Understanding the Impact of defects on catalytic CO oxidation of LaFeO$_3$-Supported Rh, Pd, and Pt single-atom catalysts

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Understanding the Impact of Defects on Catalytic CO Oxidation of LaFeO₃-Supported Rh, Pd, and Pt Single-Atom Catalysts

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ABSTRACT: Understanding the intrinsic catalytic properties of perovskite materials can accelerate the development of highly active and abundant complex oxide catalysts. Here, we performed a first-principles density functional theory study combined with a microkinetics analysis to comprehensively investigate the influence of defects on catalytic CO oxidation of LaFeO₃ catalysts containing single atoms of Rh, Pd, and Pt. La defects and subsurface O vacancies considerably affect the local electronic structure of these single atoms adsorbed at the surface or replacing Fe in the surface of the perovskite. As a consequence, not only the stability of the introduced single atoms is enhanced but also the CO and O₂ adsorption energies are modified. This also affects the barriers for CO oxidation. Uniquely, we find that the presence of La defects results in a much higher CO oxidation rate for the doped perovskite surface. A linear correlation between the activation barrier for CO oxidation and the surface O vacancy formation energy for these models is identified. Additionally, the presence of subsurface O vacancies only slightly promotes CO oxidation on the LaFeO₃ surface with an adsorbed Rh atom. Our findings suggest that the introduction of La defects in LaFeO₃-based environmental catalysts could be a promising strategy toward improved oxidation performance. The insights revealed herein guide the design of the perovskite-based three-way catalyst through compositional variation.

1. INTRODUCTION

The development of new low-cost and highly active catalysts for automotive emission control is of great importance to the protection of the environment. Among practical solutions, supported platinum group metals (PGMs) are widely used to catalyze reactions to abate the emission of noxious gases from gasoline engines.1−6 The cost of PGMs and their low-temperature performance as well as their aggregation into larger particles when operated at elevated temperatures pose significant challenges in developing better catalysts.7,8 These aspects explain why already for a long time substantial efforts have been made to reduce the content of precious metals in these catalysts.9−15 In the extreme case, catalysts contain these precious metals in an atomically dispersed form, which in recent years has become a topic of frontier research.16−22

Another solution to the problem of costly precious metals is to replace them by a cheaper class of materials. Recently, perovskite (ABO₃ type) materials have been explored as a potential replacement for conventional three-way catalysts.23−26 As in general these materials are not active enough, one strategy is to promote these base metal-based oxides with precious metals. This only makes sense when these are present in high dispersion. Early studies indicated that the noble metals can retain good dispersion on perovskite surfaces.27,28 For instance, LaFeO₃ (LFO) perovskites exhibit excellent resistance against sintering of precious metal overlayers.29 The most prominent reaction investigated in this respect is CO oxidation.30−32 Previous studies demonstrated that the physical and chemical and, accordingly, catalytic properties of perovskites can be tuned by partial substitution of the A and B sites with transition-metal ions.32−36 For example, Pd doping of LFO can strongly improve the CO oxidation activity.37 Another recent experiment highlighted that the catalytic activity of CO oxidation on LFO-supported Rh and Cu catalysts was enhanced by the presence of La defects.38 Onn and co-workers reported about a high-surface-area LFO-supported Pd catalyst obtained by atomic layer deposition with good catalytic performance.39

There are very few studies that focus on the underlying chemical aspects of the surface reactivity of perovskites by computational chemistry. Some studies have dealt with the stability of transition-metal atoms and adsorption of simple molecules on these complex oxide surfaces.40−43 This represents a lack of the fundamentals of the reaction mechanism and the relation with the electronic structure that is modified by aspects such as common defects and hinders the guided development of more active systems.

