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Linear Activation Energy-Reaction Energy Relations for LaBO₃ (B = Mn, Fe, Co, Ni) Supported Single-Atom Platinum Group Metal Catalysts for CO Oxidation

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ABSTRACT: Single-atom catalysts are at the center of attention of the heterogeneous catalysis community because they exhibit unique electronic structures distinct from nanoparticulate forms, resulting in very different catalytic performance combined with increased usage of often costly transition metals. Proper selection of a support that can stably keep the metal in a high dispersion is crucial. Here, we employ spin-polarized density functional theory and microkinetics simulations to identify optimum LaBO₃ (B = Mn, Fe, Co, Ni) supported catalysts dispersing platinum group metals as atoms on their surface. We identify a strong correlation between the CO adsorption energy and the d-band center of the doped metal atom. These CO adsorption strength differences are explained in terms of the electronic structure. In general, Pd-doped surfaces exhibit substantially lower activation barriers for CO₂ formation than the Rh- and Pt-doped surfaces. Strong Brønsted–Evans–Polanyi correlations are found for CO oxidation on these single-atom catalysts, providing a tool to predict promising compositions. Microkinetics simulations show that Pd-doped LaCoO₃ is the most active catalyst for low-temperature CO oxidation. Moderate CO adsorption strength and low reaction barriers explain the high activity of this composition. Our approach provides guidelines for the design of highly active and cost-effective perovskite supported single-atom catalysts.

■ INTRODUCTION

Platinum group metals dispersed on metal oxide supports are quintessential in automotive exhaust control, employing more than half of the annual production of noble metals such as Pt, Pd, and Rh. CO oxidation is a key reaction in this respect and is also regarded as an archetypical model reaction in heterogeneous catalysis. The current generation of automotive three-way catalysts used in gasoline cars is based on Rh and Pt or Pd nanoparticles supported on alumina and ceria-zirconia. The cost of platinum group metals, their relatively low performance during cold start and their tendency to sinter at elevated temperature pose challenges in developing improved catalysts to comply with increasingly stringent environmental legislation related to exhaust gas abatement. Catalytic performance depends strongly on the surface morphology, particle size, and the reducibility of the support. Despite their good performance, the metal atom utilization in these catalysts is rather low because only the exposed surface metal atoms are involved in catalyzing CO oxidation.

To achieve good catalytic performance in combination with the highest possible metal atom utilization efficiency, single-atom catalysts (SACs) have been recently proposed. A key aspect of SACs is the under-coordinated nature of the single metal atom stabilized on typically metal oxide supports. In practice, single atoms anchored to oxide supports are susceptible to sintering. Therefore, there is a need to identify metal-support combinations that allow for stabilization of the metal in atomic form and high activity. In their pioneering work, Qiao et al. reported a stable anchored single Pt atom on Fe-oxide with excellent performance of CO oxidation. A very recent study indicated that activation of the surface oxygen species of ceria-supported Pt single atom catalysts can drastically improve the CO conversion rate at low temperature. Many factors need to be considered when designing highly active SACs, such as the type and oxidation state of the metal atom, and its location on the surface.

As general in heterogeneous catalysis, it would be useful if catalytic properties of candidate SACs could be estimated from simple activity descriptors by theoretical methods. An early study in this direction reported that the CO oxidation activity on transition metal surfaces and clusters correlates well with the adsorption energy of the adsorbate. A recent study reported a linear relation between the transition-state energies and adsorption energy of CO and O₂ reactants. Many computational studies reported the utility of Bronsted–Evans–Polanyi (BEP) relations for various chemical reactions occurring on transition metal surfaces.
as well as transition metal oxide surfaces. However, such correlations have not been explored yet in detail for SACs.

Recently, perovskites have been receiving increased attention in the field of catalysis owing to their remarkable electronic properties, relatively high structural stability and tunability in terms of composition and, therefore, catalytic function. Relevant to the present study, perovskite has been mentioned as a potential material to replace platinum group metals for environmental catalysis. A recent study emphasized the role of single atoms of Pt stabilized on perovskite for catalytic CO oxidation. Among perovskites, LaBO₃ perovskites have received increased attention in the field of catalysis owing to their remarkable electronic properties, relatively high structural stability and tunability in terms of composition and, therefore, catalytic function. In the present study, we systematically investigated the catalytic properties with respect to CO oxidation of a series of single metal (M) atoms (M = Rh, Pd, and Pt) supported by LaBO₃ (B = Mn, Fe, Co, and Ni) using density functional theory (DFT) and microkinetics simulations. We identify a strong correlation between the CO adsorption energy and the d-band center of the doped metal atom and, for the first time, a linear dependence of the activation barrier for CO₂ formation and the reaction enthalpy as a strong BEP relation for SACs. Microkinetics simulations predict that CO oxidation rates are much higher on Pd-doped surfaces than on Rh- or Pt-doped surfaces. In particular, Pd-doped LaCoO₃ exhibits a promising activity for low-temperature CO oxidation. These insights provide guidance in the design of cost-effective and highly active perovskite-based catalysts for oxidation reaction.

