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Adsorption of CO on the oxygen defective LaCoO$_3$ (001) surface: A first-principles study

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ABSTRACT

Adsorption of CO molecule on the oxygen defective LaCoO$_3$ (001) surface is studied by the first-principles calculation based on the density functional theory. Calculation results reveal that when CO molecule adsorption on the oxygen defective LaCoO$_3$ (001) surface, the most stable configuration is the defect-CO structure. The adsorption configurations, electrons transferred in the adsorption process, adsorption energy and the Density of States (DOS) are investigated. The oxygen defective LaCoO$_3$ (001) surface shows better gas sensing properties to CO molecule than the perfect LaCoO$_3$ (001) surface.

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1. Introduction

As a kind of colorless, tasteless, widespread and toxic gas, carbon monoxide (CO) could cause serious harm to human beings. Detection of the CO gas becomes more and more important since the worsening environmental pollution [1,2]. Moreover CO molecule has been widely used to investigate the interaction between gas molecule and surfaces of gas sensitive material [3–7]. In order to find better gas sensor materials for CO gas, it is critical to study of the reactions between CO molecule and oxide surfaces.

Recently increasing research efforts have been devoted to ABO$_3$ perovskites due to their potential application in gas sensor [8–10]. Previous studies have proved that the ABO$_3$ perovskites are excellent material for detecting some poisonous gas such as methane, acetone, CO and ethanol gases [11–13]. Gas sensing properties of the ABO$_3$ perovskites could be affected by oxygen vacancy in the surface. For example, Zhang et al. have found that electrical valence compensating and oxygen vacancy compensating can affect the conduction hole concentration in the substituted semi-conductor [14]. Delgado and Michel suggested that the partial substitution of Sm^{3+} by Ba^{2+} produces in the oxide an increase in oxygen vacancies, which is the explanation of the sensing mechanism in Sm$_{0.9}$Ba$_{0.1}$CoO$_3$ [15]. Therefore the oxygen vacancy is a key factor affecting gas sensing performance of the ABO$_3$ perovskites. For example, our previous study has demonstrated that the oxygen

vacancy could change the adsorption properties of LaFeO$_3$ (010) surface to CO molecule [16].

LaCoO$_3$ has the typical perovskites structure, which is a perfect model for studying the interaction between gas molecule and the surface. (001) surface are generally the most stable in the perovskites [17–19]. In our precious study we have investigated the adsorption of CO molecule on the perfect LaCoO$_3$ (001) surface [20]. Now we further explore the adsorption of CO molecule on the oxygen defective LaCoO$_3$ (001) surface. Emphasis is placed on the changes in adsorption properties by the introduction of oxygen vacancy.

2. Theoretical methods and models

The calculations were performed at the spin unrestricted generalized gradient approximation (GGA) level to density functional theory (DFT) using the program package DMol^3 [21,22]. The Perdew–Burke–Ernzerhof (PBE) method was employed to describe the exchange and correlation energy. Double numerical basis sets with polarization functions (DNP) and a hardness conserving semilocal pseudopotential, density functional semicore pseudopotential (DSSP) were employed. Global orbital cut off of 5.0 Å and a Fermi smearing of 0.005 Ha were used to improve the computational performance. The sampling of the Brillouin zone was done using a $2 \times 2 \times 2$ Monkhorst–Pack grid, which gave the converged results for all the properties. The convergence criteria of optimal geometry based on the energy, force and displacement convergence, were 2×10^{-5} Ha, 2×10^{-3} Ha/Å and 5×10^{-3} Å,

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respectively. Electrons transfer was calculated based on the Milliken Population Analysis (MPA) [23]. The electrons transfer (Q) was defined as the electrons difference between the adsorption and isolated CO molecules. Following equation was used to express the adsorption energy: $E_{ads} = E_{sub} + E_{ad} - E_{tot}$, where E_{tot} is the total energy of the adsorbate–substrate system in the equilibrium state, E_{sub} and E_{ad} are the total energy of substrate and adsorbate respectively. The calculation methods in this paper are consistent with the previous study to ensure the calculated results comparative [20].

The bulk LaCoO$_3$ with cubic structure is simulated by $2 \times 2 \times 2$ super cell with 40 atoms. After optimized bulk LaCoO$_3$, the (001) surface was cleaved, and a 10 Å vacuum layer was added to the unit cell to simulate periodic boundary conditions. There are LaO and CoO-terminated layer along the (001) direction. The simulated model includes four atomic layers in this paper: two LaO layers and two CoO layers. In the calculation process, the internal coordinates of the atoms were fully relaxed. There are LaO and CoO-terminated (001) two different surfaces for the LaCoO$_3$ (001), one surface oxygen atom was removed in these two surfaces to obtain the oxygen defective LaCoO$_3$ (001) surface, which are shown in Fig. 1.

