

Article

# On the Effects of Doping on the Catalytic Performance of (La,Sr)CoO<sub>3</sub>. A DFT Study of CO Oxidation

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**Abstract:** The effects of modifying the composition of LaCoO<sub>3</sub> on the catalytic activity are predicted by density functional calculations. Partially replacing La by Sr ions has beneficial effects, causing a lowering of the formation energy of O vacancies. In contrast to that, doping at the Co site is less effective, as only 3d impurities heavier than Co are able to stabilize vacancies at high concentrations. The comparison of the energy profiles for CO oxidation of undoped and of Ni-, Cu-m and Zn-doped (La,Sr)CoO<sub>3</sub>(100) surface shows that Cu is most effective. However, the effects are less spectacular than in the SrTiO<sub>3</sub> case, due to the different energetics for the formation of oxygen vacancies in the two hosts.

**Keywords:** heterogeneous catalysis; surface science; materials science; perovskites; CO oxidation; DFT calculations; transition metal doping

## 1. Introduction

As internal combustion engines are likely to power most world vehicles for at least the next two decades, while legislations are tightening the emission limits, the reduction of noxious components in the exhaust gas stands as a priority for the automotive industry. The main tool for achieving this result is provided by three way catalysts (TWCs) installed downstream of engines. Unfortunately, state-of-the-art TWCs typically contain platinum group metals and/or other elements such as rare earths, whose demand is rapidly rising, and whose production occurs in unevenly distributed areas. Hence, finding new and sustainable materials for TWCs is a current issue for research in catalysis. In this regard, a convenient and well known approach to tune the electronic and, consequently, the catalytic properties of materials, is doping with transition metal atoms [1]. In fact, experimental and theoretical investigations [2–4] have shown that even inert compounds, such as SrTiO<sub>3</sub>, can be turned into effective catalysts for CO oxidation if doped with transition metals, such as Co or Cu. Furthermore, it has been established that the primary role of doping is that of enhancing the surface oxygen atoms activity, which is gauged by the formation energy of surface oxygen vacancies. In fact, the rate determining step of the CO oxidation reaction is the extraction of surface oxygen by CO [3]. On the other hand, a more active host, such as LaCoO<sub>3</sub>, can improve its performance as a TWC material by partially replacing Co with Cu [5]. This is, however, most effective for high doping levels, when copper oxides segregate at the surface. Hence, it is not clear whether a low concentration of Cu dopant can actually improve the activity of LaCoO<sub>3</sub> for TWC applications. Furthermore, we are not aware of systematic studies comparing the effects of different transition metals as dopants on the catalytic properties of LaCoO<sub>3</sub>. The aim of the present work is to understand whether doping can improve the performance of LaCoO<sub>3</sub> as a material for three-way catalytic converters. In particular, we want to assess whether the vacancy formation energy is a good descriptor for the catalytic properties of perovskites, as it was found in our recent studies on the prototypical SrTiO<sub>3</sub> perovskite.

## 2. Results

### 2.1. $\text{LaCoO}_3$ vs. $(\text{La,Sr})\text{CoO}_3$

As the stoichiometry of perovskites can be changed by replacing both the A-site and the B-site ions, the range of possible stoichiometries is quite large. Thus, we decided to adopt a simple approach where we first compare the properties of the  $\text{LaCoO}_3$  (LCO) and of  $(\text{La,Sr})\text{CoO}_3$  (LSCO) hosts. For the latter, we assumed a  $\text{La}_{0.75}\text{Sr}_{0.25}\text{CoO}_3$  stoichiometry, which has been computed to be a stable phase by Fuks et al. [6]. We considered the formation of both single and double oxygen vacancies ( $V_{\text{O}}$ ), as well as the adsorption of CO and NO molecules at the CoO-terminated (100) surface, testing all the configurations allowed by a  $2 \times 2$  supercell. The main results are reported in Table 1.

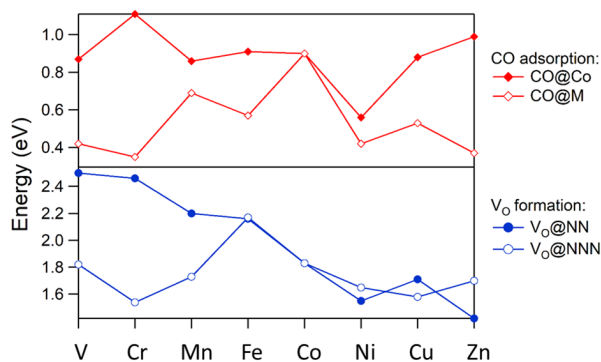
**Table 1.** Formation energy for surface vacancies and CO adsorption energies (eV) at the (100) surface of LCO and LSCO.