## COMPUTATIONAL METHODS

### DFT Calculations

All spin-polarized DFT calculations reported here were carried out using the Vienna Ab Initio Simulation Package (VASP version 5.3.5). The Perdew–Burke–Ernzerhof (PBE) functional was used to account for exchange and correlation effects. A Hubbard-like term, U, describing the on-site Coulombic interactions, was introduced. We employed effective U values of 4.0, 4.0, 3.3, and 6.4 eV for Mn, Fe, Co, and Ni, respectively. These values were taken from previous computational studies, which provided a good description of the electronic structures of the corresponding LaBO₃ perovskites.

The cutoff energy for the plane-wave basis was set at 400 eV. The Gaussian smearing method with a smearing width of 0.05 eV was adopted to determine partial occupancies. VdW interactions were considered via DFT-D3 corrections in all our calculations.

To optimize the lattice constant of bulk LaBO₃, a Pbnm symmetry unit cell was used in the calculations. We first evaluated the influence of different magnetic structures on the total energy and determined that the most stable magnetic structures for LaMnO₃ and LaFeO₃ are of the antiferromagnetic A- and G-type, respectively. Ferromagnetic structures were the most stable ones for bulk LaCoO₃ and LaNiO₃. The optimized lattice parameters are listed in Table S1. For the surface calculations, we constructed a BO₂-terminated LaBO₃(001) slab model, which is known to be a stable and exposed facet of this material in catalytic reactions. Here, we

constructed a 2 × 2 unit cell with the following sizes: 11.29 × 11.12 Å for LaMnO₃, 11.29 × 11.11 Å for LaFeO₃, 10.92 × 10.93 Å for LaCoO₃, and 10.76 × 10.92 Å for LaNiO₃. A six atom-layer slab separated by a 12 Å vacuum was used for all surface calculations. The top four atomic layers were relaxed, and the bottom two layers were fixed. The LaBO₃ (001) slab model contains 24 La atoms, 24 B atoms, and 72 O atoms. A B atom in the surface of these LaBO₃ supercells was replaced by a platinum group metal (Rh, Pd, or Pt). As a consequence, the dopant concentration in the perovskite lattice is 4.2% with respect to the number of B atoms in the unit cell. This computational setup is adequate to avoid interactions between periodic images that would affect the results of the predicted surface catalytic properties involving the single atom dopant and small adsorbates. For the Brillouin zone integration, a Monkhorst–Pack k-point mesh of 1 × 1 × 1 was used. Geometries optimization was achieved until the residual Hellmann–Feynman forces were smaller than 0.05 eV/Å.

In order to explore the reaction mechanism, we calculated the location and total energy of transition states by the climbing-image nudged elastic band (CI-NEB) method. A frequency analysis was done to make sure that each transition state has a single imaginary frequency in the direction of the reaction coordinate (Table S3). Adsortion energies of CO and O₂ are computed by

$$E_{ads} = E_{surf+g} - (E_{surf} + E_{g})$$

where $E_{surf}$ is the total energy of the adsorbed surface, the empty surface, and the corresponding gas phase species, respectively.

The d-band center ($ε_d$) was computed as

$$ε_d = \frac{\int_{-∞}^{0} \rho(ε)de}{\int_{0}^{∞} \rho(ε)de}$$

where $\rho(ε)$ is the partial density of states (PDOS) of the d orbital at a particular energy $ε$. We determined $ε_d$ by integrating $\rho(ε)$ for the dopant from −20 to 5 eV relative to the Fermi level.

### Microkinetics Simulations

Microkinetics simulations were carried out on the basis of the computed energetics for the explored CO oxidation pathways. These were employed to determine the reaction rates and the composition of the adsorbed layer. For surface reactions, the calculated activation barriers were used to estimate the forward and backward rate constant using the Eyring equation

$$k = \frac{k_BT}{h}f^*_e e^{-E_a/k_BT}$$

where $k$ is the reaction rate constant, $k_B$ is the Boltzmann constant, and $h$ is the Planck constant. $T$ is the temperature (in K), and $E_a$ is the activation barrier (in J), $f^*$ and $f$ are the partition functions of the transition state and the ground state, respectively. Here, all vibrational partition functions were assumed to be a unity. This yields a prefactor for all surface elementary reaction steps of $\sim 10^{13}$ s⁻¹.

For the adsorption process, we use the approximation that the molecule loses one of its translational degrees of freedom with respect to the gas phase. Then, the rate for molecular adsorption is given by
\[ k_{\text{ads}} = \frac{PA'}{\sqrt{2\pi nk_bT}}S \]

Here, \( P \) refers to the partial pressure of the reactant in the gas phase, and \( A \) represents the surface area of the adsorption site. \( S \) and \( m \) are the sticking coefficient and the mass of the reactant, respectively. The surface area was set to the area of a square planar doped site, i.e., \( 7.3 \times 10^{-20} \text{ m}^2 \). The sticking coefficients were set to unity in all the simulations.

