Adsorption of CO_2 on Bi_2MoO_6 (010) surface: A density functional theory study

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Abstract. The adsorption of CO_2 on Bi-end and MoO-end Bi_2MoO_6 (010) surfaces has been investigated by density functional theory (DFT) calculations. The results indicate that CO_2 exhibits physical absorption on both of the two surfaces, and Bi-end surface is more slightly active than MoO-end surface. Our results confirm that Bi_2MoO_6 has the potential for CO_2 decrease from the atmosphere and further conversion.

Introduction

Carbon dioxide (CO_2) as the main greenhouse gas that results from the fossil fuel utilization and human activities, makes global warming and climate change [1,2]. So to reduce the accumulation of CO_2 in the atmosphere is extremely urgent. Photocatalytic conversion of CO_2 into valuable chemicals by using the solar energy is considered as a green and potential strategy [3,4], which not only decreases the concentration of CO_2 in the air, but also use the solar energy at the same time to provide sustainable energy resources.

Semiconductor-based photocatalytic reduction of CO_2 has received an amount of attention due to its potential applications in clean energy and environmental cleanup [5,6]. Among various semiconductors, TiO_2 and Bi_2WO_6 have been demonstrated to exhibit excellent photocatalytic reduction of CO_2 into useful fuels, such as CH_4, CH_3OH and HCOOH [7,8]. Compared to them, the flat-band potential of Bi_2MoO_6 (-0.32 V vs NHE at pH = 7.0) is comparable to TiO_2 (-0.31 V) and Bi_2WO_6 (-0.33 V) [9], and it is more negative than the redox potential of CO_2/CH_4 (-0.24 V) which indicates that the photogenerated electrons of Bi_2MoO_6 can reduce the adsorbed CO_2 to CH_4. However, there are few reports about the photocatalytic conversion of CO_2 into useful fuels by using Bi_2MoO_6 materials. Therefore, it is essential to identify the effect of surface structure of Bi_2MoO_6 on CO_2 adsorption for developing better photocatalysts.

In this work, DFT calculation was performed to investigate the adsorption of CO_2 on Bi_2MoO_6 one of the most experimentally accessed surface, (010) surface [16-17]. Both the Bi-end and MoO-end (010) surfaces were considered. It is shown that these two surfaces can react with CO_2 molecules. The reactivity of Bi-end surface is stronger than that of MoO-end surface. The results will be useful to understand in great detail the chemistry of the Bi_2MoO_6 (010) surface.

Models and Computational Methods

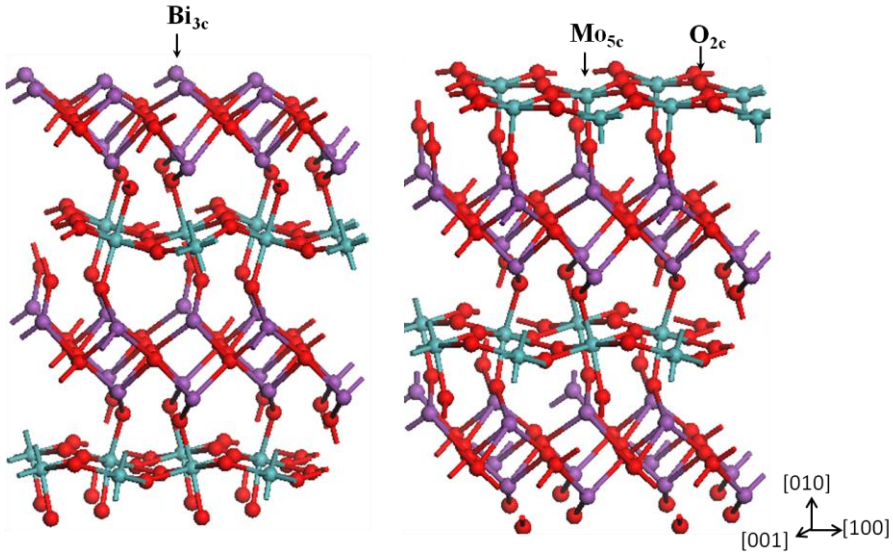
In this paper, all the calculations were carried out by Dmol3 package in Material Studio [10,11]. Exchange-correlation function is used by Perdew-Bruke-Ernzerhof (PBE) of generalized gradient approximation (GGA) [12]. The valence orbital of the atoms are described by the double-numeric-quality basic set with polarization functions (DNP) [13], and the core electrons are substituted by DFT semi-core pseudopotentials (DSPPs) [14]. The geometries are considered to be

converged until the energy difference dropped below 1.0 $\times 10^{-4}$ Ha/atom, the force dropped below 0.02 Ha/Å and the max displacement dropped below 0.05 Å. The optimized lattice parameters of the Bi_2MoO_6 crystal are a = 5.482 Å, b = 16.199 Å, and c = 5.509 Å. They are agreement with the corresponding experimental values: a = 5.4822 Å, b = 16.1986 Å, and c = 5.509 1 Å [15]. The results implied that our calculation results were reliable.