Compound	1 $V_{\text{O}}$ /cell	2 $V_{\text{O}}$ /cell	CO Adsorption	NO Adsorption
LCO	2.12	5.15	0.98	1.10
LSCO	1.83	4.37	0.90	1.16

Interestingly, the partial substitution of La by Sr atoms enhances the stability of vacancies, while having minor (and contrasting) effects on the adsorption of CO and NO. Hence, this replacement is in principle suitable for tuning the catalytic properties of  $\text{LaCoO}_3$ . Another interesting finding is that when two vacancies are introduced in the supercell, they prefer to cluster together.

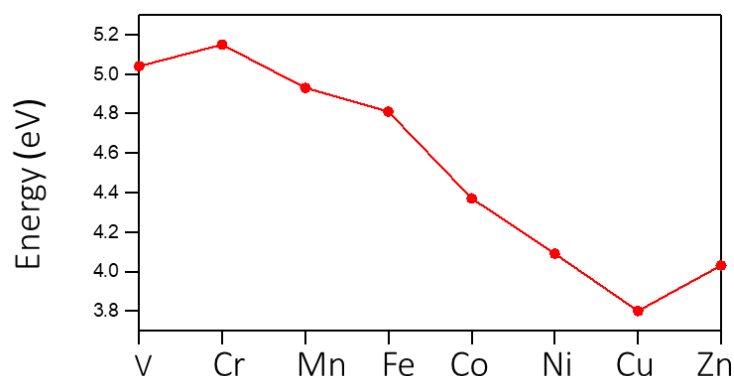
### 2.2. Doping LSCO at the Co Site

On the basis of the above presented results, it seems interesting to investigate the effects of doping LSCO at the Co site, once more taking the vacancy formation energy as a gauge of the catalytic activity. To this end, we replace one of the surface Co atoms of the supercell by another 3d atom, namely V, Cr, Mn, Fe, Ni, Cu, and Zn. Next, we compute the stability of oxygen vacancies, taking into consideration both the sites adjacent (NN) and those not-adjacent (NNN) to the 3d-impurity. The same slab models are used to compute the adsorption energy of CO, which is in turn evaluated both at the impurity site ( $\text{CO@M}$ ) and at regular cobalt sites ( $\text{CO@Co}$ ). We resume the results of these calculations in Figure 1, from which the difference in the behaviour of the investigated systems can be inferred. In particular, it appears that though the formation of vacancies is favored both by light and by heavy 3d metal impurities (with the exception of Fe), vacancies are attracted only by light dopants. Furthermore, CO adsorption is always favored at regular (unsubstituted) Co sites.



**Figure 1.** CO adsorption energies (top) and vacancy formation energies (bottom) computed for TM-doped LSCO(100) surfaces. The  $\text{CO@M}$  and  $\text{CO@Co}$  lines indicate adsorption at impurity and at regular Co sites, respectively. Vacancies created at the nearest site and at the next nearest site of the impurity are labelled NN and NNN, respectively.

We now consider the effect of Co-site doping on the formation of double vacancies. This is done starting from the structure of single vacancies, and exploring the stability of the possible configurations corresponding to the creation of a second vacancy. The results, shown in Figure 2, indicate that, in contrast to the case of single vacancies, the formation of double vacancies is favored only by heavy 3d impurities, namely, Ni, Cu, and Zn. In contrast to that, doping with light 3d metals is detrimental, as it increases the formation energy of double vacancies by  $\sim 0.5$  eV wrt the undoped LSCO host (corresponding to the Co label in Figure 2) which in turn indicates a worse performance for NO reduction. Therefore, doping with light 3d impurities, such as V, Cr, Mn, and Fe, is not a wise choice for improving the properties of LSCO in TWC converters.

