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A theoretical investigation of the α-MnO_2 (1 1 0) surface

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ABSTRACT

Density functional theory calculations have been carried out to investigate the α-MnO_2 (1 1 0) surface. It is shown that the energies of nonmagnetic (NM) and ferromagnetic (FM) states are higher than that of the antiferromagnetic (AFM) states, and at the same time some AFM states have similar stabilities. Using a 27-layer thick periodically repeated slab model, the (1 1 0) surface with all kinds of no reconstruction terminations have been calculated. The AFM surface T1 with the lowest surface energy of 0.77 J m^{-2} is the most stable surface, which exposes the crystal 2 × 2 semitunnel to air. When we put OH^- ions onto the surface T1, our computed results agree with the experimental atomic force microscopy results. We hope that our calculations would be helpful for the understanding of the α-MnO_2 (1 1 0) surface and further exploration of some adsorptions and reactions on it.

1. Introduction

α-MnO_2 can act as an efficient and robust water oxidation catalyst under visible light in strong acidic conditions [1], and O_2 reduction catalyst in a KOH solution [2]. Based on our experiments of dimethyl ether combustion, MnO_2 catalytic activities are mainly dominated by the crystalline phase, and α-MnO_2 is better than γ-MnO_2 and β-MnO_2 [3]. The α-MnO_2 crystal structures can be found from XRD pattern (JCPDS 44-0141) and the recent reports [4,5]. In terms of magnetism, the ground state of α-MnO_2 is considered to be antiferromagnetic or helical magnetic [6,7]. Using atomic force microscopy (AFM), Yamamoto et al. determined the atomic configuration and topography of the α-MnO_2 surface [8].

Computational chemistry and molecular modelling tools are capable of simulating crystal and surface structures and advancing our understanding of adsorption and catalysis behaviors on solid surfaces. In 2007, Franchini et al. reported the structural, electronic, magnetic, and thermodynamical properties of MnO, Mn_3O_4, α-Mn_2O_3, and β-MnO_2 crystals by density functional theory (DFT) methods [9]; in 2008, Kwon et al. reported the calculations of layered δ-MnO_2 [10]; in 2011, Oxford and Chaka reported the calculations of many kinds of β-MnO_2 surfaces [11]. For α-MnO_2 crystal, Cockayne and Li calculated the atomic, electronic, and magnetic properties in 2012 [12]; Duan et al. calculated Ni/Co/Fe-doped α-MnO_2 in 2012 and 2013 [13,14]. For α-MnO_2 surface, Tang et al. used the oxygen-rich and oxygen-lean α-MnO_2 surface model to explain the surface structure sensitivity of manganese oxides for low-temperature selective catalytic reduction of NO with NH_3 in 2011 and 2012 [15,16].

To achieve a deeper understanding of the α-MnO_2 crystal and surface, DFT with periodic boundary conditions have been applied to calculate α-MnO_2 crystal structures with different magnetic arrangements and different kinds of α-MnO_2 (1 1 0) surface terminations. The next section gives details of the computational model and the parameters used. The results section examines the crystal and surface structures. Then the most favorable crystal and surface structures are confirmed.

2. Computational method

The calculations were performed with DFT with periodic boundary conditions [11]. The exchange–correlation interaction was treated within the generalized gradient approximation (GGA) with the functional parameterized by Perdew, Burke and Enzerhof (PBE) [17]. Atomic basis sets were applied numerically in terms of a double numerical plus polarization function [18] and a global orbital cutoff of 4.7 Å was employed. The geometry optimization convergence tolerances of the energy, gradient, and displacement were 10^{-5} Hartree, 2×10^{-3} Hartree $Å^{-1}$, and 5×10^{-3} Å, respectively. All the structures were optimized at the same level of theory unless otherwise mentioned. The surface energy γ (J m^{-2}) is used to estimate the surface stability as follows:

$$\gamma = (U_{\text{surf}} - U_{\text{bulk}})/S_{\text{surf}} \tag{1}$$

where U_{surf} and U_{bulk} are the energies of the surface and crystal with the same number of bulk ions, respectively, and S_{surf} is the surface area. It is necessary to ensure that a sufficient number

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of layers are modelled so that the energy of the bulk has converged.

Although using effective on-site coulomb value (*U*) and exchange value (*J*) such as in Ref. [19] or some hybrid functionals such as in Ref. [9] may make some calculations fit to the experimental results. However, based on the computations of Franchini et al. [9], hybrid functionals and DFT + U tend to favor oxygen-poor compounds, leading to incorrect trends in calculated relative formation energies for various manganese oxides. Oxford et al. [11] also reported that the structures and energies would be better agreement with experimental results when the *U* correction was not included during the calculations of β-MnO_2 surfaces. By comparing our computational results of α-MnO_2 crystal (without using *U* and *J*) with the results from Cockayne et al. [12] (using *U* and *J*) in Section 3.1, we also find that our structure results are more near the experimental results such as in JCPDS 44-0141. Therefore, we did not include the *U* and *J* parameters in our DFT calculations. In addition, there was no uniformed *U* for MnO_2. Liechtenstein et al. [19] suggested *U* to be 2.8 eV for β-MnO_2. Franchini et al. [7] also tested different *U* such as 3 eV, 4 eV and 6 eV to get that 4 eV was better than the others, while the structure and energy results of 4 eV were not better than that of without using *U* in their Figs. 2 and 5, respectively for β-MnO_2. For α-MnO_2 crystals, Cockayne and Li [12] used 2.8 eV, but Duan et al. used 2.5 eV for Fe doped α-MnO_2 [13] and 2.8 eV for Co/Ni doped α-MnO_2 [14]. There would be different *U* and *J* values needed for different kinds of MnO_2 crystals and surfaces. For our system, there would be different *U* and *J* for α-MnO_2 crystal and its (1 1 0) surface. Then the surface energy γ would be no means when we used different *U* to calculate the energies of crystal and surface. In the present paper, all the simulations were based on the same method (without *U* correction), the comparison of the surface energies can provide an insight into the surface stabilities. All electron DFT calculations were performed using a DMol3 package [20–22] in Materials Studio (version 5.5).

