



A DFT-based study of surface chemistries of rutile TiO₂ and SnO₂(110) toward formaldehyde and formic acid



Miru Tang^a, Zhenrong Zhang^b, Qingfeng Ge^{a,*}

^a Department of Chemistry and Biochemistry, Southern Illinois University, Carbondale, IL 62901, United States

^b Department of Physics, Baylor University, Waco, TX 76798, United States

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ABSTRACT

Rutile TiO₂ and SnO₂ are two structurally similar metal oxides found applications in catalysis and solid-state sensory devices as well as optics and electronics. In present work, we studied the adsorption and conversion of formaldehyde and formic acid on the (110) surfaces of rutile TiO₂ and SnO₂ based on density functional theory computational results. As oxygen vacancy is one of the most important and common defects on these metal oxides, the effect of the oxygen vacancy on adsorption and transformation were also examined. The results show that the adsorption of formaldehyde and formic acid resulted in similar adsorption configurations on SnO₂(110) and TiO₂(110). On the stoichiometric surface, SnO₂ exhibits a stronger binding toward the adsorbates than TiO₂. On the other hand, TiO₂(110) with one bridge-bonded oxygen vacancy shows a stronger binding toward the adsorbates than SnO₂(110) with the same type of defects. The bridge-bonded oxygen vacancy played important roles in adsorption and conversion and the Vo-bidentate formate species is the key intermediate in the oxidation of formaldehyde to formic acid. TiO₂(110) has a higher activity than SnO₂(110) for the reactions examined herein.

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1. Introduction

SnO₂ and TiO₂ are important oxides for many technologically important applications such as catalysis, solid-state gas sensor, thin-film coating and transistors [1,2]. These oxides have similar crystalline structures and metal-oxygen distances. Rutile is one of the stable phases of both oxides. The electronic band gaps of the rutile phase of the two oxides are also similar. However, Sn is a main group metal and Ti is a 3d metal. This intrinsic difference in their electronic structures will inevitably result in different physicochemical properties and reactivity.

There have been extensive studies, both experimentally and computationally, on various properties and different applications of these oxides [3–6]. In particular, the most stable (110) surface of the rutile phase has been a focus for TiO₂ and treated as prototypical model of metal oxides for many fundamental surface studies [1]. Both TiO₂ and SnO₂ are considered as reducible metal oxide and the bridge-bonded oxygen vacancy (Vo) sites are the most prevalent defects on the (110) surface [1,2]. The Vo sites may act as an electron donor to modify the surface electronic structure and result in stronger binding of the adsorbates and/or higher reactivity [7–9].

The volatile organic compounds such as formaldehyde and acetone are the main indoor pollutants. Their detection and remediation are important to maintain a healthy living environment [10]. SnO₂ and TiO₂ are often the active ingredients in solid state gas sensor materials that detects these compounds and in catalysts that are used in photochemical treatment of the pollutants. In addition, formaldehyde and formic acid are commodity chemicals and are widely used to produce value-added compounds through various heterogeneous catalytic processes, in which TiO₂ and SnO₂ are important components of the catalysts. Furthermore, formaldehyde and formic acids are small organic molecules and often serve as probe molecules in researches under well-defined condition to understand the underlying physical/chemical origins of the complex chemical processes. Therefore, the study of the adsorption and conversion of formaldehyde and formic acid is of great interests not only in terms of fundamental research but also the practical applications. Previously, we reported combined density functional theory (DFT) and scanning tunneling microscopic (STM) studies of the diffusion of Vo on TiO₂(110) [11] as well as its role of the vacancy in adsorption and diffusion of acetone [12] and formaldehyde [13,14]. For acetone adsorption and diffusion, we found an almost perfect agreement between STM and DFT results [12]. In contrast, the relative stabilities and adsorption configurations for formaldehyde on TiO₂(110) predicted by DFT, although agrees with

* Corresponding author. Fax: +1 618 453 6408.
E-mail address: qge@chem.siu.edu (Q. Ge).