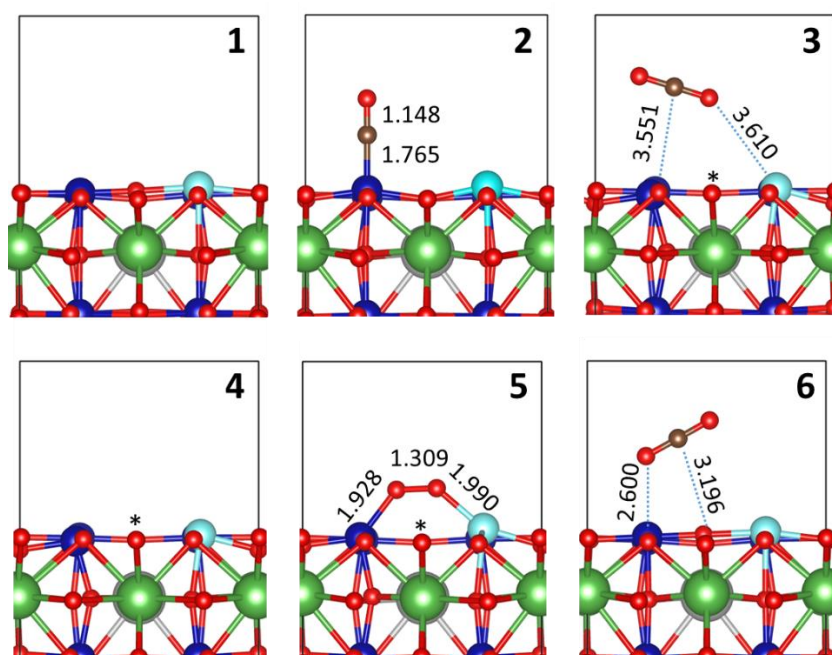


**Figure 2.** Formation energy for double vacancies (i.e.,  $2 V_{\text{O}}/\text{cell}$ ) for LSCO doped at the Co site.

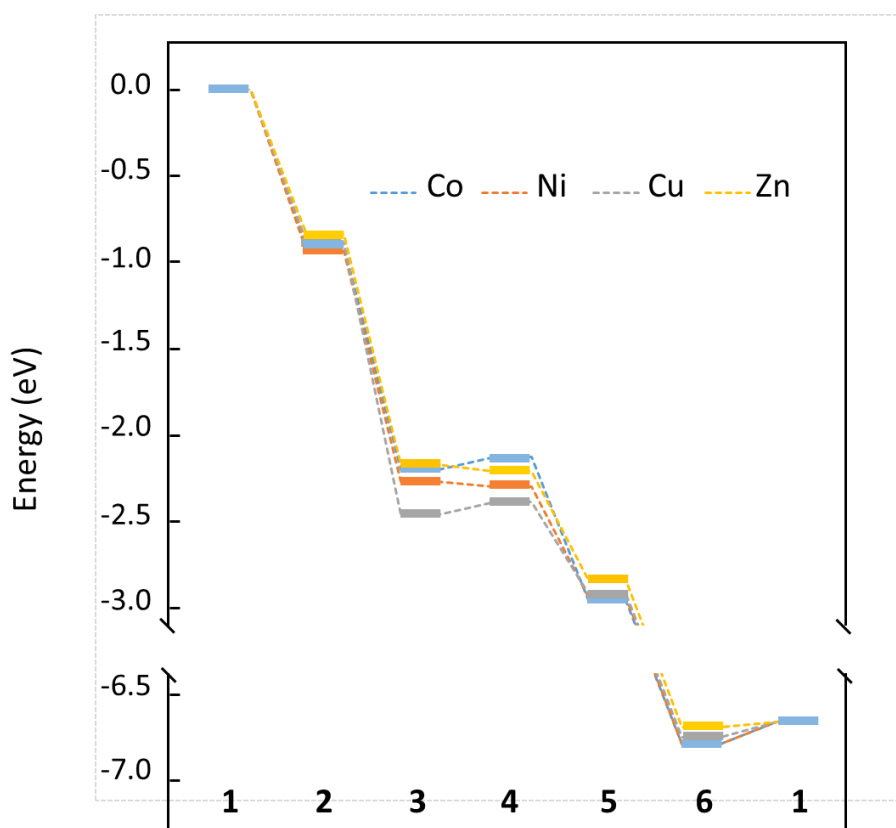
### 2.3. CO Oxidation at LSCO: Effects of Doping at the Co Site

