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A Linear Scaling Relation for CO Oxidation on CeO$_2$-Supported Pd

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ABSTRACT: Resolving the structure and composition of supported nanoparticles under reaction conditions remains a challenge in heterogeneous catalysis. Advanced configurational sampling methods at the density functional theory level are used to identify stable structures of a Pd$_8$ cluster on ceria (CeO$_2$) in the absence and presence of O$_2$. A Monte Carlo method in the Gibbs ensemble predicts Pd-oxide particles to be stable on CeO$_2$ during CO oxidation. Computed potential energy diagrams for CO oxidation reaction cycles are used as input for microkinetics simulations. Pd-oxide exhibits a much higher CO oxidation activity than metallic Pd on CeO$_2$. This work presents for the first time a scaling relation for a CeO$_2$-supported metal nanoparticle catalyst in CO oxidation: a higher oxidation degree of the Pd cluster weakens CO binding and facilitates the rate-determining CO oxidation step with a ceria O atom. Our approach provides a new strategy to model supported nanoparticle catalysts.

INTRODUCTION

Supported nanoparticle catalysts, which are pivotal to many chemical processes, can be optimized by tuning the interface of the nanoparticles with oxide supports. 1,2 The interface depends on the shape and composition of the nanoparticles, which is influenced by adsorbates leading to promotion of the catalytic performance or deactivation. For instance, nanoparticles are prone to partial or complete transformation to corresponding oxide structures for CO oxidation than the corresponding metallic surfaces. There is also growing evidence that the surface of supported precious group metals nanoparticle catalysts is oxidized during CO oxidation. 3,4 Despite widespread research on controlling the morphology and composition of nanoparticles, 9,10 we lack molecular understanding of the evolution of the active phase during the ongoing catalytic reaction. Experimentally, the relatively small amount of precious group metals used in environmental catalysts presents a considerable challenge in determining the active phase composition and structure during CO oxidation. 11–15 Nanoparticle-support interactions further complicate the understanding of the relation between size, shape and composition of nanoparticles and catalytic performance. A suitable model for supported nanoparticle catalysts in which metal–support interfaces play a role is ceria-supported palladium. Pd/CeO$_2$ has attracted widespread attention due to its excellent catalytic performance in combustion processes. 14

Pd is nowadays a common ingredient of three-way catalyst (TWC) convertor technology, mainly because of its relatively low cost and excellent low-temperature CO oxidation performance. 5 The high catalytic performance is usually understood in terms of strong metal–support interactions (SMSI), 6 which maintain a high Pd dispersion. An important property of ceria is its ability to release O atoms, allowing TWCs to retain a good oxidation performance under fuel-rich operating conditions. 16 The oxidation state of the Pd nanoparticles is also affected by these strong particle-support interactions. Consequently, many investigations have attempted to relate low-temperature CO oxidation on Pd/CeO$_2$ to the oxidation state of Pd, the role of ceria O vacancies, and the specific topological features of the Pd-CeO$_2$ interface. 17,19 For instance, there is an ongoing debate regarding whether the active phase in Pd/CeO$_2$ is oxidic. 17 The view that both metallic and oxidic Pd contribute to the activity suggests that a thin oxide overlayer on small Pd nanoparticles may be important. 20

Density functional theory (DFT) has become a powerful tool to predict the rates of elementary reaction steps. 21 By correlating surface topology and catalytic performance, computational chemistry contributes to the design of new and improved catalysts. 22–28 Detailed knowledge of the structure of the catalytically active phase is essential for meaningful modeling of surface kinetics. The structure of CeO$_2$-supported transition metals during CO oxidation has not been unequivocally determined, which explains the variety of surface models employed in computational modeling of these catalysts. 33–45 The majority of such studies employ a small