The Bi_2MoO_6 (010) surface was simulated by the periodic slab models composed of Bi-O-Mo layers with (2×2) supercell. During the geometric optimization, the six bottom layers were fixed equivalent to bulk structure, while the rest of the atoms were allowed to relax freely. For the free CO_2 molecule, a 10×10×10 Å unit cell was used. There was only threefold coordinated Bi (Bi_{3c}) adsorption site on the Bi-end (010) surface (see Fig.1a), while on MoO-end surface, two adsorption sites were exposed, including Mo_{5c} and O_{2c} (see Fig.1b).T he adsorption energy E_{ads} was calculated as following:

$$E_{ads} = E_{CO2} + E_{surface} - E_{CO2/surface}. \quad (1)$$

where E_{CO2} was the energy of an free CO_2 molecule in the vacuum, $E_{surface}$ was the energy of clean (010) surface and $E_{CO2/surface}$ was the total energy of the surface with CO_2 adsorption. According to the equation, a positive value of E_{ads} indicates a favorable adsorption configuration.



(a) Bi-end surface (b) MoO-end surface

Fig.1 Slab models of Bi_2MoO_6 (010) surfaces: (a) the Bi-end surface, (b) the MoO-end surface. Purple spheres represent Bi atoms, green ones represent Mo atoms and red ones represent O atoms.

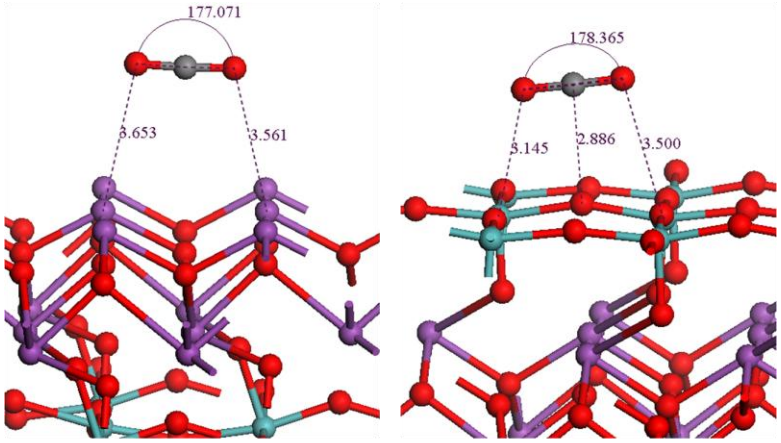
Results and discussion

Many experimental results have been to find that the Bi_2MoO_6 with (010) surface exposure exhibited the enhanced photocatalytic performance [16,17]. To correlate surface structures with photocatalytic activity, interaction between CO_2 and (010) surface of Bi_2MoO_6 was examined.

CO_2 adsorption on the Bi-end Bi_2MoO_6 (010) surface

As mentioned above, the (010) surfaces of Bi_2MoO_6 have two different terminated surfaces including Bi layer and MoO layer. We firstly performed the CO_2 interaction with the Bi-end Bi_2MoO_6 (010) surface. In this part, four configurations were calculated including one O atom of CO_2 molecule towards the surface Bi_{3c} vertically (OCO-Bi_{3c}-V), C atom of CO_2 molecule towards the Bi_{3c} horizontally (O_2C-Bi_{3c}-H), two O atoms of CO_2 towards two Bi_{3c} atoms horizontally (CO_2-Bi_{3c}-H) and CO_2 decomposition to CO and O atom on (010) surface (CO+O-Bi_{3c}-D). The adsorption energy for different adsorption configurations are shown in Table 1. We found that molecularly adsorption occurred for CO_2 molecule with the Bi_2MoO_6 (010) surface.

As we can see from Table 1, the adsorption energies of OCO-Bi_{3c}-V and CO+O-Bi_{3c}-D configurations are negative, which indicate that these adsorption cannot occur unless the addition of energy or any other auxiliary conditions. So these configurations are neglected. The adsorption energies for O_2C-Bi_{3c}-H and CO_2-Bi_{3c}-H configurations are 0.083 and 0.196 eV, respectively, which indicate that the CO_2 molecules are favorable to adsorb horizontally on the Bi-end (010) surface. In this configuration, the Bi-end Bi_2MoO_6 (010) surface provides chance to CO_2 molecules to be stayed. This adsorption, although not so strong, still can be a sign of the CO_2 to be decreased from air, if the working condition is slightly enhanced (e.g. not too high temperature). The CO_2-Bi_{3c}-H configuration is the most stable adsorption structure. It is reasonable because two O atoms of CO_2 molecule interact with two Bi_{3c} atoms generating bidentate structure as shown in Fig 2a. While for O_2C-Bi_{3c}-H configuration, CO_2 molecule absorbs via the C atom to form a monodentate structure. Thus, we will discuss the adsorption properties of CO_2-Bi_{3c}-H configuration in details.