In this study, we aim for this kind of understanding by employing density functional theory (DFT) in combination with microkinetics analysis to understand the chemical and
catalytic properties of single Rh, Pd, and Pt atoms dispersed on or in the stable (001) surface of LFO with a view on CO oxidation catalysis. We investigate the stability, CO₂ adsorption energies, and CO oxidation activation barriers for stoichiometric and defective surfaces. Especially, La and O defects can improve the stability of the introduction of precious metal atoms and tune the electronic structure toward high CO oxidation activity. A general finding is that La defects can lead to highly active CO oxidation catalysts based on the three explored precious metals, while the presence of subsurface O vacancies boosts the performance of single Rh atoms adsorbed to the LFO surface.

2. COMPUTATIONAL METHODS

2.1. DFT Calculations. We employed spin-polarized DFT calculations using the projector-augmented wave approach as implemented in VASP. To account for the effect of the exchange–correlation and on-site Coulomb interaction, the Perdew–Burke–Ernzerhof functional with the Hubbard U correction was used. We set U_{O} to 4 eV for the Fe atoms. In order to accurately describe the electronic structure of LFO, we consider its G-type antiferromagnetic structure. To understand the catalytic properties, we constructed the FeO₂-terminated (001) surface, which is known to be a stable and ordered (001) surface, where the adsorption of a single M atom on the surface of the LFO slab model.

Different adsorption sites were considered for the latter purpose. Here, the constructed slab models are 2 × 2 unit cells with six atomic layers and a slab thickness of 9.93 Å. The top four layers were relaxed and the bottom two layers were frozen to the configuration of the bulk. A vacuum thickness of 12 Å was used to avoid spurious interactions of adsorbates between neighboring super cells. For the Brillouin-zone integration, a 1 × 1 × 1 Monkhorst–Pack k-point was used. The geometry optimizations were assumed converged when the Hellmann–Feynman forces acting on atoms were below 0.05 eV/Å. Further, computational details including a discussion of the magnetic structure of the LFO models are provided in the Supporting Information.

The formation energies of M atom-doped LFO surfaces are defined as

\[ E_{\text{form}} = E_{\text{M+surf}} + E_{\text{Fe}} - (E_{\text{surf}} + E_{\text{M}}) \]  

Herein, \( E_{\text{M+surf}} \), \( E_{\text{surf}} \), and \( E_{\text{M}} \) are the electronic energies of the M-doped LFO surface, the empty LFO surface, the bulk Fe atom, and the bulk M atom, respectively.

Here, the adsorption energies are calculated by

\[ E_{\text{ads}} = E_{\text{M+surf}} - (E_{\text{surf}} + E_{\text{M}}) \]  

where \( E_{\text{M+surf}} \) and \( E_{\text{M}} \) are the electronic energies of the adsorbed system and the corresponding gas-phase species, respectively.

2.2. Microkinetics Simulations. On the basis of the DFT calculations, we carried out microkinetics simulations to gain the kinetic properties for CO oxidation on LFO-supported Rh, Pd, and Pt single-atom catalysts. For instance, the reaction rate, the rate-determining step, and species distribution are investigated. For surface reactions, the calculated activation barriers are used to estimate the forward and backward rate constants using the Eyring equation

\[ k = \frac{k_{B}T}{h} \left( \frac{f^T}{f} \right) e^{-E_{a}/k_{B}T} \]  

where \( k \) represents the reaction rate constant, \( k_{B} \) and \( h \) are Boltzmann and Planck’s constants, respectively, \( T \) is the temperature (in K), and \( E_{a} \) refers to the electronic activation energy (in J). \( f^T \) and \( f \) indicate the partition functions of the transition state and the ground state, respectively. We assumed that all vibrational partition functions equal unity which gives a prefactor for all surface elementary reaction steps of \( \sim 10^{13} \text{ s}^{-1} \).

In the case of adsorption reactions, there is an assumption that the molecule loses only one of its translational degrees of freedom with respect to the gas phase. Accordingly, the rate of molecular adsorption was calculated as

\[ k_{\text{ads}} = \frac{PA'}{\sqrt{2\pi mk_{B}T}} S \]  

Herein, \( P \) indicates the pressure of the adsorbate in the gas phase, \( A' \) is the surface area of the adsorption site, \( m \) is the mass of the adsorbate, and \( S \) refers to dimensionless sticking coefficient.