For product desorption from the surface, we assumed that the activated complex has two translational and three rotational degrees of freedom. Accordingly, the rate for molecular desorption can be defined as \[ k_{\text{des}} = \frac{k_BT^3}{k_B^3} A'(2\pi nk_bT) \]

Here, \( \sigma \) is the symmetry number, \( \theta_{\text{rot}} \) is the characteristic temperature for rotation, and \( E_{\text{des}} \) represents the desorption energy. The symmetry number of CO is 1. The symmetry numbers of \( \mathrm{O}_2 \) and \( \mathrm{CO}_2 \) are 2. The characteristic temperature of rotation for \( \mathrm{CO}, \mathrm{O}_2, \) and \( \mathrm{CO}_2 \) are 2.73, 2.08, and 0.56 K, respectively.

The details of the microkinetics simulations have been described in our previous studies and briefly mention the main aspect of the approach.\(^5,6\) The rate constants of the elementary steps are used to construct the differential equations for all surface reaction intermediates. For each of the \( X \) components involved in the reaction pathway, a single differential equation is defined as

\[ r_i = \sum_{j=1}^{N} k_j \left( \prod_{k=1}^{X} c_k^{\nu_k} \right) \]

Herein \( k_j \) refers to the elementary reaction rate constant, \( \nu_k \) to the stoichiometric coefficient of component \( i \) in elementary reaction step \( k \), and \( c_k \) indicates the concentration of component \( k \) on the reaction surface.

In order to identify the elementary steps that determine the overall reaction rate of the CO oxidation, a degree of rate control (DRC) analysis \(^5\) was implemented. To a specific elementary step \( i \), the DRC coefficient \( \chi_{\text{RC},j} \) is calculated by

\[ \chi_{\text{RC},j} = \frac{k_j \left( \frac{dr}{\partial k_j} \right)_{k_j=K_j} \left( \frac{dl_k}{\partial n_k} \right)_{k_j=K_j}}{r} \]

In eq 7, \( r \) is the overall reaction rate and \( k_j \) and \( K_j \) are the forward rate and the equilibrium constants for step \( i \), respectively. The first-principles-based microkinetics simulations were performed using the in-house-developed MKMCXX program.\(^3\) The overall \( \mathrm{CO}_2 \) formation rate reaction, steady-state coverage, and product distribution were computed as a function of temperature by integrating the ordinary differential equations with respect to time using the backward differentiation formula method.\(^4,5,6\)

**RESULTS AND DISCUSSION**

**CO and \( \mathrm{O}_2 \) Adsorption.** We first investigated the structure and relative stability of M-doped \( \text{LaBO}_3 \) surfaces \((\text{LaBO}_3-\text{M})\). To estimate their relative stability, we computed the exchange energy associated with replacing a B atom in the stoichiometric \( \text{LaBO}_3 \) surface with an M atom compared to bulk B and M (Figure 1). The M-doped \( \text{LaMnO}_3, \text{LaFeO}_3, \text{LaCoO}_3, \) and \( \text{LaNiO}_3 \) surfaces are denoted in the following as \( \text{LaMnO}_3-\text{M}, \text{LaFeO}_3-\text{M}, \text{LaCoO}_3-\text{M}, \) and \( \text{LaNiO}_3-\text{M} \), respectively. From Table S2, it can be seen that the exchange energies for \( \text{LaCoO}_3-\text{M} \) and \( \text{LaNiO}_3-\text{M} \) are smaller than those for \( \text{LaMnO}_3-\text{M} \) and \( \text{LaFeO}_3-\text{M} \). This means that the incorporation of Rh, Pd, and Pt into the surfaces of \( \text{LaCoO}_3 \) and \( \text{LaNiO}_3 \) is more favorable than into those of \( \text{LaMnO}_3 \) and \( \text{LaFeO}_3 \). Previous computational and experimental works studied the stability of transition metal in different layers of \( \text{LaFeO}_3 \) and \( \text{LaMnO}_3 \) and showed that the B site can be substituted by Rh, Pd, and Pt. Among these, Pd surface doping in the first layer of such perovskites surfaces is preferred.\(^5\) We then investigated the adsorption of CO and \( \mathrm{O}_2 \) on the \( \text{LaBO}_3-\text{M} \) surfaces in order to identify structures relevant to CO oxidation. Top coordination of CO on the doped transition metal atoms is preferred in all cases. We also found that CO adsorption on the M atoms at B sites is much stronger than on the other native B sites (Table S4). For Rh, we determined the following CO adsorption energies, i.e., \(-2.49\) eV (\( \text{LaMnO}_3-\text{Rh} \)), \(-2.14\) eV (\( \text{LaFeO}_3-\text{Rh} \)), \(-1.87\) eV (\( \text{LaCoO}_3-\text{Rh} \)), and \(-1.70\) eV (\( \text{LaNiO}_3-\text{Rh} \)). Despite the fact that CO binds strongly to Rh, there is a strong influence of the reactivity of the B substituent on the adsorption strength. When the perovskite lattice contains a more reactive 3d transition metal B ion, the CO binding is stronger. Similar trends are observed for the Pt- and Rh-doped \( \text{LaBO}_3 \) surfaces. On the Pd-containing surfaces, the CO binding strengths are weakest. By comparing the CO adsorption energy for the different Pd-containing models, we find that CO binds with comparable strength to \( \text{LaMnO}_3-\text{Pd} \) (\(-1.19\) eV) and \( \text{LaCoO}_3-\text{Pd} \) (\(-1.22\) eV) as to Pd-doped CeO\(_2\) (\(+1.11\)).