The results presented in the preceding section encourage us to investigate in more detail how doping LSCO with heavy 3d dopants, i.e. Ni, Cu, and Zn, can influence the energetics of the CO oxidation reaction. To this end, we consider the mechanism reported in Ref. [3], consisting of the following elementary steps: i. Adsorption of CO; ii. Abstraction of lattice O atom and formation of  $\text{CO}_2$ ; iii. Desorption of  $\text{CO}_2$ ; iv. Adsorption of  $\text{O}_2$ ; v. Capture of a second CO molecule and formation of  $\text{CO}_2$ ; and vi. Desorption of  $\text{CO}_2$  and restoration of the stoichiometry of the starting surface. On the basis of the above presented findings, CO has been assumed to be adsorbed at a regular Co site, and to abstract a nearby O oxygen to form  $\text{CO}_2$ . We optimized all the intermediate species and labelled them with consecutive numbers, starting from the clean surface (1). The optimized structures of these species turn out to be quite similar for the pure and for the doped systems, and are sketched in Figure 3 for the case of the Cu-doped surface. Actually, the structures are also similar to those of the analogous intermediates computed for  $\text{SrTiO}_3$  [3] in the case of Cu doping. In particular, both  $\text{O}_2$  and  $\text{CO}_2$  lay parallel to the surface.

The analysis of the energy profiles relative to the investigated systems, reported in Figure 4, reveals that, similarly to what has been observed for the structures of the intermediates, the reaction energetics is also scarcely perturbed by doping, which is in striking contrast to the  $\text{SrTiO}_3$  case [3]. In fact, step ii, where a surface O atom is abstracted by CO, is always exothermic by 1.2–1.3 eV for all the systems, with the exception of the Cu-doped system, where it is even more exothermic ( $\sim 1.5$  eV). Overall, the energy profile of the reaction is qualitatively very similar to that computed for Cu-doped  $\text{SrTiO}_3$ : all the steps are exothermic, with the exception of those corresponding to the desorption of weakly adsorbed molecules, which are slightly endothermic



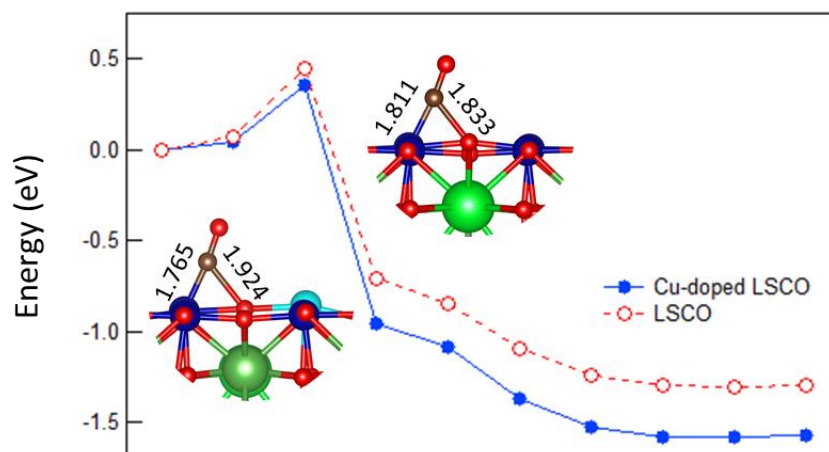
**Figure 3.** Intermediate species in the CO oxidation process on the Cu-doped LSCO(100) surface. The color codes are red = O, blue = Co, green = La, gray = Sr, cyan = Cu, brown = C. Asterisks mark the position of O vacancies.



**Figure 4.** Energy profiles reporting all the intermediates (see Figure 3) in the CO oxidation reaction occurring on the pure as well as on the Ni-, Cu-, and Zn-doped LSCO(100) surfaces.

We now want to compare the potential energy (PE) curves of the O abstraction process (step ii, *viz.* 2  $\rightarrow$  3) for the undoped and for the Cu-doped LSCO surfaces as obtained from nudged elastic band

(NEB) calculations. In tune with the analogies found both in the structure of the intermediates, and in the energy profiles (see Figure 4), the PE curves, shown in Figure 5, appear to be quite similar, the barrier being slightly lower for the Cu-doped case (0.35 vs. 0.45 eV). Because of the exothermicity of the step, we find “earlier” transition states, with respect to the case of  $\text{s SrTiO}_3$ . In fact, transition state (TS) structures (see Figure 5) are similar to semi-bridging CO molecules, whereas  $\text{CO}_2$ -like structures were computed in the latter case [3]. For analogous reasons, the C-Co distance of the TS becomes shorter (1.811 vs. 1.765 Å) on passing from the undoped to the Cu-doped surface, while a slight shortening is computed also for the C-O distance (1.159 vs. 1.156 Å).