For the CO₂ desorption process, we assumed that the activated species has two translational and three rotational degrees of freedom. Therefore, the molecular desorption rate is defined as

\[ k_{\text{des}} = \frac{k_{B}T^{3}}{h^{5}} \frac{A'(2\pi mk_{B})^{3/2}}{\sigma \theta_{v}} e^{-E_{a}/k_{B}T} \]  

where \( \sigma \) refers to the symmetry number, \( \theta \) is the characteristic temperature for rotation, and \( E_{\text{des}} \) is the desorption energy.

The details for the microkinetics modeling have been described in our previous works. To calculate the reaction rate of all surface reaction intermediates, we constructed the differential equations by using the rate constants of the elementary reaction steps. For each of the X components presented in the reaction network, a single differential equation is defined as

\[ \frac{dX_i}{dt} = \sum_{j=1}^{N} \left( k_{ji} \prod_{k=1}^{X} c_{k}^{1/2} \right) \]  

In the above equation, \( k_{ji} \) is the elementary reaction rate constant, \( c_{k} \) indicates the stoichiometric coefficient of component \( i \) in elementary reaction step \( kj \), and \( c_{k} \) refers to the concentration of component \( k \) on catalyst surface.

To identify the rate-determining step of the CO oxidation reaction, Campbell’s degree of rate control (DRC) analysis was employed. For a specific elementary step \( i \), the coefficient of DRC \( \chi_{\text{RC},i} \) is determined by

\[ \chi_{\text{RC},i} = \frac{k_{i} \left( \frac{\partial r}{\partial k_{j}} \right)_{k_{j},k_{i}}}{r \left( \frac{\partial k_{j}}{\partial k_{i}} \right)_{k_{j},k_{i}}} \]  

Herein, \( r \) refers to the overall reaction rate and \( k_{i} \) and \( k_{j} \) indicate the forward rate and the equilibrium constants for step \( i \), respectively.

The first-principles-based microkinetics simulations were carried out using the MKMCXX code. The overall conversion rates of CO oxidation, steady-state coverages, and
products distribution were calculated as a function of temperature by integrating the ordinary differential equations with respect to time using the backward differentiation formula method.55–57

3. RESULTS AND DISCUSSION

3.1. Geometry and Stability of LFO-Supported Rh, Pd, and Pt Single-Atom Catalysts. We first investigated the structure and stability of Rh-, Pd-, and Pt-doped LFO surfaces. Figure 1a,b shows the structures of the stoichiometric doped LFO surfaces and the same surfaces with VLa. The M atom-doped stoichiometric LFO and VLa-promoted LFO structures are denoted in the following as LFO-M and LFO-VLa-M, respectively. The structures of the corresponding models with an O vacancy are denoted as LFO-VLa (color code: light blue, La; lavender, Fe; O, red; blue, M = Rh, Pd, and Pt).

Accordingly, we used a model for LFO-VSO-M which includes the subsurface O vacancy to investigate stability and catalytic properties. Compared with LFO-M, the formation energies for LFO-VSO-Rh, LFO-VSO-Pd, and LFO-VSO-Pt are lower, that is, −0.60, −2.16, and −1.39 eV, respectively. These data confirm the expected trend that creating oxygen vacancies in doped LFO structures is more facile because the noble metal dopants are less reactive than Fe.

For the adsorption structures, we find a preference for M adsorption on the hollow site of the LFO surface (Figures 1c,d and S2). We denote the adsorption of M on different LFO surfaces as Mads-LFO, Mads-LFO-VLa, and Mads-LFO-VSO. The stability of the different models is compared on the basis of the adsorption energy. Table 1 shows that VLa enhances strongly the adsorption energies of Rh (−2.69 eV), Pd (−2.58 eV), and Pt (−2.48 eV) compared with the stoichiometric LFO surface. The data also show that the presence of an O vacancy also results in lower adsorption energies of Rh (0.71 eV), Pd (0.70 eV), and Pt (1.06 eV) in comparison to the stoichiometric surface. Thus, we can conclude that La and O defects increase the stability of isolated noble metal atoms at the LFO surface.

