FIRST PRINCIPLE INVESTIGATION OF O₂ ADSORPTION ON THE LAMNO₃ (001) SURFACE

Zhi Guo Yan*, Hui Wang, Ai Guo Xuan, Ming Qi Chen and Yuan Xin Wu

Key Laboratory for Green Chemical Process of Ministry of Education,
Key Lab of Novel Reactor & Green Chemical Technology,
Wuhan Institute of Technology, Wuhan, 430073, P.R.China

Summary

In this paper, first-principle calculations is used to research the process of O₂ adsorption on the clean, defect-free stoichiometric MnO₂- terminated LaMnO₃ (001) surface. The calculations are based on the density-functional theory (DFT) pseudo potential approach, which has already proved highly successful in many previous studies of SrTiO₃ surfaces.

Keywords

density-functional theory, Adsorption, LaMnO₃ (001) surface

Abstract

In this paper, first-principle calculations is used to research the process of O₂ adsorption on the clean, defect-free stoichiometric MnO₂- terminated LaMnO₃ (001) surface. The calculations are based on the density-functional theory (DFT) pseudo potential approach, which has already proved highly successful in many previous studies of SrTiO₃ surfaces. Vanderbilt-type ultrasoft pseudopotentials (USPP) were employed to describe the electron–ion interactions. The exchange and correlation terms were described with the generalized gradient approximations (GGA) in the scheme of PBE; the charges on the atoms were estimated by projecting the occupied one electron eigenstates onto a localized basis set with a subsequent mulliken population. In all the calculations, the kinetic energy cutoff (600 eV for the bulk LaMnO₃, 300 eV for the adsorption mode) and the density of the Monkhorst-pack k-point for the bulk LaMnO₃ and adsorption model was 8×8×8, 3×5×1, respectively. Which were high enough to ensure convergence of the computed structures and energetic.

In order to verify the method used in our calculation, we first calculated the lattice constant of LaMnO₃ and the length of O-O of O₂. Results obtained in our calculation are in well agreement with the experiment value. We also found that: LaMnO₃ presents half-metal properties by calculating the band structure and density of states (DOS); in the MnO₆ octahedron the O-Mn-O bond is mainly covalent, on the contrast, O-La-O bond is mainly ionic. The adsorption of oxygen on the ABO₃ perovskite oxide was studied by three possible modes: O₂ forms bonds with one Mn site (M1) or two O binds to two Mn sites (M2) or one O interact with two Mn (M3). The adsorption energy of the three modes are all negative, indicating they may be the stable adsorption mode. E_M2 > E_M1 > E_M3, so, the M2 mode may be the most stable mode from the energy point of view; The bond length of O-O was lengthened apparently in the process of oxygen adsorption on the LaMnO₃ (001) surface. The bond length is similar with the bond length of calculated by the same method used in the calculation of free oxygen molecular, these indicate that: molecular oxygen can adsorb on the LaMnO₃ (001) surface, and the adsorption process leads to the formation of O₂⁻.

The valence of Mn is very important for the process of Pd⁰-Pd²⁺ for the synthesis of diphenyl carbonate (DPC), the changes valence of Mn in the adsorption process can

* To whom all correspondence should be addressed: zhgyan@mail.wit.edu.cn
be calculated quantitatively by Integrating for the curve of the PDOS of Mn-3d from -7.09~4.14eV($t_{2g}$), the results show that: the integral value of $t_{2g}$ band for M1 and M2 is smaller than that of the bulk by 0.24 and 0.31, so the valence of Mn for M1 and M2 is Mn$^{3+0.24}$ and Mn$^{3+0.31}$ after O$_2$ adsorption, so, M2 may be the most adsorption mode that can make Pd$^0$-Pd$^{2+}$ more quickly in the process of direct synthesis of diphenyl carbonate (DPC) using the catalyst -Pd supported on the LaMnO$_3$.

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References