To understand the properties of CO adsorption on \( \text{LaBO}_3-\text{M} \), we analyze the partial density of states (PDOS) of these models. From the PDOS of CO adsorbed on \( \text{LaBO}_3-\text{M} \), we observe that the overlap between CO orbitals and d orbitals of the doped M atoms depend on the M atom (Figure 2 and Figure S1). We find strong correlations between the CO adsorption energy and the integrated crystal orbital Hamiltonian population (ICOHP) between the M atom and C atom (of CO) for the \( \text{LaBO}_3-\text{M} \) models (Figure 3 and Table S6). These correlations indicate that CO binds stronger to Rh and Pt than to Pd. \( \text{LaMnO}_3-\text{Rh} \) exhibits the strongest CO adsorption among the \( \text{LaMnO}_3-\text{M} \) models because the Rh 4d orbitals are less filled than the Pt 5d orbitals of \( \text{LaMnO}_3-\text{Pd} \), which leads to a different ICOHP. Similar to the ICOHP of \( \text{LaMnO}_3-\text{M} \), Rh doping in \( \text{LaFeO}_3, \text{LaCoO}_3, \) and \( \text{LaNiO}_3 \) also results in more negative values than Pt doping.
In order to understand the effect of the support on CO adsorption, we compare the PDOS as well as the d-band center of Pd for different LaBO$_3$-Pd models. We note that the d-band stems from the electronic interaction between the doped atom and perovskite lattice, and there are similarities between our d-band model and the one from Nørskov et al.\textsuperscript{63} To our model, the d-band center reflects the location of the d states of the doped atom relative to the E$_F$. Thus, it is reasonable to introduce this concept to rationalize the properties of CO adsorption on different models. In fact, the combined analysis of the PDOS and the d-band center is widely accepted to understand the relation between catalytic activity and electronic structure.\textsuperscript{64–66} In Figure 4a, we can clearly observe that the Pd 4d states in LaMnO$_3$-Pd and LaCoO$_3$-Pd are shifted to energy positions closer to the Fermi level compared to the corresponding states in LaFeO$_3$-Pd and LaNiO$_3$-Pd. The location of d states closer to the Fermi level provides more empty d orbitals for CO adsorption. This is also in line with the relatively high d-band center of Pd atoms in LaMnO$_3$ and LaCoO$_3$ compared to LaFeO$_3$ and LaNiO$_3$ (Figure 4a and Table 1). It is worth noting that the d-band center reflects the location of the d states of the doped M atom relative to the E$_F$. The closer the d-band center of the dopant is to the E$_F$, the easier electron transfer from d orbitals to CO orbitals will be.

Figure 2. PDOS of doped M atom (M = Pd, Pt, and Rh) and adsorbed CO on (left) LaMnO$_3$-M and (right) LaFeO$_3$-M. The states marked in green, red, and blue are the PDOS of adsorbed CO, the Pd atom of CO adsorbed LaBO$_3$-Pd, and the Pd atom of LaBO$_3$-Pd, respectively.

Figure 3. Correlation between the CO adsorption energy and the average ICOHP value of doped M atom (M = Rh, Pt, and Pd) and C atom in (a) LaMnO$_3$-M, (b) LaFeO$_3$-M, (c) LaCoO$_3$-M, and (b) LaNiO$_3$-M.
and the stronger the bond between M and CO. Interestingly, we find a linear correlation between the d-band center and the CO adsorption energy for these Pd-doped LaBO3 models (Figure 4b). Such a linear relation is also observed for CO adsorption on Rh- and Pt-containing models (Figure 5a,b). The PDOS for these two models are plotted in Figure 5c,d. A clear variation in Rh-occupied states in different LaBO3-Rh models is evident, and the computed d-band center trend of LaMnO3-Rh > LaFeO3-Rh > LaCoO3-Rh > LaNiO3-Rh tracks the trend in CO adsorption energy. A similar trend of the PDOS and d-band center is obtained for LaBO3-Pt as follows from Figure 5b,d. In general, the models with their d-band center shifted to higher energies exhibit a higher CO adsorption strength.