To understand the electronic nature of these LFO surfaces, we analyzed their partial density of states (PDOS). We focus in Figure 2 on the bonding of the different stoichiometric and defective LFO surfaces with an Rh atom. The bonding is governed by hybridization of Rh 4d and O 2p orbitals. The O 2s orbitals lie too low in energy to be involved in the bonding. In all cases, the overlap between Rh 4d and O 2p orbitals is higher for Rh-doped LFO structures than for Rh adsorbed on LFO. For the LFO-VLa surface, the calculated Bader charges of the Rh atom in LFO-VLa-Rh and Rhads-LFO-VLa are +1.85e and +1.31e, respectively, consistent with the lower occupancy of the 4d states. Thus, we can say that Rh transfers effectively electrons to O 2p orbitals. For LFO-VSO-Rh and Rhads-LFO-VSO, the Rh atom and the nearest O atoms form a stable square-planar configuration. Figures S3 and S4 confirm that similar trends occur for Pd and Pt doping in LFO-VLa. We note however that the overlap for the d orbitals of Pd and Pt is smaller than for Rh, explaining the generally observed higher stability of Rh-doped structures.

3.2. Adsorption of CO and O2. Before we explore the reaction mechanism of CO oxidation, we first investigate the adsorption properties of CO and O2 on these surfaces. All relevant data are collected in Tables S2 and S3. Our calculations indicate that the stoichiometric LFO surface cannot bind CO or O2. Therefore, we predict that the stoichiometric surface should present a low activity. This is in line with the early experimental result.50 Notably, the surface O vacancy formation energy for the LFO surface is as high as 2.18 eV, which implies that spontaneous formation of surface O vacancies will only take place at relatively high temperature. Accordingly, we did not consider CO adsorption on such O-deficient LFO structures.

Table 1. Stabilities of the Different Surface Models Used for the DFT Calculationsa

<table>
<thead>
<tr>
<th>model</th>
<th>formation energy (eV)</th>
<th>adsorption energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>LFO-M</td>
<td>LFO-VLa-M</td>
</tr>
<tr>
<td>Rh</td>
<td>0.09</td>
<td>−1.44</td>
</tr>
<tr>
<td>Pd</td>
<td>1.41</td>
<td>0.30</td>
</tr>
<tr>
<td>Pt</td>
<td>0.79</td>
<td>−0.31</td>
</tr>
</tbody>
</table>

aFor the doped models, formation energies are reported; for the models consisting of a noble metal adsorbed on the LFO surface, the adsorption energies are listed.
vacancies. For LFO-Rh, the CO adsorption energy is $-2.14$ eV, which is stronger than for CO adsorption on LFO-Pd ($-0.53$ eV) and LFO-Pt ($-1.38$ eV). The stronger CO adsorption on Rh can be correlated to the enhanced donation of CO electron density into the more unoccupied Rh d-orbitals. In the catalytic mechanism to be discussed below, the

<table>
<thead>
<tr>
<th>model</th>
<th>LFO-M</th>
<th>LFO-V_{La}-M</th>
<th>LFO-V_{SO}-M</th>
<th>M_{ads}-LFO</th>
<th>M_{ads}-LFO-V_{La}</th>
<th>M_{ads}-LFO-V_{SO}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rh</td>
<td>2.42 (2.10)</td>
<td>1.00</td>
<td>2.72</td>
<td>3.02</td>
<td>2.82</td>
<td>3.07</td>
</tr>
<tr>
<td>Pd</td>
<td>2.28 (1.53)</td>
<td>0.41</td>
<td>2.62</td>
<td>2.40</td>
<td>2.14</td>
<td>2.49</td>
</tr>
<tr>
<td>Pt</td>
<td>2.47 (1.56)</td>
<td>0.73</td>
<td>2.77</td>
<td>2.31</td>
<td>2.65</td>
<td>2.42</td>
</tr>
</tbody>
</table>

Values in parenthesis are corresponding subsurface oxygen formation energies.

