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A theoretical study of stability and vacancy replenishing of $MoO_3(0\,1\,0)$ surfaces in oxygen atmosphere

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ABSTRACT

Oxygen vacancies on transition metal oxide surfaces are catalytically very important. The stability, shape and replenishing process of the vacancies are critical to understanding reactions happening on the surfaces. In this paper we investigate the stability of various defective $MoO_3(0\,1\,0)$ surfaces and examine the influence of environmental oxygen on the stability as well as the active sites for the replenishing process. Our calculations reveal that the line oxygen defect along *a* (asymmetric oxygen) direction is thermodynamically most favorable at higher defect concentration whereas point defect surfaces are unfavorable. Under normal experimental conditions the perfect surface dominates the $MoO_3(0\,1\,0)$. We show that for stoichiometric surfaces of any oxides (A_xO_y) the formation energy per vacancy controls the favorable defect shape (line or point defects). Calculations indicate that O_2 can dissociate readily on the surfaces that double vacancies share one Mo atom. The replenishing process of the oxygen vacancies through O_2 dissociation most likely occurs on the double-vacancy containing one terminal and one asymmetrical oxygen vacancies.

1. Introduction

Many transition metal oxides are important catalysts or supports of catalysts. As catalysts, their catalytic properties are strongly affected by the surface defect [1]. Oxygen vacancy is a special type of defect and plays an important role in catalysis. Surface oxygen vacancies not only affect the surface structure and electronic properties of the host system and thus influence the surface reactions, but also may directly take part in reactions. Hence studies of the stability and creation and annihilation of surface oxygen vacancies of metal oxides are of significance [1].

MoO_3 is one of the main components of the catalysts used to selectively oxidize propene to acrolein, acrylic acid and acrylonitrile [2,3]. It has also been widely used in anode/cathode interfacial layers in optoelectronic devices [4,5]. Selective catalytic oxidation itself is also very important in chemical industry because about 25% organic chemicals and intermediates are produced with this method [6,7]. The oxidation process is thought to obey the Mars–van Krevelen mechanism [8,9] which contains two stages. The first one is the oxidization of reactants by lattice oxygen and the reduction of the metal oxides. After the departure of the oxidation products, lattice oxygen vacancies are formed in the reduced metal oxides. In the second stage, the oxygen vacancies are annihilated by adjacent lattice oxygen (either at surface sites or in subsurface sites); Concomitantly, anion vacancies migrate toward the reoxidation site where dioxygen is dissociated and incorporated into the bulk, thereby re-establishing the original, fully oxidized state of the metal oxide. The two stages can be carried out totally independently.

Most theoretical studies on MoO_3 deal with the first stage, that is, oxidation of the reactants by the lattice oxygen. For example, propene oxidation and C—H bond activation of methane on MoO_3 surface have been theoretically investigated [10–14]. These studies provided useful information for us to understand the role of MoO_3 in the oxidation processes. Influence of vacancy on surface chemical properties has been verified theoretically by investigation of adsorption of hydrogen and methyl [15]. Relatively speaking, less work has been done regarding the second stage, creation and, especially the annihilation of the vacancy or the regeneration of the oxidization state of the surface by oxygen. Previously the point vacancy formation energies of oxygen atoms are studied using various methods and models [16–22]. Tokarz-Sobieraj et al. calculated the vacancy energy, 6.8–7.6 eV, for different oxygen sites at $MoO_3(0\,1\,0)$ surface with cluster models and found that oxygen binds to the substrate quite strongly [16]. Using slab model and DFT+U method, Coquet and Willock computed the vacancy energy

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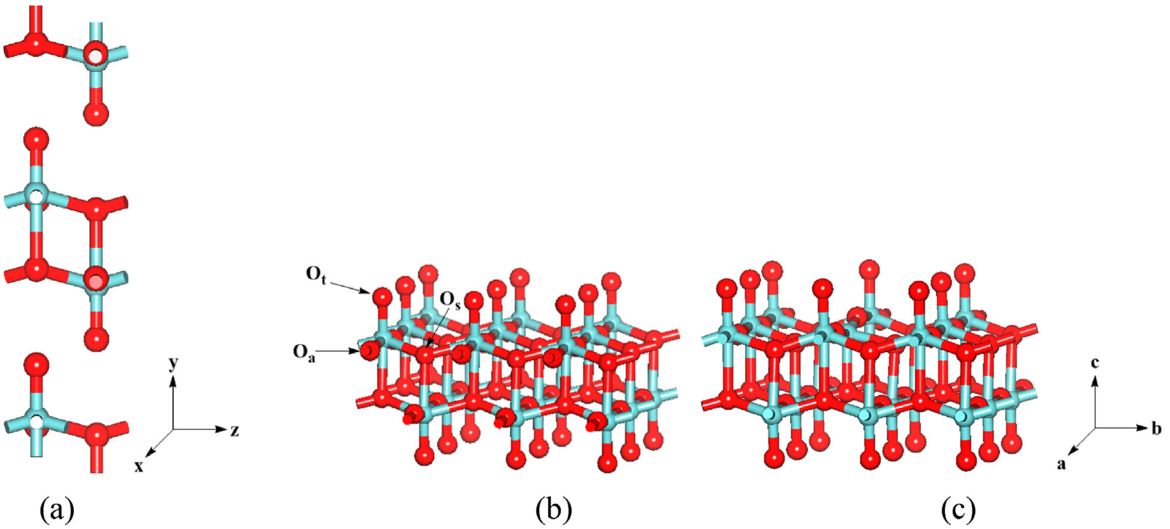

