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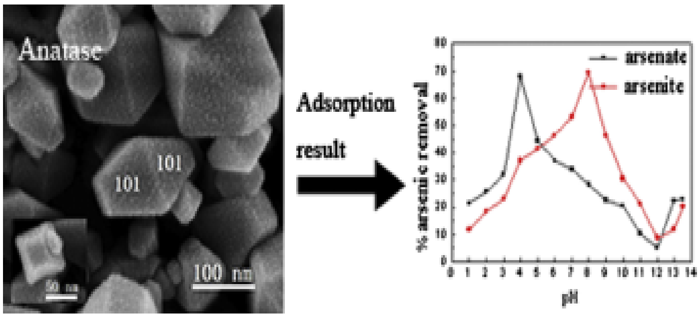
The effect of pH on the adsorption of arsenic(III) and arsenic(V) at the TiO_2 anatase [1 0 1] surface

Zhigang Wei [a,*], Kai Liang [a], Yang Wu [b], Yandi Zou [a], Junhui Zuo [a], Diego Cortés Arriagada [c], Zhanchang Pan [a], Guanghui Hu [a]

[a] *School of Chemical Engineering and Light Industry, Guangdong University of Technology, Guangzhou 510006, PR China*
[b] *College of Chemistry, Liaoning University, Shenyang 110036, PR China*
[c] *Laboratorio de Química Teórico-Computacional, Departamento de Química-Física, Pontificia Universidad Católica de Chile, Chile*

GRAPHICAL ABSTRACT



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ABSTRACT

Octahedral TiO_2 nanocrystals (OTNs) have been prepared by a hydrothermal method with the main surface of (1 0 1). Then the arsenic adsorption behavior on OTNs is investigated in a broad experimental pH range from 1.0 to 13.5. The maximum adsorptions of arsenite (As(III)) and arsenate (As(V)) appear at pH values 8 and 4, respectively. It is interesting to see that the minimum adsorptions of As(III) and As(V) are both at pH 12 and then their adsorptions increase again at higher pH values such as 13.0 and 13.5. To our best knowledge, it is quite new to report the arsenic adsorption on the controlled TiO_2 surface especially at very high pH values. These results might be helpful to understand the adsorption mechanism. On the other hand, periodic slab models of TiO_2 anatase (1 0 1) surface with some H^+ cations, some water molecules or some OH^- ions are suggested to simulate the pH effect. Using these models, the adsorptions of As(III) and As(V) are simulated by the density functional theory (DFT) method. Qualitatively, the adsorption abilities of arsenic species, water and OH^- follow the order of $AsO_3^{3-} > OH^- > HAsO_3^{2-} > H_2AsO_3^- > H_2O > H_3AsO_3$ for As(III) and $AsO_4^{3-} > OH^- > HAsO_4^{2-} > H_2AsO_4^- > H_3AsO_4 > H_2O$ for As(V). It implies that $H_2AsO_3^-$ should be the major As(III) species at pH 8 and $H_2AsO_4^-$ should be the major As(V) species at pH 4, and the most negative charged ions AsO_3^{3-} and AsO_4^{3-} should correspond to the adsorptions at the high pH values 13 and 13.5.

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* Corresponding author.
E-mail address: weizg2003@126.com (Z. Wei).

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ARTICLE

Importance of Metal Cations and Water for Stability of MnO_2 Crystals

Zhi-gang Wei[a,b*], Jia-hong Yan[a], Yang Wu[c], Yue Liu[a]

a. School of Chemical Engineering and Light Industry, Guangdong University of Technology, Guangzhou 510006, China
b. Institute of Theoretical Chemistry, Jilin University, Changchun 130023, China
c. College of Chemistry, Liaoning University, Shenyang 110036, China

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Metal cations as well as water are important factors to control the synthesis of MnO_2 crystal nanostructures. In this work, systemic Density functional theory calculations about α, β, δ-MnO_2 are presented to show the importance of metal cations and water for the structure stability and energy stability of MnO_2. It is shown that the α-MnO_2 crystal and its (110) surface will crash without the tunnel cations such as K^+, and the distance between the layers of the δ-MnO_2 will be significantly lower than that of the experimental results without the interlayer metal cations and water. At the same time, α-MnO_2 and δ-MnO_2 can be more stable than β-MnO_2 with metal cations and water, and vice versa.