We also performed a Bader charge analysis on these models (Table 2). From the Bader charges for Pd atoms, we determined the amount of electrons transferred from Pd to the support, i.e., 1.41 e (LaMnO3), 1.52 e (LaFeO3), 1.21 e (LaCoO3), and 1.90 e (LaNiO3). Thus, Pd in LaMnO3 and LaCoO3 hold more valence electrons than in LaFeO3 and LaNiO3. It should be noted that CO adsorption on Pd results in a redistribution of the charge. After CO adsorption, the amount of Pd valence electrons are decreased by 0.45, 0.15, 0.64, and 0.05 e in LaMnO3-Pd, LaFeO3-Pd, LaCoO3-Pd, and LaNiO3-Pd, respectively. This means that the Pd atoms in LaMnO3 and LaCoO3 transfer more electrons to the adsorbed CO compared to Pd atoms in LaFeO3 and LaNiO3. This strong back-donation of electrons results in a strong chemical bond between Pd and CO. Moreover, the charge density difference for CO adsorbed on LaBO3-Pd surfaces (Figure 4c) confirms that the Pd atoms lose more electrons in LaMnO3-Pd than in LaFeO3-Pd and LaNiO3-Pd upon CO adsorption. For the charge distribution in Rh- and Pt-containing models (Table 2), there are apparently less valence electrons on doped Rh or Pt than on Pd, which is consistent with the higher amount of unoccupied d states of Rh and Pt. The stronger CO adsorption on LaBO3-Rh and LaBO3-Pt can be ascribed to the enhanced donation of CO electron density into the less occupied Rh or Pt d orbitals. The increased electron donation is reflected by the accumulation of electrons between CO and Rh or Pt, as shown in Figure S2.

In the catalytic reaction mechanism to be discussed below, adsorbed CO reacts with a surface lattice O atom to produce CO2. This constitutes a Mars-van Krevelen (M-vK) mechanism. Molecular oxygen will then bind on the formed surface oxygen vacancy. The O2 adsorption energies on the vacancy sites of LaMnO3-Rh, LaMnO3-Pd, and LaMnO3-Pt are −1.56 eV, −1.10 eV, and −0.46 eV, respectively. The strength of O2 adsorption is strongly associated with the surface O vacancy formation energies, as follows from the calculated surface O vacancy formation energies for LaMnO3-Rh (2.02 eV), LaMnO3-Pd (1.67 eV), and LaMnO3-Pt (0.84 eV). For O2 adsorption on LaFeO3-M, we determined the following adsorption energies: −2.09 eV (LaFeO3-Rh), −1.53 eV (LaFeO3-Pd), and −2.17 eV (LaFeO3-Pt). The surface O vacancy formation energies for LaFeO3-Rh, LaFeO3-Pd, and

![Figure 4.](image)

**(a)** PDOS of adsorbed CO and doped Pd in LaBO3-Pd (B = Mn, Fe, Co, Ni). The states marked in green, red, and blue are PDOS of adsorbed CO, Pd atom of CO adsorbed LaBO3-Pd, and Pd atom of LaBO3-Pd, respectively. The blue line refers to the d-band center of the Pd atom of LaBO3-Pd. (b) A linear relation between the CO adsorption energy and the d-band center of the Pd atom on the corresponding surfaces. (c) Charge density difference between LaBO3-Pd surfaces after and before CO adsorption (charge density isosurface 0.07 e/Å3). Yellow: increase of electron density. Blue: decrease of electron density.

**Table 1. Calculated d-Band Center (eV) for the Different Surface Models (M = Rh, Pd, and Pt)**

| Model   | LaMnO3-M | LaFeO3-M | LaCoO3-M | LaNiO3-M |
|---------|----------|----------|----------|----------|
| Rh      | −0.48    | −0.82    | −2.35    | −3.07    |
| Pd      | −1.86    | −3.56    | −2.05    | −3.15    |
| Pt      | −0.65    | −2.58    | −2.65    | −3.26    |
LaFeO₃-Pt are 2.42, 2.28, and 2.47 eV, respectively, in line with the trend of O₂ adsorption energies. In comparison with LaMnO₃-M and LaFeO₃-M models, LaCoO₃-M and LaNiO₃-M models exhibit relatively weak O₂ adsorption. This can be ascribed to the lower surface O vacancy formation energies for the latter surfaces.

**CO Oxidation.** We first established that coadsorption of CO and O₂ on the stoichiometric LaBO₃-M surfaces is unfavorable. Accordingly, a Langmuir–Hinshelwood reaction mechanism for CO oxidation is not likely for our models. As experimental work has shown that the oxygen species of perovskite participates in O₂ formation,⁶⁷ we considered CO oxidation involving a surface lattice O atom. The reaction starts with CO adsorption followed by migration of CO to allow CO₂ formation. Subsequently, CO₂ desorbs from the surface, resulting in an oxygen vacancy. Molecular oxygen can then adsorb on this vacancy, followed by adsorption of another CO on the M atom. This CO adsorbate migrates to the adsorbed O₂ to form CO₂ via a transition state in which the oxygen–oxygen bond of adsorbed O₂ is further elongated. Afterward, the second CO₂ molecule is spontaneously released from the surface.

