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Computational prediction of hydrogen sulfide and methane separation at room temperature by anatase titanium dioxide

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ABSTRACT

Removal of hydrogen sulfide (H_2S) is a key step for biogas purification. Herein, the adsorption of H_2S and methane (CH_4) on anatase titanium dioxide (TiO_2) has been studied by first principle calculations. It is found that TiO_2 offers excellent capacity for the H_2S/CH_4 separation. Using force-field molecular dynamics, this high separation capacity has been examined at room temperature.

1. Introduction

Biogas, generated from the anaerobic digestion of biological wastes, has been viewed as a promising renewable energy source [1,2]. Generally the major compositions of biogas are methane (CH_4) and carbon dioxide (CO_2), together with small amount of impurities, such as hydrogen sulfide (H_2S), moisture, nitrogen oxides, volatile organic compounds, etc. [1]. Among those impurities, H_2S is the most problematic contaminant due to its high toxicity and corrosivity. Therefore, efficient removal of H_2S is critical for the large-scaled applications of biogas.

In the industry, the technology most commonly employed for H2S removal involves the use of active media, such as iron oxides (Fe_2O_3 and Fe_3O_4), zinc oxide (ZnO), alkali solution, etc. [3,4]. Although such treatment is simple and effective, the removal is actually based on the consumption of the media. Using Fe_2O_3 as an example, $Fe_2O_3 + 3H_2S \rightarrow Fe_2S_3 + 3H_2O$; as a result, the used media needs to be renewed and safely disposed from time to time, which gets rise to additional cost and environmental concerns [5]. Another well-established technique is based on the Claus process, $H_2S + 1/2O + 2 \rightarrow S + H_2O$ [6]. Apparently, this process recovers elementary sulfur and no additional solid media has to be sacrificed, while the environmental issues associated with its by-products, like SO_x, are seriously concerned [7]. To address the environmental problems, it is desirable to develop clean technologies for H_2S-removal.

Photo-induced H_2S splitting, $H_2S \rightarrow S + H_2$, is attractive, because it not only recovers elementary sulfur as Claus process does, but also generates hydrogen fuel with sunlight as the only energy input. Therefore, photocatalytic decomposition H_2S over semiconductors has been proposed as an option to produce solar-hydrogen [8]. Using CdS-based photocatalysts, H_2S-splitting has been realized even under visible light [9], which can harvest more sunlight and thus reduce the purification cost. To make this feasible for biogas purification, it is essential to ensure that H_2S can be efficiently captured by photocatalysts, which underlines the importance of the separation of H_2S. Under this context, we investigated the adsorption of H_2S on anatase titanium dioxide (TiO_2), one of the mostly widely employed photocatalysts. The initial motivation is to investigate whether H_2S can be efficiently separately from CH_4 and strongly captured by TiO_2, which is the basis for photocatalytic H_2S-splitting. As shown below, anatase TiO_2 is an excellent media for H_2S/CH_4 separation, especially when they are dominated by minority surface (001). The photocatalytic splitting of H_2S over TiO_2 photocatalysts is out of the scope of this letter, but will be studied experimentally in the future. In nature, anatase TiO_2 crystals are dominated by the majority surface (101) [10], but if special controlling agents (e.g., fluorine acid) are employed, well-defined crystals with high percentage of minority surface (001) can be synthesized readily [11–14].

2. Computational methods

In nature, anatase TiO_2 crystals are dominated by the majority surface (101) [10], but if special controlling agents (e.g., fluorine acid) are employed, well-defined crystals with high percentage of minority surface (001) can be synthesized readily [11–14]. In this letter, both (101) and (001) have been investigated and modeled by slab models, as shown in Figure 1.