**Figure 5.** Potential energy surfaces for the oxygen abstraction step (2 → 3) on the pure and on the Cu-doped LSCO(100) surfaces. Inset pictures show the structure of the transition states. The colors are the same as in Figure 3.

### 3. Theoretical Methods

Similarly to our previous investigations of  $\text{SrTiO}_3$ , we used the PWSCF code of the QUANTUM-ESPRESSO package [7] to solve the spin-polarized Kohn-Sham equations with the generalized gradient approximation (GGA), adopting the PBE exchange-correlation functional [8]. We point out that our aim is not giving accurate descriptions of the electronic structure, nor quantitative predictions of any kind. Hence, we rely on standard GGA calculations, which have been successfully tested in similar cases [9,10], and are certainly affordable when comparing trends, instead of performing GGA+U calculations, which are time-consuming and often problematic to converge. The valence-core interaction were described by ultrasoft pseudopotentials taken from the Garrity–Bennett–Rabe–Vanderbilt library [11]. All the calculations have been initialized in the ferromagnetic state. Though most of the calculations have been carried out using the recommended 40 ryd plane wave kinetic energy cutoff, for transition state calculations (vide infra) a 30 ryd cutoff was used. We actually found that reducing the cutoff from 40 to 30 ryd has minor effects on the geometries, and produces a general 0.02–0.05 eV reduction of the adsorption energies. Lattice constants of  $\text{LaCoO}_3$  and of  $\text{La}_{0.75}\text{Sr}_{0.25}\text{CoO}_3$  have been optimized and kept fixed for all the subsequent calculations, as dopants have been treated as diluted impurities. Bulk structures have been studied with cubic supercells containing 40 atoms. For LSCO, Sr ions were assumed to occupy the lattice positions as in the structure proposed by Fuks et al. [6], i.e., they were placed at the farthest possible distance in a  $2 \times 2 \times 2$  supercell. We have considered the (100) surfaces, which have been modelled with a  $2 \times 2$  slab consisting of seven atomic layers of  $\text{CoO}_2$  and  $\text{LaO}$  stacked alternately. Only the top ( $\text{CoO}_2$ -terminated) surface of the slab was used to model adsorption and reactions. The top three atomic layers are relaxed, whereas the bottom four atomic layers were kept fixed to simulate bulk. Effects of impurities and oxygen vacancies were evaluated by modifying the composition of the top surface. Thanks to the symmetric termination, a 12 Å thick vacuum space is sufficient to decouple the surfaces. Increasing

the vacuum thickness to 18 Å changes adsorption energies by less than 0.01 eV. The surface Brillouin zone was sampled using a  $2 \times 2$  k-point mesh. Transition states (TSs) were located using the climbing image nudged elastic band (CI-NEB). Zero-point energy and entropic contributions were not included, as they cannot change the computed trends. In computing the formation energy of oxygen vacancies, a correction was applied to compensate the well-known DFT-GGA tendency to overestimate the O<sub>2</sub> dissociation energy [12].

#### 4. Conclusions

We have investigated the effects of modifying the composition of LaCoO<sub>3</sub> using DFT calculations. The vacancy formation energy, taken as a gauge of the catalytic activity, is reduced both by introducing Sr atoms at the La site and by doping with 3d atoms at the Co site. Only heavy 3d atoms are able to promote high density of vacancies, which is needed for NO reduction. Overall, Cu-doped and Ni-doped (La,Sr)CoO<sub>3</sub> appear to be the best materials for preparation of catalysts suitable for three-way converters. It should, however, be pointed out that, due to the early nature of the transition state for the vacancy formation step in LSCO, the increased stability of oxygen vacancies obtained by doping is predicted to have a reduced influence on the catalytic properties when compared to that found for SrTiO<sub>3</sub>. Clearly, this work represents a first step towards a full understanding of the catalytic properties of these complex systems. More efforts, both on the theoretical and on the experimental side, is needed to extend and corroborate our conclusions.

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