Supporting Information

CO oxidation activity

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metallic cluster (e.g., Pt, Pd, Au) placed on an oxide support (e.g., CeO2, TiO2) as the model of the active phase. A more involved method for determining the exposed surfaces of catalytically active phases involves coupling DFT modeling with ab initio atomistic thermodynamics.44,45 This approach is especially suitable for extended surfaces encountered in single crystal studies44 or (large) Wulff-type nanoparticles.46 However, the selection of candidate structures for small supported clusters or nanoparticles placed on a support, which lack well-defined facets, is not straightforward. Then, manually generating a sufficient number of potential configurations becomes intractable. Accordingly, more systematic configurational sampling algorithms such as evolutionary algorithms, basin hopping and molecular dynamic simulations are required. A standard evolutionary algorithm for efficiently identifying the global minimum energy structure of particles was presented by Deaven and Ho.47 In practice, the particle is in contact with a gaseous atmosphere, which may change its chemical composition. The latter can be taken into account by grand-canonical Monte Carlo (GCMC) insertion and deletion of atoms in a basin-hopping approach.48 Janik and co-workers used this method to study the active phase of Pd/ CeO2 for CH4 activation.49 These authors predicted an Pd-oxide structure for a ceria-support Pd cluster exposed to O2 by combining a GCMC approach with a reactive force field (ReaxFF). Drawbacks of using reactive force fields is that these are less accurate and cannot describe the transfer of electrons between the active phase and a reducible support like CeO2.49

In the present study, we employed a genetic algorithm (GA) according to the Deaven–Ho scheme to identify the minimum energy structure of a Pd8 cluster on CeO2(111), the most stable surface termination of ceria, at the DFT level (GA-DFT). We compared a stoichiometric and a defective CeO2 surface with an O vacancy. A basin hopping approach in the Gibbs ensemble (GCMC-DFT) was used to optimize the structure of the Pd8/CeO2(111), the most stable surface termination of ceria, at the DFT level (GA-DFT). We compared a stoichiometric and a defective CeO2 surface with an O vacancy. A basin hopping approach in the Gibbs ensemble (GCMC-DFT) was used to optimize the structure of the Pd8/CeO2(111) system in equilibrium with a gaseous O2 atmosphere. This simulation is connected to experiment by an equation of state that relates the chemical potential of O2 to temperature and pressure. In this way, we confirmed the oxidation of Pd during CO oxidation. For three DFT-GA-optimized Pd8/CeO2 as well as two GCMC-DFT optimized Pd8O-x/CeO2(111) structures, we then computed the kinetic barriers for all relevant steps involved in CO oxidation at the Pd-CeO2 interface. Microkinetics simulations demonstrate that the fully oxidized Pd8 catalyst has the highest activity in CO oxidation. The catalytic performance is strongly correlated to the binding strength of CO to the active Pd phase and first scaling law for a supported nanoparticle catalyst is presented. This work presents an advanced approach for determining the active phase structure and composition under practical reaction conditions, which we expect to become a standard given the rapid advances in computational power.

## RESULTS AND DISCUSSION

### Optimal Pd8/ CeO2 Structure.

To identify the minimum energy structure of a Pd8 particle on CeO2, we used a genetic algorithm at the DFT-GGA-PBE level. The fitness function is the minimization of the electronic energy. This implies that we neglect the contribution of the configurational entropy of the solid as a first approximation.56 The GA approach typically uses Lennard-Jones or other potentials to compute the energy.57,58 DFT has also been used, mostly for determining the optimal structure of unsupported metal clusters.59 The actual choice for Pd8 is a pragmatic one based on selecting a system with a large enough Pd cluster that resembles the structure of a Pd nanoparticle and small enough to be computationally tractable. Also, experiments have shown that Au8 and Pd8 clusters can be synthesized on MgO and Al2O3, respectively, displaying high activity in low-temperature CO oxidation and oxidative dehydrogenation of propane.60,61 The surface model consisted of a Pd8 cluster placed on the stoichiometric CeO2(111) surface (Pd8/CeO2) and a defective CeO2(111) surface, which contains one O vacancy (Pd8/CeO2-x). We also optimized the structure of a free Pd8 cluster. The structures of the six lowest-energy isomers are presented in Figure S1. Figure 1a shows that the lowest energy structure of the free Pd8 cluster has a bicapped octahedral geometry with D2d symmetry. The surface Pd atoms of this cluster have coordination numbers of 4 and 5, which is consistent with the structure of gas-phase clusters.62