Fig. 1. The structures of MoO_3 bulk (a), perfect (b) and terminal defective (c) (0 1 0) surface.

to be 4.85–5.34 eV [21], which differs from the results by Tokarz-Sobieraj et al. by about 2.0 eV. Such large difference is likely due to the introduction of on-site electron-electron interaction, as indicated by ref. [21]. Witko et al. demonstrated that the pre-existing vacancy affects the formation of the second vacancy [18]. In particular, their work showed that the vacancies can be re-oxidized by gaseous oxygen, and di-vacancy formation from isolated vacancies is energetically favorable at MoO_3(0 1 0) surface while appearance of di-vacancy from isolated vacancies is unfavorable on V_2O_5(0 1 0). In addition, Witko et al. also investigated the re-oxidation process of vacancy on the single vacant MoO_3(0 1 0) and V_2O_5(0 1 0) surfaces. It is noted that studies reveal that the double vacancies mechanism has lower barrier than the single vacancy mechanism for the re-oxidation of the defective surfaces transition metal oxide, such as Co_3O_4 and TiO_2 [23,24].

In this paper, we concentrate on the stability of the perfect and defective MoO_3(0 1 0) surfaces and the annihilation process of the vacancies in oxygen atmosphere. We show that energetically point defects are unfavorable compared to aggregated ones and they prefer to form lines along the asymmetrical oxygen direction. We further demonstrate that the favorable vacancy shape (line or point defects) is determined by the formation energy per vacancy, a conclusion holding true for any stoichiometric surfaces of A_xO_y compounds. Finally we show that the di-vacancies containing a terminal vacancy and an asymmetrical oxygen vacancy are the most probable site for O_2 dissociation to annihilate the surface vacancies.

2. Computational method

The most stable structure of MoO_3 is orthorhombic, belonging to P_{bmn} space group with the experimental lattice parameters $a = 3.964$, $b = 13.863$ and $c = 3.699$ Å [25]. It has layered structure along the (0 1 0) direction (Fig. 1). There are three types of oxygen atoms in MoO_3. The terminal oxygen (O_t) only bonds to one Mo atom with a distance of 1.67 Å. The asymmetric oxygen atom (O_a) bonds to two Mo atoms. The two O_a-Mo bond lengths are 1.74 and 2.25 Å, respectively. The symmetrically bridging oxygen atom (symmetric oxygen, O_s) binds to three Mo atoms with two horizontal bonds of distance of 1.95 Å and one vertical bond with a longer length of 2.33 Å (Fig. 1).

All the calculations were performed using Vienna ab initio simulation program [26,27] (VASP). Widely used approximations for the exchange and correlation energy in density functional theory are mainly based on parameterization of nearly homogeneous electron gas. For the systems such as transition metal oxides, the electronic band gap may be underestimated and even a qualitatively wrong metallic ground state may be predicted. DFT + U approach [28,29] has proved to be able to study a large variety of strongly correlated compounds with considerable improvement with respect to LDA or GGA results. In this work, DFT (Perdew, Burke, and Ernzerhof (PBE) functional [30]) + U approach of Dudarev et al. [31] was applied to the molybdenum centers. A value of 6.3 eV was chosen for U–J parameter [21]. PBE + U predicted the total atomic spin density of 1.98 e on the Mo atom when the bound terminal oxygen is removed, compared to no spin density with PBE functional only. The electron-ion interaction was described by the projector augmented wave (PAW) method [32,33]. The Kohn–Sham equations were solved using a plane-wave basis set with a cut-off energy of 400 eV. Gaussian smearing method was adopted with a width of 0.2 eV to determine how the partial occupancies are set for each wavefunction. Dipole correction was considered where necessary. The (3 × 3) surface cells slab was used to model MoO_3(0 1 0) surface and Monkhorst–Pack (3 × 3 × 1) grids is used to sample the K-points. The vacancy formation energy E_f is defined as: $E_f = (E_{def} + n \times E_O - E_{perf})/n$, where E_{def} and E_{perf} are the total energies of the MoO_3 slab with and without defects. E_O is the energy of atomic oxygen. n is the number of oxygen lost in the defect surface. Transition states were searched by the nudged elastic band (NEB) method [34]. A total of eight images from the linear interpolation between the reactant and product states were used as the initial guesses for the reaction coordinates.

The stability of surfaces is characterized by Gibbs free energy per unit area $\gamma(T, P)$, and its calculation method has described in detail for other refs. [35–37]. The Gibbs free energy per unit area $\gamma(T, P)$ of a slab with two equivalent surfaces at temperature T and partial pressure P is calculated by:

$$\gamma(T, P) = \frac{1}{2A}[G^{slab} - N_{Mo}\mu_{Mo}(T, P) - N_O\mu_O(T, P)] \qquad (1)$$

Here A is the area of the surface unit cell, G^{slab} is the total Gibbs free energy of the slab, N_{Mo} and N_O are the numbers of Mo and O atoms in the supercell, μ_{Mo} and μ_O are the chemical potentials of a Mo atom in solid state and an O atom in gas phase, respectively. From the definition of Gibbs free energy, we can get

$$\gamma(T, P) = \frac{1}{2A}[E^{slab} + PV - TS - N_{Mo}\mu_{Mo}(T, P) - N_O\mu_O(T, P)] \qquad (2)$$