3. Results and discussion

3.1. Adsorption of CO on the oxygen defective LaO-terminated LaCoO$_3$ (001) surface

The location of the oxygen vacancy may affect adsorption results. In this section we calculate the E_{ads} when oxygen vacancy is located in the first, second and third layer of the LaO-terminated LaCoO$_3$ (001) surface. The O–CO configuration was selected as the instance, which is the most stable configuration when CO adsorption on the perfect LaO-terminated LaCoO$_3$ (001) surface [20]. From our calculated results, the E_{ads} of the first, second and third layer are 1.25 eV, 1.12 eV, and 1.07 eV respectively. This implies that when oxygen vacancy is located in the first layer, it has the greatest influence effect on the adsorption of CO molecule. Therefore we will focus on the situation that when oxygen vacancy is located in the first layer.
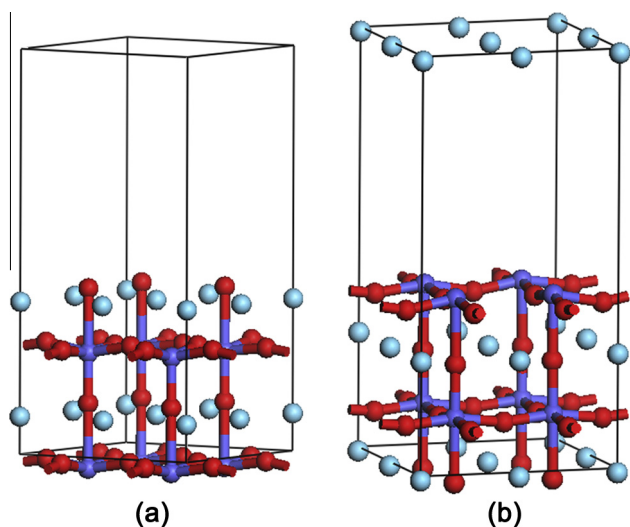

Fig. 1. Oxygen defective LaO and CoO-terminated LaCoO$_3$ (001) surface after relaxed: (a) LaO-terminated surface; (b) CoO-terminated surface. La atoms are shown in blue, Co atoms in purple and O atoms in red. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
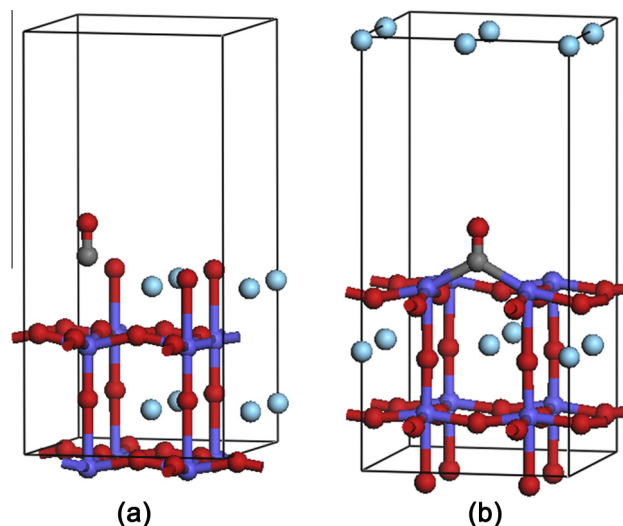

Fig. 2. Optimized configurations of defect-CO structure: (a) LaO-terminated LaCoO$_3$ (001) surface; (b) CoO-terminated LaCoO$_3$ (001) surface.

The O–CO structure is the most stable when CO adsorption on the perfect LaO-terminated LaCoO$_3$ (001) surface [20], However it is no longer the most stable configuration after introduction of oxygen vacancy. After optimized, the CO molecule gets away from the surface and do not form any bond with the surface. The elongation of C–O bond after adsorption is also very small. Although the adsorption energy and electrons transferred in the adsorption process increase, which are 1.25 eV and 0.26e respectively, they are not the highest compared with the defect-CO configuration. The defect-CO configuration is found to be the most stable structure when CO adsorption on the oxygen defective LaO-terminated LaCoO$_3$ (001) surface. Fig. 2(a) shows the defect-CO configuration after optimization. From our calculation, equilibrium distance between the CO and oxygen vacancy after optimization is 0.73 Å, suggesting that oxygen vacancy has strong adsorption capacity to CO molecule and the CO molecule enters into the oxygen vacancy after optimization. Bond length of the CO molecule is elongated from 1.15 Å to 1.21 Å after adsorption, demonstrating that the adsorption could activate the C–O bond of the CO molecule. The elongation of C–O bond is associated with the electrons transferred between the CO molecule and the surface. In the adsorption process, the CO molecule acts as accepter and the electrons transfer from the surface to it, which is consistent with the calculated results of the LaO-terminated LaCoO$_3$ (001) [20]. The electrons transferred in the adsorption process is 0.48e, greater than that in O–CO structure. The E_{ads} of defect-CO configuration is 1.77 eV, which is the biggest, showing that the defect-CO configuration is the most stable in the investigated configurations. In conclusion, when CO molecule adsorption on the oxygen defective LaO-terminated LaCoO$_3$ (001) surface with the defect-CO configuration, introduction of oxygen vacancy can increase the adsorption energy and electrons transferred in the adsorption process. The oxygen defective LaO-terminated LaCoO$_3$ (001) surface has better gas sensing properties to CO molecule than the perfect LaO-terminated LaCoO$_3$ (001) surface.

Further insight into bonding mechanism of the defect-CO structure can be obtained by analyzing Density of States (DOS). DOS of adsorbed CO molecule before and after adsorption in the defect-CO configuration is shown in Fig. 3. After adsorption, $1\pi^*$, 5σ and $2\pi^*$ orbits of CO are all delocalized and move to the low energy state, implying that these orbits do take part in the bonding progress. The 5σ band of the adsorbed CO shifts to −0.2 Ha and overlaps with the $1\pi^*$ Band, which is also broadened by the electrons