The same method was used to obtain the minimum-energy structures of Pd8/CeO2 (Figure 1b) and Pd8/CeO2-x (Figure 1c). A comparison to the optimized Pd8 cluster shows that the Pd-CeO2 interactions result in a completely different structure.
On CeO₂, the cluster adopts a bilayer structure and retains the bulk FCC-Pd structure in the first three coordination shells as follows from inspection of the radial distribution functions (Figure S2). Bilayer structures have been frequently observed for supported nanoparticles, e.g., Au/TiO₂, Pd/MgO, and Cu/ZnO.⁶⁰⁻⁶⁵ For Pd₈/CeO₂, the topmost Pd layer comprises three Pd atoms, while the remaining five Pd atoms interact with five ceria oxygen atoms. In these calculations, we assumed that the support does not change its shape. We explored the impact of an O vacancy in the CeO₂(111) surface. The Pd₈ particle will then preferentially locate on this defect and adopt a slightly different geometry compared to Pd₈/CeO₂. For the sake of comparison, we also selected from the pool of optimized Pd₈/CeO₂ₓ configurations a less stable structure, Pd₈/CeO₂₋ₓ (ΔE = +0.21 eV, Figure 1d), in which Pd₈ has the same structure as in the global minimum structure of Pd₈/CeO₂. Analysis of the electronic structure, which is possible because of the use of the DFT+U method ensuring proper localization of excess electrons in Ce-4f orbitals, shows that one Ce³⁺ ion is generated in Pd₈/CeO₂. A Bader charge analysis estimates the charge on Pd₈ + 0.57e (Figure S3). For Pd₈/CeO₂₋ₓ, the CeO₂ surface contains two additional Ce³⁺ ions and the charge on Pd₈ is +0.40e. The slightly less stable Pd₈/CeO₂₋ₓ structure also contains three Ce³⁺ ions and the charge on Pd₈ is +0.29e. These charge differences are qualitatively consistent with an earlier computational study of Au/CeO₂.³⁶ The three Ce³⁺ ions are located close to the cluster due to the choice of a 3 × 3 surface unit cell.³⁷,³⁸ These results demonstrate that the presence of an O vacancy has a strong impact on the structure of the supported metal cluster and the charge transfer from the particle to the ceria support.

We used a GCMC approach to also take into account possible compositional changes of Pd₈/CeO₂ due to contact with gaseous O₂. In our GCMC-DFT approach, we accept trial moves (insertion, deletion, translation) on the basis of the Metropolis algorithm in which we use the Gibbs free energy

![Figure 1](image1.png)

Figure 1. Structures of Pd₈ and CeO₂ supported Pd₈ and Pd₈Oₓ nanoparticles. (a–c) Optimized structure of Pd₈ as a free particle, and on the stoichiometric and defective ceria surfaces (optimized by GA-DFT). (d) Metastable structure of Pd₈ on the defective ceria. (e,f) Structures of Pd₈Oₓ/CeO₂ (x = 12 and 6) obtained by GCMC-DFT at 300 K with oxygen atmospheres of 1 atm and 10⁻²⁰ atm, respectively. Color coding: cyan, red, white, and small yellow spheres represent Pd, O, Ce⁴⁺, and Ce³⁺ atoms, respectively; the purple spheres in defective ceria represent Ce³⁺ atoms adjacent to O vacancy sites. This notation is used throughout this paper.

![Figure 2](image2.png)