3. Results and discussion

3.1. Calculations of α-MnO_2 crystal

Although α-MnO_2 has been shown to exhibit an antiferromagnetic or helical magnetic spin arrangement [6,7], an idealized collinear arrangement was modeled in this study, as has been done in previous studies [9,11]. An ideal α-MnO_2 supercell ($2 \times 1 \times 4$, $Mn_{32}O_{64}$) with a tetragonal structure was used to simulate the nonmagnetic (NM), ferromagnetic (FM), and four kinds of antiferromagnetic (AFM1–AFM4) states, as shown in Fig. 1 (where the O^{2-} ions are shown in red, the NM, FM and spin 'up' Mn^{4+} ions are in lavender, and the spin 'down' Mn^{4+} ions are in green). It should be noted that NM, AFM1, AFM2 and AFM4 are shown from top view in Fig. 1, and the rear Mn^{4+} ions possess the same spin state as the ions seen in the top view. AFM3 has the same top view as AFM1, but the behind Mn^{4+} ion possesses different spin state as shown in Fig. 1E. The Monkhorst–Pack *k* point sampling was set as $3 \times 3 \times 3$ in the supercell [23]. The optimized lattice parameters and energies are collected in Table 1.

From Table 1, we can see that the crystal energy is dramatically influenced by the magnetic arrangement. The NM and FM structures are 722.473 and 87.633 meV per formula unit higher in energy than AFM1. The AFM1 state is the ground state. It lies 3.096, 18.723 and 18.938 meV per formula unit lower than AFM2, AFM3 and AFM4 states, respectively. It should be noted that the energy difference between AFM1 and AFM2 is small, and Cockayne and Li [12] and Duan et al. [13,14] calculated α-MnO_2 and Ni/Co/Fe-doped α-MnO_2 crystal with the AFM2 state. The optimized bulk lattice constants of 9.8349 Å (−0.2%) and 2.8805 Å (+0.6%) for the AFM1 state are in excellent agreement with experimental JCPDS 44-0141 values (percent error shown in parentheses) and other experimental results [4,5]. It is clear that our structures are better than that of 9.702 Å (−1.52%) and 2.856 Å (−0.30%) from the DFT + U computations

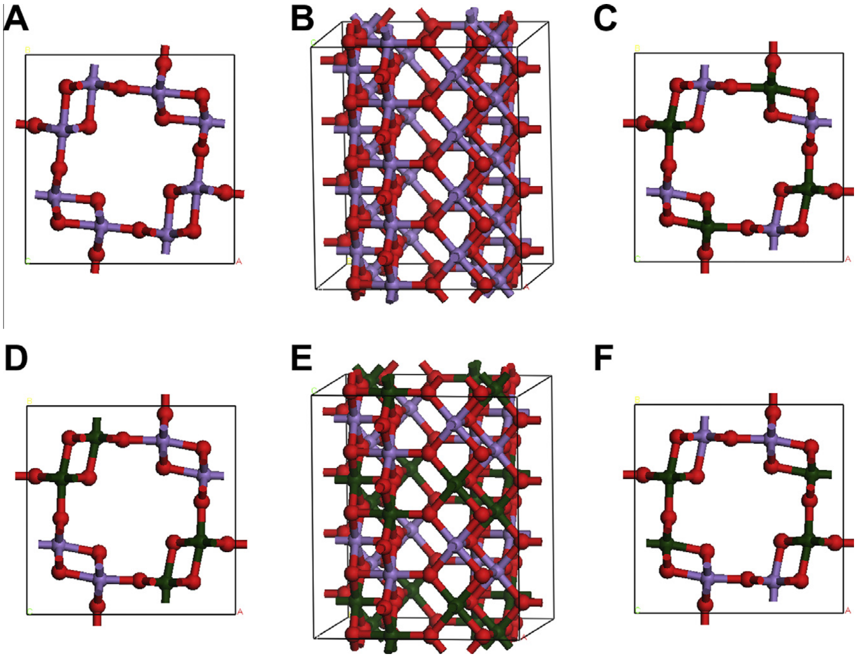

Fig. 1. The optimized α-MnO_2 crystal with the supercell $Mn_{32}O_{64}$, where the O^{2-} ions are shown in red, the NM, FM and spin 'up' Mn^{4+} ions are in lavender, and the spin 'down' Mn^{4+} ions are in green. (A) top view of NM state; (B) side view of FM state; (C) top view of AFM1 state; (D) top view of AFM2 state; (E) side view of AFM3 state; and (F) top view of AFM4 state. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)