(a) CO_2-Bi_{3c}-H **(b) O_2C-O_{2c}-H**

Fig.2 Optimized the stable adsorption structures of CO_2 on different terminated surface: (a) bidentate structure of Bi-end (010) surface O_2C-Bi_{3c}-H, (b) tridentate structure of MoO-end (010) surface O_2C-O_{2c}-H. Purple spheres represent Bi atoms, green ones represent Mo atoms and red ones represent O atoms.

Table 1 Adsorption energies for different configurations on the two surfaces

Systems	Configurations	Adsorption energy (E_{ads})[eV]
Bi-end (010) surface	OCO-Bi_{3c}-V	-0.350
	O_2C-Bi_{3c}-H	0.083
	CO_2-Bi_{3c}-H	0.196
	CO+O-Bi_{3c}-D	-1.411
MoO-end (010) surface	OCO-Mo_{5c}-V	-0.036
	O_2C- Mo_{5c}-H	0.056
	O_2C-O_{2c}-H	0.170

Note: V denotes the vertical configuration of CO_2 molecule toward the surface. H denotes the horizontal configuration and D denotes the dissociated condition.

It is easy to find that there is no obvious structure perturbation for CO_2-Bi_{3c}-H configuration comparing with the surface before CO_2 adsorption. And the bond length of C-O has a little stretch from 1.166 Å to 1.167 Å, and all the atoms of Bi-end (010) surface have not deformed obviously with displacement change less than 0.01 Å. The Bi_{3c} atoms interacting with CO_2 molecule have the most obvious displacement change of only about -0.002 Å. These results indicate that there is a relatively weak interaction between CO_2 and Bi-end (010) surface and CO_2 adsorption does not change the surface structure obviously. The distances of O_a-Bi_{3c} and O_b-Bi_{3c} between CO_2 molecule and the surface are 3.653 Å and 3.561 Å, respectively. The distances are much longer than the bond length of

Bi-O (2.197 Å). Then we can conclude that there is a physical adsorption occured. Zhou et al. [8] reported that CO_2 dissociation was thermodynamically favorable on the Bi-end Bi_2WO_6 (001) surface which was similar surface structures with Bi-end Bi_2MoO_6 (010) surface. Initially, we consider that the Bi-end Bi_2MoO_6 maybe has the same physicochemical properties as the Bi_2WO_6 materials. However, the results exhibit that CO_2 molecule not favorable to dissociate on the surface. To further clear the possibility of the photocatalytic reduction of CO_2 by using the Bi_2MoO_6 materials, the other terminated surface (MoO-layer) will be discussed.

CO_2 adsorption on the MoO-end Bi_2MoO_6 (010) surface

Then, we investigated the adsorption of CO_2 molecule on the MoO-end Bi_2MoO_6 (010) surface. On this surface, three configurations were considered including one adsorption through O atom of CO_2 towards to the surface Mo_{5c} vertically (OCO-Mo_{5c}-V), one adsorption via C atom to surface Mo_{5c} atoms horizontally (O_2C- Mo_{5c}-H) and another adsorption via C atom to surface O_{2c} atom and two O atoms of CO_2 towards two Mo_{5c} atoms horizontally (O_2C-O_{2c}-H). The adsorption energy for different adsorption configurations are also shown in Table 1. We found that the adsorption energy of CO_2 on the MoO-end Bi_2MoO_6 (010) surface is smaller than that of CO_2 on Bi-end surface.

In OCO-Mo_{5c}-V configuration, the adsorption energy is still negative, so the CO_2 molecules are preferential to horizontally absorb on Bi_2MoO_6 (010) surface whether Bi-end or MoO-end layers. And in O_2C-Mo_{5c}-H configurations, the adsorption energy is 0.056 eV, which indicated the relatively weak interaction between CO_2 and surface atoms. In accordance with the reason of the CO_2-Bi_{3c}-H configuration, we found the adsorption energy of O_2C-O_{2c}-H configuration is 0.170 eV, which is the stable configuration on the MoO-end surface due to the tribendate structure formation. Nevertheless, the adsorption energy is slight smaller than that on Bi-end Bi_2MoO_6 (010) surface (0.195 eV), which indicates that the MoO-end surface is less reactive than the Bi-end surface. The geometry of O_2C-O_{2c}-H configuration was shown in Fig 2b.