Figure 2. Scheme of CO oxidation mechanism and computed potential energy surfaces for CO oxidation. (a) Scheme for CO oxidation without O₂ dissociation and (b) scheme for CO oxidation via O₂ dissociation at the interface of CeO₂ supported Pd nanoparticles. (c–e) Potential energy diagrams for CO oxidation without O₂ dissociation mechanism. (d–f) Potential energy diagrams for CO oxidation via O₂ dissociation on Pd₈, CeO₂ supported Pd₈, and Pd₈Oₓ nanoparticles. The elementary reaction barriers are given in eV.
μ(T, P) of existing and trial configurations. μ(T, P) is evaluated by considering the electronic energy of the solid and the Gibbs free energy of the gaseous O2 reservoir at (T, P) using data from thermodynamic tables. In 1 atm O2 and at 300 K, CeO2-supported Pd8 will be oxidized to Pd8O12 (Figure 1e). The radial distribution function of the Pd8O12/CeO2 structure in Figure S2 clearly shows that all Pd atoms are oxidized in line with a previous computational work demonstrating deep oxidation of a Pd7 cluster supported on CeO2 exposed to O2. Each Pd atom coordinates to four O atoms. At a low O2 pressure of 10−20 atm, the most stable state is Pd8O6 (Figure 1f), in which O atoms adsorb on the Pd8 surface in 3-fold and bridge sites. Some Pd−Pd bonds are retained and the Pd−O coordination number varies between 1 and 4. We also verified that GCMC-DFT will lead to rapid healing of O vacancies created in the CeO2 surface when it is exposed to O2. In this work, we did not investigate the disintegration of Pd clusters, which is known to occur at very high temperature in an O2 atmosphere.

**CO Oxidation.** In order to determine the CO oxidation activity of the optimized structures, we explored the well-accepted Mars-van Krevelen mechanism for the oxidation of CO at the Pd-CeO2 interface (Figure 2). The O atoms of the ceria are involved in CO oxidation, which will result in ceria O vacancies close to the Pd cluster. Two different reaction pathways were explored. In the first one, adsorption of molecular O2 on a ceria O vacancy precedes reaction with CO adsorbed on the nanoparticle to generate CO2 (CO_Pd + O2_Ceria → CO2 + O_Ceria). This step heals the ceria O vacancy and the catalytic cycle is closed by reaction of adsorbed CO with a ceria O atom (Figure 2a). The alternative scenario is that molecular O2 adsorbed on the O vacancy first dissociates at the Pd-CeO2 interface, resulting in healing of the ceria O vacancy and migration of the other O atom to the Pd8 nanoparticle. Both O atoms are then removed by CO in two reaction steps.
(Figure 2b). The computed potential energy diagrams and corresponding transition state configurations are presented in Figure 2 and Figure 3, respectively. A complete overview of the configurations involved in CO oxidation on the six considered structures is given in the Figure S8–S19.

We start the discussion of the catalytic cycle from the state in which the ceria surface contains an O vacancy. Figure 2c shows that O₂ adsorption is strongest at the O vacancy of Pd₈/CeO₂ (E_ads = −1.95 eV). O₂ adsorbs weaker on the defective Pd₈/CeO₂₋ₓ and Pd₈/CeO₂₋ₓ₋ₓ structures. The O₂ adsorption energy is lowest for Pd₈ (E_ads = −1.37 eV). After O₂ adsorption on the O vacancy site in ceria, the CO adsorption energy shows an opposite trend: Pd₈ (−2.01 eV) > Pd₈/CeO₂₋ₓ (−1.73 eV) > Pd₈/CeO₂₋ₓ₋ₓ (−1.63 eV) > Pd₈/CeO₂ (−1.53 eV) > Pd₈O₁₂/CeO₂ (−1.26 eV) > Pd₈O₁₂/CeO₂ (−0.88 eV). The variation of the CO adsorption energy of the reduced Pd₈ clusters correlates strongly with the positive charge on Pd₈.

Oxidation of Pd₈ results in weaker CO adsorption. The strong dependence of CO and O₂ adsorption energies on the structure and composition of Pd₈/CeO₂ has a profound impact on the kinetics of CO oxidation. The overall activation barrier for CO oxidation without O₂ dissociation on the free Pd₈ nanoparticle is 1.73 eV. We considered two steps for this structure: COₙ + O_ads → CO₂ + O_ads (E_act = 1.73 eV) and COₙ + O_ads → CO₂ (E_act = 1.45 eV). For the pathway involving only atomic O₂ dissociation must also be considered (E_act = 0.99 eV). Accordingly, the reaction cycle will proceed according to the textbook Langmuir–Hinshelwood mechanism for CO oxidation on metal surfaces, involving O₂ dissociation and CO+O reaction events. Under typical reaction conditions, the metallic surface will be poisoned by CO and high overall reaction barriers are predicted, which will result in low catalytic performance. In a similar manner, the Pd₈ cluster placed on CeO₂ will be covered mainly by CO as it binding strength is 1.19 eV higher than that of O₂. Therefore, the contribution of CO oxidation pathways occurring exclusively on the Pd₈ particles can be neglected.

