexes. In fact, the stabilizations of Pt\((CO)\) on CeO\textsubscript{2−x}(110) and (100) and Pt\((CO)\)\textsubscript{2} on the CeO\textsubscript{2−x} are so strong that they even enable the disintegration of the infinitely large bulk Pt (Figure S20).

Note that, compared to those on the Pt\textsubscript{C} complexes, the Pt\textsubscript{1} complexes on these surfaces are energetically more favorable. On CeO\textsubscript{2−x}(110), the difference in energy was small (less than 0.19 eV) (Figure S20), indicating that both complexes could coexist on these surfaces, as was the case for CeO\textsubscript{2−x}(111). However, on the CeO\textsubscript{2−x}(100) and CeO\textsubscript{2−x} step surfaces, the Pt\textsubscript{1} carbonyl complexes will be the dominant sites. The calculated reaction rates for these three surfaces show that the Pt\textsubscript{8} carbonyl complexes are more active than the Pt\textsubscript{1} carbonyl complexes and Pt NPs at \( T \) ranging from 270 to 380 K (Figure 4b–d). However, on CeO\textsubscript{2−x}(110), the activity of the Pt\((CO)\)\textsuperscript{n} complex is approximately 6 orders of magnitude lower than that of the Pt\textsubscript{C} complexes by at least 1.19 eV. In other words, on the CeO\textsubscript{2−x}(100) and CeO\textsubscript{2−x} step surfaces, the Pt\textsubscript{1} carbonyl complexes will be the dominant sites. Accounting for metastable Pt\textsubscript{x} isomers might widen the activity gap between these forms and cannot alter the conclusion that Pt clusters are more active than single-atom catalysts over CeO\textsubscript{2−x}(110), (100), and stepped (111) surfaces.

Our theoretical modeling validates recent research in experiments and reveals dynamic transformations, migrations, and redistributions among single atoms, clusters, and nanoparticles, particularly during CO oxidation over the Pt/CeO\textsubscript{2} catalyst\textsuperscript{14,32} which offers a comprehensive scenario for rationalizing the experiments required for further investigation. Specifically, Pt clusters exhibit higher CO oxidation activity than Pt\textsubscript{1} at elevated temperatures due to the presence of reactive interfacial oxygen species.\textsuperscript{9,16,17} Moreover, the high activity observed for CO oxidation in the Pt\textsubscript{C}/CeO\textsubscript{2} catalyst\textsuperscript{31} can be attributed to Pt\((CO)\), whereas the low activity observed for CO oxidation\textsuperscript{31} may be linked to Pt\textsubscript{1}/Ce\textsuperscript{3+}O\textsubscript{2−x}.

Degree-of-rate-control (DRC) analysis\textsuperscript{35} was employed to elucidate the disparities in activity for CO oxidation across the Pt\textsubscript{C} and Pt\textsubscript{C} carbonyl complexes and Pt NPs over the various surfaces considered. The greater the value of the DRC is for a particular step, the more significant is the impact of its rate.
constant on the overall reaction rate. A positive value indicates that increasing the rate constant will lead to an increase in the net reaction; such steps are referred to as RDS. Our investigation unveils several potential RDSs for CO oxidation, including oxygen migration from CeO$_2$ to a single Pt site, removal of oxygen species from Pt sites, and O$_2$ adsorption/dissociation, and these results are particularly evident for the Pt$_1$(CO)$_{1/2}$ and Pt$_8$(CO)$_{8/9}$ catalysts (Figures S25 and S26). This exploration further established a correlation between reactivity, quantified by the TOF, and the binding strength of surface lattice oxygen species across different Pt/CeO$_2$ structures with variations in the CeO$_{2-x}$ surfaces (illustrated in Figure 5). The enhanced lattice oxygen binding strength on the CeO$_{2-x}$ support corresponds to a heightened CO oxidation TOF, suggesting that the binding energy of surface lattice oxygen serves as an indicator of oxidation activity on Pt/CeO$_2$ catalysts. Therefore, strategies aimed at augmenting oxidation performance over Pt/CeO$_2$ catalysts may involve manipulating the binding strength of the surface lattice oxygen.

**CONCLUSIONS**

In summary, our comprehensive theoretical investigations have illuminated the reactant-mediated transitions in the structure and composition of Pt/CeO$_2$ catalysts under the reaction conditions, shedding light on CO oxidation. The CO-stabilized Pt$_1$ atom, instead of the Pt single atom alone, on the defective CeO$_2$(111) surface, was identified as the active site for CO oxidation at low temperature and was much more active than the Pt-doped CeO$_2$(111) (Pt$_1$/Ce$_{1-x}$O$_2$) catalyst. At higher temperatures, CO-stabilized multinuclear Pt$_n$(CO)$_2$ clusters dominate the process of driving CO oxidation. The presence of oxygen defects not only reinforces the stability of these single-molecule and multinuclear complexes but also significantly amplifies their activity via the facile MvK mechanism. The clusters exhibit greater activity than single atoms on the (110), (100), and stepped (111) ceria supports. This work not only offers a promising theoretical blueprint for deciphering reactant-induced highly dispersed catalysts under reaction conditions but also extends its relevance to diverse catalytic systems involving CO as reactants, intermediates, or products.