Figure 2. PDOS of Rh 4d, O 2p, and O 2s orbitals (the O atom adjacent to Rh) in (a) LFO-Rh, (b) Rh_{ads}-LFO, (c) LFO-V_{La}-Rh, (d) Rh_{ads}-LFO-V_{La}, (e) LFO-V_{SO}-Rh, and (f) Rh_{ads}-LFO-V_{SO}.

Figure 3. Potential energy diagrams for CO oxidation on (a) LFO-Rh, LFO-V_{La}-Rh, and LFO-V_{SO}-Rh, (b) Rh_{ads}-LFO and Rh_{ads}-LFO-V_{La}, and (c) corresponding geometries for CO oxidation on the different models. The structures of stable and transition states are indicated by corresponding numbers in the different panels.
adsorbed CO molecule reacts with a surface O atom to form CO$_2$. This constitutes an M$^{-}$V$_K$ mechanism. Molecular oxygen will then adsorb on the created O vacancy. Its adsorption energy on the defect sites of LFO-Rh, LFO-Pd, and LFO-Pt are $-2.09$, $-1.53$, and $-2.17$ eV, respectively. We find that the strength of O$_2$ adsorption correlates strongly to the surface O vacancy formation energy as follows from the computed surface O vacancy formation energies for LFO-Rh (2.42 eV), LFO-Pd (2.28 eV), and LFO-Pt (2.47 eV).

We also considered the effect of V$_{La}$ on the CO and O$_2$ adsorption energies for the LFO-M surfaces. The presence of a La defect results in a substantial decrease of the CO adsorption strength on the Rh-doped surface and a decrease of the O$_2$ adsorption strength on the O defect obtained after one catalytic CO$_2$ formation cycle. On the other hand, the CO adsorption strengths on LFO-V$_{La}$-Pd and LFO-V$_{La}$-Pt are enhanced with respect to the corresponding stoichiometric surfaces. The O$_2$ adsorption strengths are however decreased, similar to the Rh case. The different influence of a La defect on the CO adsorption strength for Rh on the one hand and Pt and Pd on the other has to do with the degree of hybridization between the CO and Rh 4d orbitals. For Rh, this leads to a lower hybridization, lowering the CO adsorption strength. For Pd and Pt, the shift of the relevant d orbitals due to the La defect causes a stronger hybridization with the CO orbitals. Finally, we determined that the presence of a subsurface O vacancy upon Rh doping in LFO-V$_{SO}$ decreases both the CO and O$_2$ adsorption energies. Neither Pd- nor Pt-doped LFO-V$_{SO}$ can bind CO or O$_2$. The reason is that the square-planar coordination of Pt and Pd with O atoms precludes CO adsorption, which is not the case for Rh. We also investigated CO and O$_2$ adsorption on Rh$_{La}$-LFO. CO adsorbs weakly on Rh$_{La}$-LFO ($-0.99$ eV) than on Rh$_{La}$-LFO-V$_{La}$ ($-1.30$ eV), while O$_2$ adsorption is slightly weakened for Rh$_{La}$-LFO-V$_{La}$ compared to its stoichiometric counterpart. CO does not adsorb on the Pd$_{La}$-LFO and Pt$_{La}$-LFO surfaces. The main reason for this is that the Pd and Pt atoms are coordinatively saturated in their square-planar geometry.

In summary, the above results show that the presence of La and subsurface O vacancies has a profound effect on the CO and O$_2$ adsorption energies. We expect that the CO oxidation rate should benefit from intermediate adsorption strengths of the reactants (Sabatier principle). To investigate this in detail, we determined the complete potential energy diagrams for the CO oxidation on the various LFO surfaces. To this end, we explored all relevant stable and transition states. We also included CO oxidation involving lattice O atoms, as experimental results indicate that the structural O atoms of transition metal-substituted LFO participate in CO$_2$ formation. Moreover, the modeling of adsorption complexes showed that co-adsorption of CO and O$_2$ is unfavorable on the modified LFO surfaces explored in this work. Accordingly, a Langmuir–Hinshelwood reaction mechanism is less likely.