The adsorption of H_2S and CH_4 on (001) and (101) surfaces has been studied by density functional theory (DFT) [15]. The calculations were carried out using DMol3 package [16,17]. The exchange and correlation terms were treated under the generalized gradient

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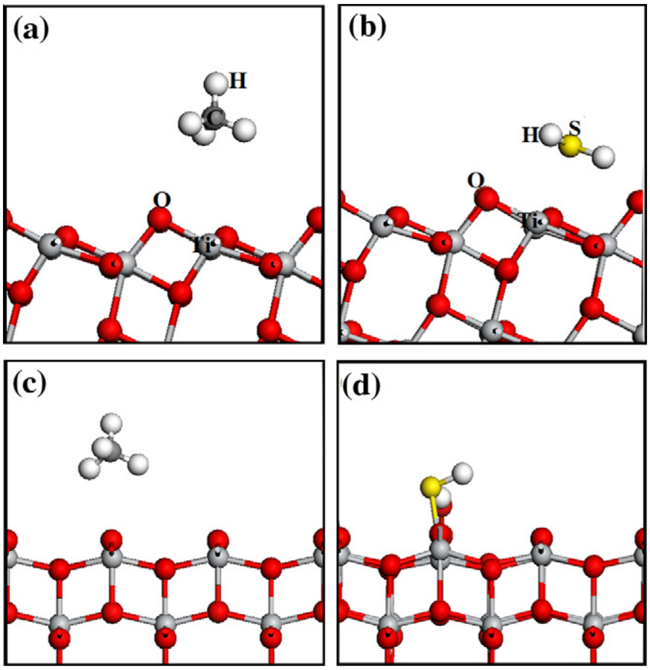

Figure 1. Optimized geometries for (a) CH_4 and (b) H_2S on $TiO_2(101)$, (c) CH_4 and (d) H_2S on $TiO_2(001)$.

approximation (GGA) functional by Perdew et al. [18]. A double numerical quality basis set with polarization function (DNP) were utilized for all geometric optimization and total energy calculations [19]. K-space was sampled by the gamma point due to the large size of the supercells. Along the z-direction, a vacuum space of 20 Å was employed to avoid the interaction between neighboring images. The gas–TiO_2 interaction was described by the averaged adsorption energy, Eads, which is defined by

$$E\text{ads} = E(\text{gas}) + E(\text{TiO}_2) - E(\text{gas—TiO}_2)$$

where E(gas), $E(TiO_2)$ and E(gas–TiO_2) are total energies of single gas molecule, clean TiO_2 slab and the interacting gas–TiO_2 system. By this definition, positive Eads indicates that the adsorption is stable.

Force-field molecular dynamics (FFMD) has been further employed to simulate the separation of H_2S from CH_4 based on periodical boundary models, as shown in the Support information (Figure S1). FFMD was performed in the NVT ensemble at 298.0 K, with a timestep of 1.0 fs. The overall simulation time is up to 400 ps (1 ps = 10^{-12} s), which is long enough to show the separation of H_2S as shown below. The random velocities were generated from the Boltzmann distribution and the temperature was maintained using the Andersen method [20] with a collision ratio of 1.00. The gas–gas and gas–TiO_2 interactions were described by the COMPASS force field [21].

3. Results and discussion

Figure 1 shows the optimized geometries of H_2S and CH_4 over (001) and (101) surfaces. As indicated by the adsorption energies (Eads), CH_4 can only weakly adsorb on both (001) and (101) with Eads = 0.02 and 0.03 eV, respectively, which is typical physisorption, being line with previous report [22]; however, H_2S can be strongly captured by anatase TiO_2, with Eads = 0.56 eV via molecular adsorption on (101), agreeing well with the report by Lin and coworkers (Eads = 0.49 eV) [23]. With respect to $TiO_2(101)$, (001) is more reactive and Eads is up to 1.43 eV. H_2S actually spontaneously dissociates on $TiO_2(001)$. On (101), there is a barrier of 0.37 eV for the dissociation of H_2S [23]. In fact, similar difference of the adsorption capacity between (101) and (001) has been well known for water on TiO_2 [10,24–26]. From the optimized geometries (see Figure S2 in the Support information), it is found that both five-coordinated titanium (Ti_{5c}) and two-coordinated oxygen (O_{2c}) are involved in H_2S dissociation on $TiO_2(001)$; moreover, short Ti_{5c}–O_{2c} distance plays a critical role for the formation of H–O_{2c} hydrogen bonds (HBs). Based on the above calculated data, it appears that TiO_2 surfaces, especially minority surface (001), can offer strong capacity to separate H_2S from CH_4 effectively.