**COMPUTATIONAL METHODS**

Spin-polarized DFT calculations were performed using the Vienna Ab initio Simulation Package code (VASP). The projector augmented wave potentials and revised Perdew–Burke–Ernzerhof (RPBE) functional were used to describe the electron–ion and exchange–correlation interactions. The DFT + U approach was adopted to describe strongly correlated cerium 4f states in partially reduced ceria. In our DFT calculations utilizing the RPBE, PBE, and PBE + vdW functionals, we set the U value specifically at 5 eV. The plane-wave cutoff energy was set to 300 eV for the genetic algorithm (GA), GCMC, and AIMD simulations. Geometry optimization was used to converge when the forces on each atom were less than 0.10 eV/Å to accelerate the GA-driven GCMC simulations.

A p(4 × 4) slab including two O–Ce–O atomic layers was used to model the CeO$_2$(111), (110), (100), and (111) step surfaces, where the top O–Ce–O atomic layers in the supercell, the adsorbed Pt species and adsorbates, were fully relaxed for all the DFT calculations. This choice was based on findings that extending the CeO$_2$(111) slab model to encompass three O–Ce–O layers resulted in negligible changes—less than 0.2 eV—in oxygen vacancy formation energy, Pt$_1$ adsorption energy and CO adsorption energy on Pt$_1$/CeO$_2$ and the formation energy of Pt$_8$ supported on CeO$_{2-x}$(111). We depicted the polarized CeO$_2$(100) surface as a reconstructed form of CeO$_2$(100) by eliminating half of its surface oxygen atoms, a structure that has been validated by STM characterization. Brillouin zone sampling was restricted to the Γ point. A p(4 × 4) slab with three metal layers was used to model the Pt(111) surface, where the top Pt atom layer and adsorbates were allowed to relax. The Brillouin zone was sampled with a 4 × 4 × 1 Monkhorst-Pack K-point grid for the p(4 × 4) Pt(111) surface. The neighboring slabs were separated by a vacuum of more than 10 Å. The cutoff energy and force convergence criteria were specified as 400 and 0.05 eV/Å, respectively, for the CO oxidation mechanism studies.

The transition states involved in CO oxidation were located by the climbing-image nudged elastic band method with a force tolerance of 0.05 eV/Å. The vibrational frequencies and corresponding modes were calculated to verify the identified transition states.

The electronic energy of the O$_2$ molecule was calculated by placing the O$_2$ gas molecules in a vacuum box with lattice constants of $a = 10$ Å, $b = 11$ Å, and $c = 12$ Å using the tetrahedron method with Blöchl corrections. The presence of a CO atmosphere has a significant influence on the stability of the Pt$_1$/CeO$_2$ catalyst, which can be quantified by the standard Gibbs formation energy relative to Pt nanoparticles as follows

$$ G_f = E_{Pt/CeO_2} - E_{Pt} - E_{CeO_2} - E_{NP'} $$.  

Where $E_{Pt/CeO_2}$, $E_{CeO_2}$, and $E_{NP'}$ are the energies of the CO-ligand-decorated Pt single atom over the CeO$_2$ support, the CeO$_2$ surface, a metal atom in Pt nanoparticles, and the Gibbs free energy of gaseous CO, respectively. The total energy of a Pt nanoparticle was calculated by the Gibbs–Thomson equation

$$ E_{NP} = E_{bulk} + \frac{3\Omega y}{R} $$

where $E_{bulk}$, $\Omega$, $y$, and $R$ are the DFT-calculated energy of a particle in the bulk phase, the molar volume of a Pt metal particle, the molar volume of a Pt monolayer, and the surface area of the particle, respectively.
atom, the overall surface energy of the metal particle, and the radius of the nanoparticle, respectively. The adopted values of $\Omega$ and $\gamma$ are 9.09 cm$^3$/mol and 1.59 J/m$^2$, respectively.\cite{footnote}

AIMD simulations were performed to reveal the dynamic structural evolution of Pt$_x$(CO)$_y$/CeO$_{2-x}$ and Pt$_x$(CO)/CeO$_{2-x}$ under a CO atmosphere by using the LASP code.\cite{footnote}

The Nose–Hoover thermostat\cite{footnote} was used for NVT ensemble sampling at three temperatures—273, 323, and 373 K—for 3 ps AIMD simulations. Umbrella sampling methods were employed to accelerate this process and accurately calculate the energy barriers for structural transformations. The MD time step was set to 1 fs.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/10.1021/acscatal.3c05590.

(MP4)

Detailed methodology, DFT calculation structures, potential energy surface, phase diagram, microkinetic simulation results, and calculated energetics (DOCX)

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### Author Contributions

C.C. and J.-L.C. contributed equally to this work. J.X.L. and W.X.L. conceived the idea and supervised and directed the project. C.C., C.J.L., F.L., and J.H. performed the theoretical calculations and analyzed the DFT data. All the authors discussed the results and wrote and commented on the paper.

### Notes

The authors declare no competing financial interest.

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typically accomplish this and improve the selectivity. 