Key words: MnO_2, Density functional theory, Metal cation, Formation energy, Structure simulation

I. INTRODUCTION

MnO_2 is a very useful material. It has more than 30 different crystal structures [1, 2], and can act as electrode, supercapacitor, catalyst, ion sieve, adsorbent, *etc.* [3−7]. In recent years, we tried to control the synthesis of nanostructured manganese oxide with different forms such as α, β, γ, δ, and improve their catalytic properties [8−12]. Based on these researches, we found that metal cations as well as water are important factors to control the synthesis of MnO_2 crystal nanostructures. For example, by using $MnSO_4$ and $KClO_3$ as starting materials under hydrothermal conditions, when there are sufficient K^+ and H^+, α-MnO_2 is the product; when there is no K^+ and H^+, γ-MnO_2 is the product; when there is only H^+, β-MnO_2 is the product; when there is no H^+ but Ac^-, MnOOH is the product [8]. It is obvious that metal cations and water are necessary to prevent collapse for large framework MnO_2 such as romanechite, todorokite, *etc.* [1]. In fact, these phenomena have alrealy been reported. In 1998, Fritsch *et al.* reported that the cations in the crystal tunnels were very important for the stability of MnO_2 crystals and without the tunnel cations large framework MnO_2 can not possibly be prepared [13]. In 2006, Johnson *et al.* demonstrated that the interlayer water is strongly bound to the interlayer cations, and plays an important role in the thermal stability of layered MnO_2 structures [14].

To my knowledge, there has not been a systemic theoretical study about the structure stability and energy stability of MnO_2, which corresponds to the metal cations and water in it. In the present work, we just take the framework α-MnO_2 (2×2 tunnel with metal cation K^+), β-MnO_2 (1×1 tunnel without metal cation), and layer structure δ-MnO_2 (1×∞ with and without metal cations and water) as examples to show the importance of the metal cations and water by the density functional theory (DFT) calculations.

II. METHODS

The calculations have been performed with DFT with periodic boundary conditions [15]. The exchange-correlation interaction is treated within the generalized gradient approximation (GGA) with the functional parameterized by Perdew, Burke and Enzerhof (PBE) [16]. Atomic basis sets are applied numerically in terms of a double numerical plus polarization function with a global orbital cutoff of 4.7 Å [17]. The geometry optimization convergence tolerances of the energy, gradient, and displacement are 10^{-5} Hartree, 2×10^{-3} Hartree/Å, and 5×10^{-3} Å, respectively. All electron DFT calculations in the present work are performed using a $DMol^3$ package in the Materials Studio (version 5.5) [18−20] at the same level of theory except the different Monkhorst-Pack k points [21] used for the different supercell calculations.

It is known that the hybrid and the PBE+U methods can give better electronic properties. However, we need to choose different U and different hybrid functionals for different MnO_2 crystals as well as their sur-

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[*] Author to whom correspondence should be addressed. E-mail: weizg2003@126.com

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

Yue Liu, Lin Yu *, Ming Sun, Guiqiang Diao, Bang Lan, Gao Cheng

School of Chemical Engineering and Light Industry, Guangdong University of Technology, Guangzhou 510006, PR China

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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:

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

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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* Corresponding author. Tel.: +86 20 39322202; fax: +86 20 39322231.
E-mail address: gych@gdut.edu.cn (L. Yu).

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发　明　人：魏志钢；左俊辉；潘湛昌；谢英豪；任超艳；杜欣欣；赵顺莲

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发　明　人：魏志钢；潘湛昌；肖楚民；陈世荣；胡光辉；许磊；徐艳阳
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