### 3.3. CO Oxidation

Figures 3 and 4 show the potential energy diagrams for the Rh-, Pd-, and Pt-containing LFO surfaces. For the stoichiometric doped LFO surfaces, the activation barriers for the reaction of adsorbed CO with a lattice O to CO$_2$ are 1.38 eV (Rh), 0.48 eV (Pd), and 0.52 eV (Pt). CO$_2$ desorption energies for these three cases are 0.70, 0.05, and 0.78 eV, respectively. After O$_2$ adsorption on the O vacancy (see above), another CO molecule will adsorb strongly on LFO-Rh ($-1.97$ eV) and LFO-Pt ($-1.62$ eV),...
but relatively weakly on LFO-Pd (−0.52 eV). The adsorbed CO molecule moves toward LFO-Pd, which leads to CO₂ formation; the barriers for this process are 2.33 and 2.22 eV for LFO-Rh and LFO-Pt, respectively, and are moderate for LFO-Pd (0.58 eV).

As CO and O₂ adsorption energies change due to the presence of La and subsurface O defects, we also investigated their influence on the potential energy diagrams. The overall barrier for CO oxidation on LFO-VLa₃-Rh is significantly lower (0.84 eV) compared to the value 1.38 eV for the stoichiometric LFO-Rh surface. Similar differences are found for LFO-VLa₃-Pd and LFO-VLa₃-Pt (Figure 4). In particular, CO oxidation on LFO-VLa₃-Pd involved a very low overall activation barrier of 0.42 eV. Importantly, we identified a linear correlation between the activation barrier for CO oxidation to CO₂ and the surface O vacancy formation energy for the LFO surfaces with a La defect (Figure 5). This strongly indicates that the surface O vacancy formation energy is a good descriptor for CO oxidation on transition metal-doped LFO-VLa catalysts. An experimental indication of the benefit of La defects can be found in the work on Rh- and Cu-doped LFO. The trend observed in Figure 5, therefore, might be useful to predict new nonstoichiometric LFO perovskite-based catalysts. On the other hand, we admit that such correlations were not observed with an experimental indication that La defects improve the catalytic activity of CO oxidation on Rh-doped LFO. Our modeling reveals that the increased activity on such La-deficient LFO models is due to intermediate CO and O₂.

Figure 5. Activation barriers of CO oxidation on LFO-VLa₃-M (M = Rh, Pd, and Pt) are linearly related to the corresponding surface O vacancy formation energies. (Blue dot: first half, CO oxidation; red square: second half, CO oxidation.)

The CO oxidation potential energy diagrams for the single Rh, Pd, and Pt atoms adsorbed on the LFO surfaces are quite different. CO adsorbs on Rh of Rhads-LFO relatively weakly compared to LFO-Rh, which facilitates the migration of CO during the CO₂ formation step. Indeed, the barrier for this step is only 0.93 eV, substantially lower than the value of 1.38 eV for LFO-Rh. The relatively high CO₂ desorption energy (0.64 eV) is consistent with the high surface O vacancy formation (3.02 eV) for stoichiometric Rhads-LFO. After adsorption of O₂ and CO, the following CO₂ formation step needs to overcome a barrier of 1.32 eV. In contrast to LFO-Rh, Rhads-LFO exhibits a lower overall activation barrier and CO₂ desorption energy. It is noteworthy that the square-planar local structures formed on single Pd and Pt atoms adsorbed on the LFO surfaces preclude the simultaneous binding of CO and O₂.

Next we study the influence of VSO on the catalytic properties of a Rh atom adsorbed LFO. As shown in Figure 3b, the first CO₂ formation involves a barrier of 0.35 eV. The second CO₂ formation step on this surface also exhibits a relatively low activation barrier (0.98 eV) compared to the corresponding barrier of 1.32 eV for the stoichiometric Rhads-LFO. As to the Pdads-LFO-VLa and Ptads-LFO-VLa, we find that also these surfaces cannot catalyze CO oxidation due to the very weak adsorption of CO and O₂.