We systematically examined CO oxidation on Rh-, Pd-, and Pt-doped LaBO₃ systems, involving in total 12 reaction cycles for CO oxidation. The reaction pathways for the CO oxidation on these surfaces are displayed in Figure 6. For the M-doped LaMnO₃ surfaces, the barriers of adsorbed CO reaction with a lattice O to form CO₂ are 0.88 eV (Rh), 0.52 eV (Pd), and 0.81 eV (Pt). Not surprisingly, this reaction step encounters its lowest barrier on LaMnO₃-Pd because of a relatively weak CO adsorption on the Pd atom, as shown in Figure 7a. For LaMnO₃-Rh, CO₂ desorption is more difficult than for LaMnO₃-Pd and LaMnO₃-Pt. This can be ascribed to the relatively higher surface oxygen vacancy formation energy (Eᵥₒ) for LaMnO₃-Rh (2.02 eV) compared to LaMnO₃-Pd (1.67 eV) and LaMnO₃-Pt (0.84 eV). After CO₂ desorption, a surface O vacancy is created, which is filled by O₂ adsorption. Here, the most stable configuration for O₂ adsorption is the one in which one of the O atoms fills the vacancy and the other

**Table 2. Bader Charge (|e|) of M Atoms in Different Surface Models**

| model     | LaMnO₃-M | LaFeO₃-M | LaCoO₃-M | LaNiO₃-M |
|-----------|----------|----------|----------|----------|
| Rh        | 1.75 (1.93) | 1.78 (1.94) | 1.92 (2.01) | 1.90 (2.16) |
| Pd        | 1.41 (1.86) | 1.52 (1.67) | 1.21 (1.85) | 1.90 (1.95) |
| Pt        | 1.83 (2.43) | 1.94 (2.42) | 2.05 (2.45) | 2.44 (2.58) |

Values in parentheses are the corresponding charges of the M atoms after CO adsorption.
is coordinating to the doped M atom, see Figure 6. The resulting surface O species will readily react with adsorbed CO with low barriers on LaMnO$_3$-Pd (0.47 eV), LaMnO$_3$-Pt (0.67 eV), and LaMnO$_3$-Rh (0.72 eV). Subsequently, CO$_2$ desorbs from the surface and completes the reaction cycle.

For LaFeO$_3$-M surfaces, the adsorbed CO reacts with lattice O to form the first CO$_2$ product molecule in the cycle with relatively high barriers on LaFeO$_3$-Rh (1.38 eV) and LaFeO$_3$-Pt (0.94 eV) in contrast to LaFeO$_3$-Pd (0.48 eV). The potential energy diagram in Figure 7b shows that CO$_2$ desorption on LaFeO$_3$-Pt and LaFeO$_3$-Rh is more difficult than on LaFeO$_3$-Pd. This is also in line with the lower $E_{02}$ values for LaFeO$_3$-Pd (2.28 eV) than for LaFeO$_3$-Pt (2.47 eV) and LaFeO$_3$-Rh (2.42 eV). After adsorption of O$_2$ and CO, the following CO$_2$ formation step on LaFeO$_3$-Pd only needs to overcome a barrier of 0.58 eV, substantially lower than the barrier for LaFeO$_3$-Rh (2.33 eV) and LaFeO$_3$-Pt (2.22 eV).

The CO oxidation potential energy diagrams for the LaCoO$_3$-M surfaces indicate that the first CO$_2$ formation step on LaCoO$_3$-Pd is very favorable with an activation barrier of 0.41 eV (Figure 7c). This barrier is much lower than for the other dopants, i.e., LaCoO$_3$-Rh (1.16 eV) and LaCoO$_3$-Pt (1.01 eV). The energies of CO$_2$ desorption on LaCoO$_3$-Pd (0.85 eV) and LaCoO$_3$-Pt (0.58 eV) are both higher than the value of 0.26 eV for LaCoO$_3$-Pd. This is in line with the fact that Pd doping only slightly increases $E_{02}$ by 0.05 eV, while it is increased by 0.70 and 0.81 eV upon Rh and Pt doping. The barriers for the second CO$_2$ formation step on the LaCoO$_3$-Pd (0.49 eV) are lower than on LaCoO$_3$-Rh (2.02 eV) and LaCoO$_3$-Pt (1.43 eV). The increasing barriers for Pt- and Rh-doped LaCoO$_3$ surfaces are closely associated with their $E_{02}$.