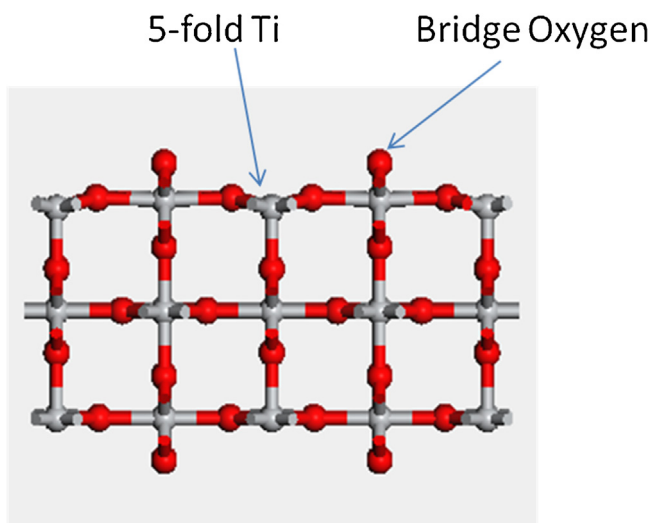


Fig. 1. A slab of three tri-layers representing the (110) surface of rutile TiO_2 and SnO_2 . Light grey sphere represent the Ti (Sn) atoms and red the O atoms. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

previous theoretical results, were not in line with the STM results [15].

Formic acid can be produced from oxidation of formaldehyde. The adsorption of formic acid on a metal oxide can be molecular or dissociative and can be used to probe the acid–base property of metal oxides [16,17]. Dissociative adsorption results in a surface formate species and a surface hydroxyl as a result of breaking the O–H bond in HCOOH and forming a O–H bond between hydrogen and bridge-bond oxygen (O_b) [18,19]. The surface formate species will further dissociate to form CO, CO_2 , H_2CO and H_2O at higher temperatures.

In the present work, we first studied the adsorption of formaldehyde and formic acid on $\text{SnO}_2(110)$ and $\text{TiO}_2(110)$. We then examined the conversion between formaldehyde and formic acid on these surfaces with a focus on the roles of O_b and Vo . Our results show that although the oxidation of formaldehyde is possible on both oxide surfaces, $\text{TiO}_2(110)$ has a higher reactivity.

2. Computational details

All calculations were performed using the Perdew–Burke–Ernzerhof (PBE) functional [35] with the Projector-Augmented Wave (PAW) method [36] implemented in the Vienne Ab-Initio Simulation Package (VASP) [37,38]. The semicore 3d and 4s states of Ti, and the 5s and 5p of Sn were treated as the valance states within the PAW method.

The cutoff energies of the plane wave basis sets were set at 400 eV. We used the same $\text{TiO}_2(110)$ model as that was used our previous study, i.e., a supercell with a dimension of $6.58 \text{ \AA} \times 11.87 \text{ \AA} \times 20.16 \text{ \AA}$ equivalent of a $p(2 \times 4)$ surface unit cell [13]. For comparison, $\text{SnO}_2(110)$ was also built from its corresponding relaxed bulk structure into a supercell with a similar dimension of $6.37 \text{ \AA} \times 13.40 \text{ \AA} \times 19.31 \text{ \AA}$. A Monkhorst–Pack K-point grid of $2 \times 4 \times 1$ was applied to both surface slabs. Each slab consists of 24 metal atoms and 48 O atoms, distributed in a three-trilayer model, shown in Fig. 1. The top trilayer was relaxed while the bottom two trilayers were fixed in the bulk positions. Bridge-bonded oxygen vacancy was created by removing one O_b atom from the corresponding stoichiometric surface. The adsorption energy was defined as:

$$E_{\text{ad}} = E_{\text{total}} - (E_{\text{sur}} + E_{\text{adsorbate}})$$

Table 1

Bond distances and adsorption energies of formaldehyde on the stoichiometric and defective TiO_2 and $\text{SnO}_2(110)$ surfaces.

