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The effects of subsurface O_v and Ti_{int} of anatase (1 0 1) surface on CO_2 conversion: A first-principles study

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ABSTRACT

Using the first-principles calculations, we explored the effects of intrinsic subsurface oxygen vacancy and Ti interstitial defects on the adsorption and reduction reaction of CO_2 at anatase (1 0 1) surface. Both PBE + U and HSE06 results show that such intrinsic defects have strong selectivity for the CO_2 binding to sites near the defects. For the most favorable site, the CO_2 adsorption energy can be greatly increased by 0.06 – 0.2 eV relative to the perfect surface. This enhancement is greatly affected by the local structure distortion and the location of the excess electrons. Furthermore, the reduction reactions of CO_2 into useful fuels such as HCOOH have also been explored. It is revealed that the energy barrier for the rate-limiting step of CO_2 activation can be greatly lowered by the intrinsic defects. These results show the important effects of the defects on the CO_2 adsorption and reduction processes.

1. Introduction

With the rapid development of world industry, tradition energy sources such as coal and fossil oil have been largely consumed, which has triggered serious energy crisis and environmental issues. Thus, it is urgent to search for alternative energy sources that are renewable and environmental friendly. Solar energy is considered as one of the inexhaustible and green energy sources, and it has drawn tremendous attentions on how to convert the incoming solar energy into available fuels. Among various strategies, photoreduction of CO_2 into chemical fuels such as CH_4, HCO_2H, CH_2O, and CH_3OH is considered as one of the most promising technologies [1,2]. Mimicking the natural photosynthesis, photoreduction of CO_2 into useful fuel is a promising approach to reduce CO_2 emission level and mitigate the energy crisis [3]. However, low conversion efficiency and weak CO_2 capture ability have greatly hindered its further real applications.

Since the pioneering research by Inoue et al. in 1979 [4], various semiconductors including TiO_2, CdS, Fe_2O_3, g-C_3N_4, Bi_2WO_6, Cu_2O, etc. have been proposed as photocatalysts to increase the efficiency for CO_2 photoreduction [5]. Among these photocatalysis, TiO_2, a prototype photo-catalyst has attracted much attention for its sufficiently high reduction potential for CO_2 conversion, low cost, and high stability. However, TiO_2 still suffers from several disadvantages that ultimately leads to the low reaction efficiency for the practical applications of CO_2 photoreduction, including the low solar energy utilization due to large band gap (3.2 eV for anatase TiO_2 and 3.0 eV for rutile TiO_2), fast recombination of electron-hole pairs, and weak interactions between CO_2 molecules and TiO_2 surfaces [6-8]. The first two limitations have been extensively researched on, and a number of solutions to them have been developed including the metal atom (such as Pt, Au) coupling, nonmetal doping [9-11], mixed phase TiO_2 [12], P-N heterojunction construction [13], photosensitizer decoration, and defect production [5,14]. However, limited attention has been focused on the last limitation, despite CO_2 adsorption being a key factor in determining CO_2 photoreduction efficiency.

So far, to enhance the CO_2 adsorption at the TiO_2 surface, surface modification, metal or nonmetal doping, and defect introduction have been mostly applied [15,16]. Among these approaches, defect introduction can most improve the adsorption of CO_2, as the defects can not only enhance the reactivity of the local surface structure but also change the electronic structure of the material [17]. During the photon-related process, the presence of defects can change the quantum yield of photonic excitation by tuning the energy band structure, modifying electron-hole separation, and carrier transport property [18,19]. For example, as for the perfect surface, the binding energy of CO_2 at rutile (1 1 0) surface is only about −0.34 eV [20,21], but for the defective

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surface with oxygen vacancies, the adsorption energy increases to −1.08 eV accompanied by a decrease in the energy barrier for the CO_2 reduction [22]. Furthermore, Luo et al. [23] have revealed that the surface oxygen vacancy can be used to effectively control the selectivity of the CO_2 reduction into CH_4.

Although the defects can greatly affect the CO_2 reduction process, the specific sites and effects of the intrinsic defects such as oxygen vacancy (O_v) and Ti interstitial (Ti_{int}) in TiO_2 are still unclear [24-27]. Scanning tunneling microscope (STM) experiment showed that the concentration of the oxygen vacancy is low at anatase (1 0 1) surface, suggesting the oxygen vacancy prefers residing on the subsurface or the inner layers [28]. Furthermore, Scheiber et al. studied the effect of temperature on O_v defect by electron bombardment [25]. Low-temperature STM result shows that the surface O_v starts to migrate to subsurface when the temperature is larger than 200 K. On the other hand, different functionals have been applied to study the stability and energetic of O_v in TiO_2 from theoretical side. Cheng et al. used pure GGA to study the formation energies and diffusion pathways of O_v and Ti_{int} at anatase (1 0 1) surface [28]. The GGA result shows that both O_v are energetically more stable by 0.5 eV in bulk or at subsurface site than that at surface, accompanied by the diffusion energy barrier of 0.74 eV from surface to subsurface. Using a more accuracy functional HSE06, Deak et al. examined the relative stability of the O_v at the different sites by calculating the formation energy of O_v. They found that the formation energy of subsurface O_v is about 5.03 eV, which is larger than that of surface one at about 4.81 eV [29]. Similar to defect O_v, Cheng et al. found that Ti_{int} is also energetically more stable by 0.5 eV in bulk or at subsurface site than that at surface by pure GGA [28]. Other result shows that the total energy of Ti_{int} closer to the surface is close to the one at deeper side, implying both sites are possible stable [30]. Based on the stable intrinsic defects, Liu et al. [31] found that the inner intrinsic defects of TiO_2 can have a significant effect on the CO_2 photoreduction. They explained that the inner intrinsic defects can also induce defect states in the band gap, which facilitates the absorption of the visible light. However, the detailed role of the inner defects in introducing the adsorption state and enhancing the photoreduction reaction of CO_2 is still unknown. Especially, the details of the surface structures upon the adsorption and the reaction processes have barely been explored at the atomistic level.