Experimentally, the adsorption of H_2S on TiO_2 has been studied for many years [27–29]. Using temperature-programmed desorption, both molecular and dissociative adsorptions have been reported over rutile surfaces [30,31], and the dissociation is believed to be resulted by defects, like oxygen vacancies [30]. Over anatase TiO_2, however, only molecular adsorption has been identified [30]. It should be clear that typical anatase TiO_2 crystals are dominated by the majority surface (101). As shown in Figure 1b, H_2S does adsorb molecularly on (101). While in the case of anatase $TiO_2(001)$, which is the minority surface with a low percentage in most TiO_2 samples and has been rarely studied before, spontaneous dissociation of H_2S is obtainable even there is no defect, as predicted in Figure 1d. This may introduce new reaction routes for the degradation of H_2S over anatase TiO_2. For instance, HS_{ads} generated by H_2S dissociation may be attacked by photo-induced holes, and form $S^\bullet$ radicals via $HS_{ads} + h^+ \rightarrow HS^{\cdot+}_{ads} \rightarrow S^{\cdot}_{ads} + H^+$, with an analogy to the general reaction pathways proposed by Portela et al. [28]. $S^\cdot$ radicals may further react with other $S^\cdot$ radicals to form elementary sulfur or be directly oxidized by adsorbed O_2 or lattice oxygen to form SO_2. The above speculations is beyond the scope of this work, but will be investigated in our following work.

Giving that gas adsorption and desorption on surfaces are strongly affected by gas–gas and gas–TiO_2 collisions, it is essential to take more gas molecules involved in the simulation, which can be explored by large-scaled FFMD simulation. At the initial state, 72 H_2S molecules are homogeneously mixed with 288 CH_4 molecules and 6 H_2S molecules adsorb on TiO_2 based on energy minimization, as shown in Figure 2a. Only after 50 ps, half of the H_2S molecules are captured by TiO_2 (see Figure S3 in the Support information) and 220 ps later all H_2S molecules are separated from CH_4 and strongly adsorb on TiO_2, as shown in Figure 2b. In the following 180 ps (t = 220–400 ps), no H_2S desorption has been observed, indicating H_2S molecules are strongly captured by TiO_2 surface, being consistent with the prediction by DFT calculations.

To minimize the cost for renewing the TiO_2 media, it is expected that TiO_2 surfaces can keep the high working efficiency even when they are partially covered by H_2S molecules. As observed in FFMD, the adsorption rate of H_2S has no notable change when more and more H_2S molecules adsorb on TiO_2 surfaces. For instance, there are 162 Ti_{5c}-sites on the two surfaces of the slab shown in Figure 2, and at t = 210 ps, 70 sites have been occupied by H_2S and all the left by CH_4; however, the adsorption of the last two H_2S molecules only takes 10 ps. Such stable performance has been contributed by two factors: (i) CH_4 desorption occurs almost at the same rate with its adsorption, obviously due to its weak adsorption (Eads = 0.03 eV, comparable to the thermal energy at room temperature 0.026 eV), which is critically important since the adsorption sites occupied by CH_4 can be quickly released for H_2S adsorption; and (ii) H_2S molecules adsorbed on TiO_2 surface are linked with H_2S molecules in the H_2S/CH_4 stream by HBs (similar with the HB network in water) and thus promote the separation of H_2S from CH_4. In fact, almost all H_2S molecules can be captured by TiO_2 surfaces immediately when the H_2S–TiO_2 distance is smaller than 3.50 Å (Ti–S bond: 2.46 Å) based on the snapshots collected in this simulation.