FIRST PRINCIPLE INVESTIGATION OF O_2 ADSORPTION ON THE $LAMNO_3$ (001) SURFACE

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Summary

In this paper, first-principle calculations is used to research the process of O_2 adsorption on the clean, defect-free stoichiometric MnO_2- terminated $LaMnO_3$ (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 $SrTiO_3$ surfaces.

Keywords

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

Abstract

In this paper, first-principle calculations is used to research the process of O_2 adsorption on the clean, defect-free stoichiometric MnO_2- terminated $LaMnO_3$ (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 $SrTiO_3$ 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 $LaMnO_3$,300 eV for the adsorption mode) and the density of the Monkhorst-pack k-point for the bulk $LaMnO_3$ and adsorption model was $8\times8\times8$, $3\times5\times1$,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 $LaMnO_3$ and the length of O-O of O_2. Results obtained in our calculation are in well agreement with the experiment value. We also found that: $LaMnO_3$ presents half-metal properties by calculating the band structure and density of states (DOS); in the MnO_6 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 ABO_3 perovskite oxide was studied by three possible modes: O_2 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 $LaMnO_3$ (001) surface. The bond length is similar with the bond length of O_2^- calculated by the same method used in the calculation of free oxygen molecular, these indicate that: molecular oxygen can adsorb on the $LaMnO_3$ (001) surface, and the adsorption process leads to the formation of O_2^- .

The valence of Mn is very important for the process of Pd^0-Pd^{2+} for the synthesis of diphenyl carbonate (DPC), the changes valence of Mn in the adsorption process can

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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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