For CO oxidation at the Pd cluster-CeO₂ interface, the activation barrier for the COₙ + O_Ceria → CO₂ + O_Ceria step is within the 1.13–1.28 eV range. The COₙ + O_Ceria → CO₂ reactions have slightly higher barriers in the range 1.36–1.53 eV. O₂ dissociation at the Pd–CeO₂ interface is facile for all three supported Pd₈ nanoparticles (E_act < 0.50 eV). The COₙ + O_Pd → CO₂ reaction has barriers of 0.80, 0.96, and 1.0 eV for Pd₈/CeO₂, Pd₈/CeO₂₋ₓ, and Pd₈/CeO₂₋ₓ₋ₓ, respectively. These differences correspond well with the differences in CO adsorption strength. Figure 2c and Figure 2d show that the dissociative mechanism should be easier than the associative mechanism. The most difficult step is the removal of the ceria surface O atom and the overall barrier for this is lowest for the defective ceria surface.

CO oxidation on Pd₈O₁₂/CeO₂ and Pd₈O₁₂/CeO₂ is much easier. As illustrated in Figure 2e, the activation barrier for COₙ + O_Ceria → CO₂ + O_Ceria is reduced from 1.22 eV for Pd₈/CeO₂ to 0.20 eV for Pd₈O₁₂/CeO₂. The barriers for O₂ dissociation and CO₂ formation are below 0.10 eV. The latter step is easier because of the weak binding of CO and O. Regenerating the O vacancy via COₙ + O_Ceria → CO₂ remains the most difficult step and involves a barrier of 1.36 eV on Pd₈O₁₂/CeO₂. The dissociative mechanism is preferred for Pd₈O₁₂/CeO₂. For Pd₈O₁₂/CeO₂ the dissociative pathway is also slightly preferred over the associative mechanism. The most difficult steps are the removal of an O atom from the Pd₈O₁₂ surface and the formation of an O vacancy with activation barriers of 0.87 and 0.83 eV, respectively. The relatively low activation barrier for O removal from Pd₈O₁₂/CeO₂ arises from weaker CO adsorption (Figure 2).

Microkinetics Simulations. CO oxidation reaction rates are predicted by microkinetics simulations based on the above potential energy diagrams. The migration of O atoms from the CeO₂ surface to the PdO₂ cluster was taken into account based on calculated reaction barriers, which are shown in Table S2. The resulting kinetic data are plotted as Arrhenius curves in Figure 4. Clearly, the active sites at the Pd-CeO₂ interface show a much higher CO oxidation rate than the surface of the free Pd₈ cluster. The apparent activation energy for the free Pd₈ cluster is 2.53 eV, while those for the supported reduced clusters are much lower, i.e., between 1.34 and 1.51 eV. Importantly, the presence of a defect in the CeO₂ surface results in a nearly 2 orders of magnitude higher activity than obtained for the defect-free CeO₂ surface. Pd₈O₁₂/CeO₂ and Pd₈O₁₂/CeO₂ exhibit the highest CO oxidation activities. The fully oxidized cluster has the highest activity with a lowest apparent activation energy of 0.90 eV. Figure 4 also illustrates that the CO oxidation rate of Pd₈O₁₂/CeO₂ declines above 400 K, which is due to a decreased CO coverage as we will discuss below. A key finding from the combined GA/GCMC-DFT and microkinetics modeling is that CeO₂-supported Pd clusters are oxidized in an O₂ atmosphere and the resulting Pd-oxide structures exhibit a much higher CO oxidation activity than metallic Pd clusters on CeO₂. These findings confirm earlier experimental suggestions that highly dispersed Pd-oxide on CeO₂ is the active phase for CO oxidation. A comparison of computed TOFs (turnover frequencies) for various Pd₈O₁₂/CeO₂ structures with experimentally reported TOF values further confirms that oxidized Pd on CeO₂ is the most likely active state in Pd/CeO₂ catalysts.