The CO oxidation potential energy diagrams for the LaNiO$_3$-M surfaces indicate that the first CO$_2$ formation step on LaNiO$_3$-Pd is very favorable with an activation barrier of 0.41 eV (Figure 7d). This barrier is much lower than for the other dopants, i.e., LaNiO$_3$-Rh (1.16 eV) and LaNiO$_3$-Pt (1.01 eV). The energies of CO$_2$ desorption on LaNiO$_3$-Pd (0.85 eV) and LaNiO$_3$-Pt (0.58 eV) are both higher than the value of 0.26 eV for LaNiO$_3$-Pd. This is in line with the fact that Pd doping only slightly increases $E_{02}$ by 0.05 eV, while it is increased by 0.70 and 0.81 eV upon Rh and Pt doping. The barriers for the second CO$_2$ formation step on the LaNiO$_3$-Pd (0.49 eV) are lower than on LaNiO$_3$-Rh (2.02 eV) and LaNiO$_3$-Pt (1.43 eV). The increasing barriers for Pt- and Rh-doped LaNiO$_3$ surfaces are closely associated with their $E_{02}$.
general, a lower $E_{\text{ad}}$ favors the migration of O species, resulting in a lower barrier for CO$_2$ formation. For CO oxidation on LaNiO$_3$-M surfaces, the activation barriers for the first CO$_2$ formation step are 0.61, 0.54, and 0.74 eV for LaNiO$_3$-Rh, LaNiO$_3$-Pd, and LaNiO$_3$-Pt, respectively (Figure 7d). CO$_2$ desorption is not difficult, which is in line with the relatively low surface O vacancy formation energies for LaNiO$_3$-Rh (1.32 eV), LaNiO$_3$-Pd (1.60 eV), and LaNiO$_3$-Pt (1.1 eV). The second CO$_2$ formation step on the LaNiO$_3$-M surface is favorable because this process is highly exothermic with very low barriers for LaNiO$_3$-Pd (0.24 eV), LaNiO$_3$-Pt (0.34 eV), and LaNiO$_3$-Rh (0.52 eV).

Brønsted–Evans–Polanyi Relations. It has been reported that activation barriers of molecular dissociation on transition metal surfaces are linearly correlated with corresponding reaction energies. Such scaling relations are rooted in Hammond’s postulate, which states that the transition state of an (organic) reaction resembles either the reactant or product state. In our study, we further analyzed the relationship between these parameters for CO oxidation on LaBO$_3$-M systems. The strong correlations identified between the activation barriers and reaction energies for CO oxidation on these models show that the BEP principle holds for CO oxidation on perovskite-supported single-atom catalysts. For the fitted dependency in Figure 8, all the correlation coefficients are high, which emphasizes their utility in accurately predicting activation barriers. In this regard, these relations provide a convenient approach to investigate trends in catalytic reactions on perovskite supported single-atom catalysts.

We observe that the activation barriers typically decrease for more exothermic reactions (more negative reaction energies). In addition, the reaction energies for the first CO oxidation event are substantially higher than those for the second CO oxidation one on corresponding surfaces. Notably, the trends in the barrier for the first CO oxidation step are very different from those for the second CO oxidation step. Figure 8a,d shows that the barriers for the first step on the LaMnO$_3$-M and LaNiO$_3$-M surfaces are higher than for the second one. On the contrary, the LaFeO$_3$-M and LaCoO$_3$-M models exhibit much lower activation barriers for the first CO oxidation step than the second one (Figure 8b,c). The slope in the linear BEP relation is usually indicated by $\alpha$ and is understood as a parameter reflecting the nature of the transition state. The $\alpha$ value close to 1 for the second CO oxidation step on the LaFeO$_3$-M can be interpreted in terms of a late transition state structure, resembling the final state along the reaction coordinate. For the first CO oxidation step on LaMnO$_3$-M and LaNiO$_3$-M, the $\alpha$ value is close to 0, pointing to an early transition state structure, which is akin to the initial state. We also note that there is poor correlation between the barriers and the reaction energies of CO oxidation on all the LaBO$_3$-M surfaces. This is most likely due to the fact that the different LaBO$_3$-M systems exhibit different electronic properties, resulting in a lack of similarity of the geometrical and theoretical structures along the reaction coordinate.

Microkinetics Simulations. To systematically evaluate the catalytic activities of these transition metal-doped LaBO$_3$ surfaces, we estimated the CO oxidation reaction rates by microkinetics simulations based on the computed potential energy diagrams. To this end, different models namely
LaMnO$_3$-M, LaFeO$_3$-M, LaCoO$_3$-M, and LaNiO$_3$-M surfaces were considered for our simulations. The predicted CO oxidation rates are displayed as Arrhenius curves in Figure 9. Clearly, the LaBO$_3$-Pd surfaces exhibit a much higher CO$_2$ formation rate than the LaBO$_3$-Pt and LaBO$_3$-Rh surfaces at low temperature. This can be ascribed to the low barriers for CO oxidation on the Pd-doped surfaces.