3.4. Microkinetics Modeling. To systematically evaluate the catalytic activities of CO oxidation on the above LFO-supported single-atom catalysts, we carried out microkinetics simulations based on the potential energy diagrams. Figure 6 shows that predicted CO₂ formation rates on the defective LFO-supported Rh, Pd, and Pt models are substantially higher than those on their stoichiometric counterparts. This is in line with an experimental indication that La defects improve the catalytic activity of CO oxidation on Rh-doped LFO. Our modeling reveals that the increased activity on such La-deficient LFO models is due to intermediate CO and O₂.

Figure 6. Microkinetics simulations for CO oxidation on LFO-supported Rh, Pd, and Pt catalysts. CO₂ formation rates r (in mol s⁻¹) as a function of temperature on different models (P = 1 atm, CO/O₂ ratio = 1): (a) LFO-Rh, LFO-VLa₃-Rh, LFO-VSO₃-Rh, Rhads-LFO, and Rhads-LFO-VLa; (b) LFO-Pd, LFO-VLa₃-Pd, LFO-Pt, and LFO-VLa₃-Pt.
adsorption energies and low overall activation barriers. Notably, our data predict that LFO-VLa-Pd is the preferred composition, indicating that replacement of Rh by Pd should be promising.

We further analyzed the kinetics in more detail. Inspection of the steady-state surface coverages (Figure 7) shows that both the Rh sites and surface O vacancy sites of LFO-Rh are occupied by CO and O₂ species, respectively, up to relatively high temperature. For LFO-VLa-Rh, adsorbed CO can already react at low temperature with adsorbed O₂ species because the associated barrier is much lower for the surface with a La defect in comparison to the stoichiometric LFO-Rh surface. A DRC analysis supports the coverage differences between LFO-Rh and LFO-VLa-Rh in the sense that the reaction of adsorbed CO with adsorbed O₂ is the rate-determining step. Similar kinetic trends are computed for the Pd- and Pt-containing LFO surfaces (Figure S5).

4. CONCLUSIONS

In summary, we investigated CO oxidation on LFO-supported Rh, Pd, and Pt single-atom models by first-principles DFT calculations and microkinetics simulations. Next to the stoichiometric LFO surface, we also explored the influence of La defects and subsurface O vacancies on the catalytic rates. Models containing such defects enhance the stability of these single atoms adsorbed at the LFO surface or doped into the surface replacing Fe. These changes also affect the CO and O₂ adsorption energies and, in this way, affect the barrier for CO oxidation surface reactions. An important finding is that LFO surfaces with a La defect result in optimum CO and O₂ binding energies with respect to CO oxidation barriers. A strong correlation between these activation barriers and the oxygen vacancy formation energy is found. Microkinetics simulations emphasize the higher CO oxidation rates for the Rh-, Pd-, and Pt-doped LFO surfaces with a La defect compared to the cases of the stoichiometric surface. Among all the considered models, Pd-doped LFO with the La defect exhibits the highest activity for the low-temperature CO oxidation. Notably, the presence of subsurface O vacancies only facilitates CO oxidation on the Rh-adsorbed LFO surface. Thus, our results demonstrate that the introduction of La defects in LFO-based environmental catalysts is a promising strategy toward improved oxidation performance.

ASSOCIATED CONTENT

* Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.9b01520.

Computational details, structures for models with subsurface O vacancy, tables for CO and O₂ adsorption energies of different models, PDOS analysis of LFO-supported Pd and Pt, and coverage distribution and DRC analysis for Pd- and Pt-doped LFO surfaces (PDF)

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Notes

The authors declare no competing financial interest.

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REFERENCES


(22) Sun, L.; Hu, J.; Qin, H.; Zhao, M.; Fan, K. Influences of Ca Doping and Oxygen Vacancy upon Adsorption of CO on the LaFeO3,


(49) Jansen, A. P. J. An Introduction to Kinetic Monte Carlo Simulations of Surface Reactions; Springer, 2012; Vol. 856.