In order to gain a deeper insight into the underlying kinetics, we analyzed the surface coverages and degrees of rate control (DRC) as a function of temperature. Figure S4a shows that CO poisons the pure Pd₈ cluster, which explains the high apparent activation energy. At low reaction temperature, the
Pd-surface of the three reduced Pd/CeO₂ catalysts will also be mainly covered by CO. As CO adsorbs weakest on Pd/CeO₂, it is observed that CO coverage starts to decrease at a relatively low temperature. Under steady-state conditions, the concentration of ceria O vacancies is low, because the reaction between COPd and Oceria controls the reaction rate. The kinetics for Pd₈O₆/CeO₂ and Pd₈O₁₂/CeO₂ are very similar: the oxidized Pd clusters is mostly covered by CO and the removal of Oceria is the rate-controlling step. However, as CO adsorbs much weaker on the oxidized structures, CO coverage will decrease at relatively low temperature. Since, under relevant conditions, the reaction between CO and Oceria will still control the overall reaction rate, the decreased CO coverage is the primary cause of the lower activity.

We find that the migration of an O atom from the ceria to the Pd₈O₆ cluster becomes rate-controlling at temperatures higher than 650 K only for Pd₈O₆/CeO₂. We then set out to determine how interactions of a Pd₈ particle with CeO₂ and O₂ impact the active phase structure and composition and, consequently, CO oxidation activity. Under catalytic conditions, Pd will be oxidized, either to a Pd-oxide surface overlayer or, for small clusters, Pd-oxide. Figure 5 shows that the activation barrier for the rate-controlling oxidation step of adsorbed CO with a ceria O atom strongly correlates with the CO and O binding energies. The negative slope indicates that weaker CO and O adsorption facilitate the association step. The adsorption energies of CO and O on Pd₈Oₓ (x = 0, 6, and 12) and CeO₂ surfaces are shown in Table S1. The O vacancy formation energies vary only slightly among the optimized structures, implying that the O binding strength is less sensitive to structure and composition than the CO binding strength. Therefore, we can draw the important conclusion that the CO oxidation rate mainly depends on the binding strength of CO with Pd. The correlations in Figure 5 constitute a first example of a scaling relation for supported metal nanoparticles, similar to scaling laws that have already proven their use in predicting periodic trends in metal nanoparticle catalysis. Given that in this particular case the final state is CO₂ in the gas phase, which has a relatively flat potential with respect to the reaction coordinate, we are able to provide a linear scaling relationship based purely on the adsorption energy rather than on the reaction energy as typically done within a Bronsted−Evans−Polanyi approximation. Under catalytic CO oxidation conditions, also out-of-equilibrium structures may exist and contribute to the catalytic performance. We computed the activation barrier for the rate-controlling step for three of such structures (Figure S6), representing Pd₈Oₓ clusters with a different shape and composition than the most stable ones. The resulting activation barriers are shown in Figure S7 and follow the scaling law in Figure 5. This result strongly underpins the validity of our conclusions and the value of the scaling law presented. Since the CO oxidation activity is largely determined by the barrier of the CO oxidation step, we can in principle determine relative contributions of such less frequently encountered structures to the overall rate.

**CONCLUSION**

In brief, our computational study predicts that oxidation of CeO₂-supported Pd leads to enhanced CO oxidation activity. In an O₂-containing atmosphere, Pd-oxide is more stable than reduced Pd particles. The lower binding energy of CO to Pd-oxide results in a lower barrier for CO₂ formation by association with a ceria O atom, which is the rate-controlling step. The linear dependence between the activation barrier for this CO₂ formation step and the CO binding energy is the first
example of a linear scaling law for a supported metal catalyst in which the reactivity of the metal—support interface features prominently.

**ASSOCIATED CONTENT**

- Supporting Information
  - The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.7b13624.

  Detailed information on GA-DFT, GCMC-DFT, DFT calculations, and microkinetics simulations; Table S1–S7 and Figure S1–S19 (PDF)

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- Notes
  - The authors declare no competing financial interest.

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