By comparing the activity of CO oxidation on different Pd-doped supports, we find that the LaMnO$_3$-Pd and LaCoO$_3$-Pd surfaces exhibit higher reaction rates than the LaFeO$_3$-Pd and LaNiO$_3$-Pd at low temperature. This is not surprising that the former two are more active for CO oxidation than the latter two because the LaMnO$_3$-Pd and LaCoO$_3$-Pd surfaces exhibit a relatively strong CO and O$_2$ adsorption and, henceforth, relatively low overall barriers for the surface reaction. In addition, CO oxidation on the LaMnO$_3$-Rh and LaNiO$_3$-Rh surfaces proceeds at higher rates than on LaMnO$_3$-Pd and LaNiO$_3$-Pd surfaces at intermediate temperatures. This is because CO only can favorably adsorb on doped atoms at low temperature. As the temperature increases, the LaMnO$_3$-Rh and LaNiO$_3$-Rh surfaces can still efficiently bind CO molecules which facilitate CO$_2$ formation. Besides, the low overall barriers for CO oxidation on LaMnO$_3$-Rh and LaNiO$_3$-Rh are relevant in this respect. Therefore, these two Rh-doped...
surfaces exhibit good performance at intermediate temperatures.

From the above analysis, we find a preference for LaBO3-Pd surfaces for CO oxidation. We then plot the steady-state coverages of surface reaction intermediate and rate-controlling steps for the LaBO3-Pd models. Figure 10a shows these surface coverages as a function of temperature for LaMnO3-Pd. At low temperatures, CO# (representing CO adsorption sites) and O# (representing O vacancy adsorption sites) are the predominant surface states. This observation is supported by a DRC analysis, which indicates that the reaction of adsorbed CO react with a lattice O atom is the rate-controlling step at low temperatures (Figure 10e). For LaFeO3-Pd, Figure 10b shows that the surface vacancy site is completely occupied by O2 at low temperatures, which is in line with strong O2 adsorption. The DRC analysis reflects that the overall CO conversion rate is limited by the second CO2 formation step. This is because the activation barrier for the second CO2 formation step is higher than for the first one. The composition of the surface adsorbed layer for LaCoO3-Pd is different from the one of LaFeO3-Pd. CO# remains preferentially on Pd at intermediate temperatures, and O2 covers the surface vacancy sites only at very low temperatures. This can be ascribed to the relatively weak O2 adsorption on LaCoO3-Pd. The DRC analysis shows that the second CO2 formation step controls the overall reaction rate because the activation barrier of the second CO2 formation is higher than that of the first one. For LaNiO3-Pd, the steady-state surface coverages as a function of temperature show that CO# occupies the Pd sites and O species covers the surface O vacancy sites at low temperatures. That is to say, the perovskite is predominantly present in its stoichiometric form. Similar kinetic trends are observed for the Rh- and Pt-containing LaBO3 surfaces (Figures S3 and S4).

**CONCLUSIONS**

Activity trends of CO oxidation on La-based LaBO3 perovskites with B = Mn, Fe, Co, and Ni surface into which single atoms of precious group Rh, Pd, and Pt metals were doped were comprehensively investigated by first-principles DFT calculations and microkinetics simulations. CO adsorption on LaBO3-Pd surfaces is weaker than on corresponding LaBO3-Rh and LaBO3-Pt surfaces. This difference in adsorption strength is rationalized by the presence of more empty d-states just above the Fermi level for systems doped with Rh or Pt, resulting in a stronger interaction between CO orbitals and d-orbitals of Pt or Rh atoms. Given the preference for Pd, the influence of the composition of the perovskite support was investigated. A strong correlation is identified between CO adsorption energy and the d-band center of the M atom for the LaBO3-M surfaces. A charge analysis for LaBO3-M indicates that oxidation state of M has a strong influence on CO oxidation and the corresponding reaction energies for these perovskite-supported single-atom catalysts. We expect that these relationships can help identify the promising perovskite catalysts for environmental catalysis. Microkinetics simulations show that LaCoO3-Pd, i.e., Pd doped in LaCoO3, is the most promising system for CO oxidation, due to moderate CO adsorption strength and the lowest activation barrier for CO oxidation. Doping LaBO3 surfaces with transition metal dopants is argued to be a promising way to modify the surface electronic structure and improve catalytic performance toward CO oxidation.

**ASSOCIATED CONTENT**

 Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcc.9b11079.

1. Optimized lattice parameters; 2. exchange energies for the different models; 3. imaginary frequencies for transition states; 4. CO adsorption energies for different adsorption sites; 5. PDOS of doped M atom and adsorbed CO for LaCoO3-M and LaNiO3-M; 6. charge density difference for LaBO3-Rh and LaBO3-Pt surfaces; 7. coverage distribution and DRC analysis for CO oxidation on LaBO3-Rh and LaBO3-Pt.

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**Notes**

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