	TiO_2		SnO_2	
	Ti–O (Å)	E_{ad} (eV)	Sn–O (Å)	E_{ad} (eV)
a) η^1 Ti-titled	2.21	–0.79	2.29	–1.00
b) η^2 Ti (Sn)-dioxyethylene	1.84	–1.66	2.04	–1.76
c) η^1 O-top	2.28/2.27	–0.93	2.37/2.43	–0.73
d) η^2 O-dioxyethylene	1.92	–1.23	2.06	–0.99

where E_{total} is the total energy of the surface with adsorbed molecule, and E_{sur} and $E_{\text{adsorbate}}$ are the energies of the clean surface slab and the isolated adsorbate molecule, respectively.

3. Results and discussion

3.1. Adsorption of formaldehyde, formate and formic acid on the (110) surface of TiO_2 and SnO_2

3.1.1. Adsorption of formaldehyde

Since we have reported formaldehyde adsorption and diffusion on $\text{TiO}_2(110)$ in a combined experimental and computational study previously [13], we only report the key features here briefly. Formaldehyde adsorbs in two stable configurations on the stoichiometric TiO_2 surface, as shown in Fig. 2a and b. In Fig. 2a, CH_2O binds the Ti site of the surface through its oxygen atom. In Fig. 2b, the adsorbed CH_2O forms a surface dioxyethylene species by bridging O_b and the five-coordinated Ti site. On the surface with one Vo , the adsorption of formaldehyde would give two additional stable configurations at the Vo site (Fig. 2c and d). In the η^1 O-top (Fig. 2c) configuration, the O atom of CH_2O occupies the Vo site with the OCH plane parallel to the O_b row. In the η^2 Ti-dioxyethylene (Fig. 2d) structure, the carbon atom bridges the neighboring O_b atom in the same row. The calculated adsorption energies and distance between O of CH_2O and the nearest surface Ti shown in Table 1 indicate that the dioxyethylene species (Fig. 2b and d) are more stable than the η^1 configuration on both stoichiometric and Vo surfaces. Detailed structural information including bond distances can be found in our previous publication [13]. We note that our calculated relative stability of these configurations is in agreement with the previous report using the PW91 functional [20], but not in line with the experimental observation that formaldehyde prefers to adsorb in the Vo sites [13].

On $\text{SnO}_2(110)$, both the stoichiometric and Vo surfaces, the adsorption of formaldehyde results in very similar adsorption configurations to those formed on $\text{TiO}_2(110)$, shown in Fig. 2. The bond distances in the optimized configurations and the calculated adsorption energies were also listed in Table 1 along with those on $\text{TiO}_2(110)$. Generally, the Sn–O distances are longer than the Ti–O distances in all four configurations. Moreover, the stoichiometric $\text{SnO}_2(110)$ has a stronger binding towards CH_2O than $\text{TiO}_2(110)$. In contrast, $\text{SnO}_2(110)$ with Vo exhibits a weaker binding than $\text{TiO}_2(110)$. This result indicates that presence of Vo makes TiO_2 more reactive towards adsorption of formaldehyde than SnO_2 .

3.1.2. Adsorption of formic acid

Similar to formaldehyde adsorption, the adsorption of formic acid on the stoichiometric and defective surfaces resulted in four stable configurations: two on each, as shown in Fig. 3. The bond distances in the optimized configurations and the calculated adsorption energies on both $\text{TiO}_2(110)$ and $\text{SnO}_2(110)$ were listed in Table 2. On the stoichiometric surface, the molecularly adsorbed formic acid binds the surface at the five-coordinated Ti(Sn) site, forming the monodentate structure shown in Fig. 3(a). In this structure, the Ti–O and Sn–O distances are 2.25 Å and 2.36 Å,

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