It can be seen from Fig 2b that the bond length of C-O has a little change from 1.166 Å to 1.165 Å and the displacement change of all surface atoms is less than 0.02 Å. The Mo_{5c} atoms interacting with CO_2 molecule has only 0.002 Å displacement change and the distance of O atoms of CO_2 to Mo_{5c} atoms are 3.145 Å and 3.500 Å, respectively, which indicate there is no former Mo-O bond broken and no new Mo-O bonds formation. In addition, the length of C-O bond is 2.886 Å, which is further larger than the C-O bond length of carbonate (1.439 Å) [18]. As a result, a molecular adsorption also occurred on the MoO-end Bi_2MoO_6 (010) surface. Compared to the Bi-end surface, the interaction between CO_2 and MoO-end Bi_2MoO_6 (010) surface is slight weaker.

It seems to realize the photocatalytic reduction of CO_2 molecule in theory, but our calculation results indicated that the interaction between CO_2 and Bi_2MoO_6 (010) surface was relatively weak. What is the reason? However, some revealed that the enhanced photocatalytic activity of Bi_2MoO_6 with exposed (010) surface originated from the oxygen defects and in-plane vacancies of MoO-end layer [16]. Thus, further studies of oxygen defects or vacancies need to be performed to reveal the mechanism of photocatalytic reduction of CO_2 on Bi_2MoO_6 materials.

Summary

Using DFT calculation, CO_2 adsorption on the Bi-end and MoO-end Bi_2MoO_6 (010) surface were performed. Calculation results show that the two surfaces have considerable reactivity to CO_2 molecule and physical adsorption occurred on Bi_2MoO_6 (010) surface. Moreover, the Bi-end surface is more active than MoO-end surface. Our results revealed the surface structure of Bi_2MoO_6 is important for CO_2 adsorption, which is useful for further experimental investigations and applications in photocatalysis.

Acknowledgements

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References

[1] J. Houghton: Rep. Prog. Phys. Vol. 68 (2005), p.1343.

[2] T. R. Karl, K. E. Trenberth: Science Vol. 302 (2003), p.1719.

[3] T. Sakakura, J. C. Choi and H. Yasuda: Chem. Rev. Vol. 107 (2007), p.2365.

[4] M. Mikkelsen, M. Jorgensen and F.C. Krebs: Energy Environ. Sci. Vol. 3 (2010), p.43.

[5] A. Mukherji, R. Marschall, A. Tanksale, C. Sun, S. C. Smith, G. Q. Lu and L. Z. Wang: Adv. Funct. Mater. Vol. 21 (2011), p.126.

[6] Z. G. Zou, J. H. Ye, K. Sayama and H. Arakawa: Nature Vol. 414 (2001), p.625.

[7] N. M. Dimitrijevic, B. K. Vijayan, O. G. Poluektov, T. Rajh, K. A. Gray, H. He and P. Zapol: J. Am. Chem. Soc. Vol. 133 (2011), p.3964.

[8] Y. Zhou, Z. P. Tian, Z. Y. Zhao, Q. Liu, J. H. Kou, X. Y. Chen, J. Gao, S. C. Yan and Z. G. Zou: ACS Appl. Mater. Interfaces Vol. 3 (2011), p.3594.

[9] M. C. Long, W. M. Cai and H. Kisch: Chem. Phys. Lett. Vol. 461 (2008), p.102.

[10] B. Delley: J. Phys. Chem. Vol. 100 (1996), p.6107.

[11] B. Delley: J. Chem. Phys. Vol. 113 (2000), p.7756.

[12] J. P. Perdew, K. Burke and M. Ernzerhof: Phys. Rev. Lett. Vol. 77 (1996), p.3865.

[13] Y. Inada and H. Orita: J. Comput. Chem. Vol. 29 (2008), p.225.

[14] B. Delley: Phys. Rev. B Vol. 66 (2002), p.155125.

[15] R. G. Teller, J. F. Brazdil and R. K. Grasselli: Acta. Cryst. Vol. C40 (1984), p.2001.

[16] Y. Zheng, F. Duan, J. Wu, L. Liu, M. Q. Chen and Y. Xie: J. Mol. Catal. A: Chem Vol.303 (2009), p.9.

[17] J. L. Long, S. C. Wang, H. J. Chang, B. Z. Zhao, B. T. Liu, Y. G. Zhou, W. Wei, X. X. Wang, L. Huang and W. Huang: Small Vol. 14 (2014), p.2791.

[18] L. Liu, W. L. Fan, X. Zhao, H. G. Sun, P. Li and L. M. Sun: Langmuir Vol.28 (2012), p.10415.