In this work, we are trying to understand the effects of subsurface O_v and Ti_{int} on the adsorption and reduction behaviors of CO_2 at anatase (1 0 1) surface by first-principles calculations. The outline of this paper is following: the structural and adsorption properties of CO_2 adsorbed at both perfect and defective anatase (1 0 1) surface will be investigated; According to the favorable adsorption structure, we will study the effects of intrinsic defects on the reduction of CO_2 into CH_4 process; Especially, we are trying to know the role of the excess electrons introduced by defects on both CO_2 adsorption and reduction process.

2. Computational method

All the results are calculated by the spin-polarized density functional theory (DFT) within periodic boundary conditions, as implemented in the CP2K/Quickstep package [32]. The CP2K implementation of DFT employs the hybrid Gaussian and plane wave (GPW) basis sets and the norm conserving Goedecker-Teter-Hutter (GTH) pseudo-potentials to describe the ion-electron interactions [33]. The Gaussian functions consisting of a double-ζ plus polarization (DZVP) basis set was used in our geometry optimization calculations. The energy cutoff for the real space grid is 500 Ry, which yields total energies converged to at least 0.001 eV per atom. Since the standard GGA functional [34] has the limitation to calculate the d-band electrons of transition metal, the GGA + U method is used with U = 3.5 eV for Ti_{3d} electrons [28]. Furthermore, the hybrid functional (HSE06) was also used for the CO_2 adsorption and electronic structure calculations. To account for the weak interaction between CO_2 and TiO_2 surface, the vdW contribution to the interaction is considered with the Grimme's empirical vdW functional (DFT-D3) [35]. In order to avoid the unphysical interactions between the adjacent images of the slab model, a vacuum spacing of 15 Å is placed for all the systems. Transition states along the reaction pathways are searched for by the Climbing Image Nudged Elastic Band (CI-NEB) approach [36]. The interaction between the adsorbed molecule and the substrate is described by the binding energy, as defined in Eq. (1),

$$E_b = E_{ab/sub} - E_{ab} - E_{sub} \tag{1}$$

where $E_{ad/sub}$ is the total energy of the adsorbed molecule and substrate, E_{ad} is the calculated energy of the isolated molecule in the same simulation box, and the E_{sub} is the energy of the substrate.

3. Results and discussions

Anatase (1 0 1) surface is the most stable and commonly exposed surface of anatase TiO_2. In the present study, a (1 × 4) supercell consisting of three tri-layers is used to represent the anatase (1 0 1) slab. At

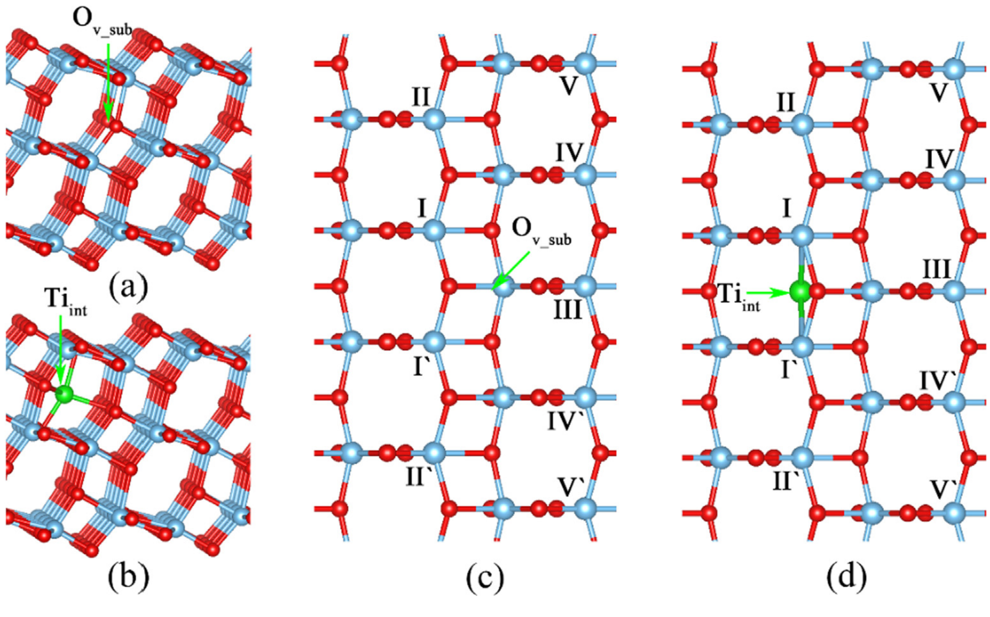

Fig. 1. The structure of defective anatase (1 0 1) surface. (a)–(b) Side view of the anatase (1 0 1) surface with subsurface O_{v_sub} and Ti_{int}, respectively. (c)–(d) Top view of the reduced anatase (1 0 1) surface with different Ti^{5c} atoms. The O atom is in red, Ti atom is in light blue for the TiO_2 system, and Ti_{int} is in green, hereinafter. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)