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

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Abstract

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.

Key words: DFT, TiO₂, SnO₂, formaldehyde, formic acid

1. Introduction

SnO_2 and TiO_2 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 TiO_2 and treated as prototypical model of metal oxides for many fundamental surface studies.[1] Both TiO_2 and SnO_2 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] SnO_2 and TiO_2 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 TiO_2 and SnO_2 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 $\text{TiO}_2(110)$ [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 $\text{TiO}_2(110)$ predicted by DFT, although agrees with 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 V_o . 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 with the Projector-Augmented Wave (PAW) method implemented in the Vienne Ab-Initio Simulation Package (VASP). 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 Figure 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:

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

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

Figure 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.

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 $TiO_2(110)$ 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 surfaces, as shown in Figure 2a and 2b. In Figure 2a, CH_2O binds the Ti site of the surface through its oxygen atom. In Figure 2b, the adsorbed CH_2O forms a surface dioxymethylene species by

Figure 2. Optimized adsorption configurations of CH₂O on rutile TiO₂(110) and SnO₂(110). (a) η^1 Ti (Sn)-titled, (b) η^2 Ti (Sn)-dioxymethylene, (c) η^1 O-top, (d) η^2 O-dioxymethylene. Light grey sphere represent Ti (Sn) atoms, dark grey C, white H and red O. See text for details.

bridging O_b and the five-coordinated Ti site. On the surface with one V_o, the adsorption of formaldehyde would give two additional stable configurations at the V_o site (Figure 2c and 2d). In the η^1 O-top (Figure 2c) configuration, the O atom of CH₂O occupies the V_o site with the OCH plane parallel to the O_b row. In the η^2 Ti-dioxymethylene (Figure 2d) structure, the carbon atom bridges the neighboring O_b atom in the same row. The calculated adsorption energies and Ti—O distances shown in Table 1 indicate that the dioxymethylene species (Figure 2b and 2d) are more stable than the η^1 configuration on both stoichiometric and V_o 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 V_o sites. [13]

On SnO₂(110), both the stoichiometric and V_o surfaces, the adsorption of formaldehyde results in very similar adsorption configurations to those formed on TiO₂(110), shown in Figure 2. The bond distances in the optimized configurations and the calculated adsorption energies were also listed in Table 1 along with those on TiO₂(110). Generally, the Sn—O distances are longer than the Ti—O distances in all four configurations. Moreover, the stoichiometric SnO₂(110) has a stronger binding towards CH₂O than TiO₂(110). In contrast, SnO₂(110) with V_o exhibits a weaker binding than TiO₂(110). This result indicates that presence of V_o makes TiO₂ more reactive towards adsorption of formaldehyde than SnO₂.

Table 1. Bond distances and adsorption energies of formaldehyde on the stoichiometric and defective TiO₂ and SnO₂ (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)-dioxymethylene	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-dioxymethylene	1.92	-1.23	2.06	-0.99

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 Figure 3. The bond distances in the optimized configurations and the calculated adsorption energies on both TiO₂(110) and SnO₂(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 Figure 3(a). In this structure, the Ti-O and Sn-O distances are 2.25 Å and 2.36 Å, respectively. In addition, formic acid can dissociate to form a bridge bidentate formate species (Figure 3(b)) on the stoichiometric surfaces by binding two oxygen atoms at the five-coordinated Ti(Sn) sites. The dissociated hydrogen atom forms a surface hydroxyl with next O_b atom. Figure 3(b) is also the commonly observed configuration of formate adsorption. On TiO₂, the Ti-O distance is 2.06 Å, reported both experimentally and theoretically.[21-25] Formic acid also can adsorb dissociatively at the Vo site with H⁺ shifting to the neighboring O_b site (Figure 3(c) and 3(d)). In Vo-bidentate structure shown in Figure 3c, one O of the formate species fills in the oxygen vacancy sites whereas the other O atoms forms a Ti(Sn)-O bond. The lengths of the two O-metal bonds are 2.13 Å and 2.27 Å on TiO₂, and 2.25 Å and 2.36 Å on SnO₂. In Figure 3(d) the O atom of the formic acid fills in the Vo site whereas the other O atom does not bind the surface directly. This monodentate formate species has its molecular plane in parallel with the bridge oxygen row of the surface. In this configuration, the Ti-O distances are 2.15 Å and 2.16 Å, and the Sn-O distances are 2.30 Å and 2.22 Å, respectively. Similar to adsorbed formaldehyde, the adsorbed formic acid on SnO₂ has a longer

Figure 3. Optimized adsorption configurations of HCOOH on the $\text{TiO}_2(110)$ and $\text{SnO}_2(110)$ surfaces. (a) Ti(Sn)-monodentate, (b) Ti(Sn)-bidentate, (c) Vo-bidentate, (d) Vo-monodentate, light grey sphere represents Ti (Sn) atoms, dark grey C, white H and red O. The insets in (b) and (c) show the side view from the perpendicular direction.

Table 2. Bond distances and adsorption energies of formic acid and formate on stoichiometric and defective TiO_2 and SnO_2 (110) surfaces. In the first column, a corresponds to the adsorbed *formic acid* configuration in Figure 3(a), and b, c, d are the corresponding *formate* configurations in Figure 3(b)-(d).

	TiO_2		SnO_2	
	O-Ti ($\text{\AA}$)	E_{ad} (eV)	O-Sn ($\text{\AA}$)	E_{ad} (eV)
a	2.25	-0.8	2.36	-0.95
a + Vo	-	-	2.36	-0.52
b + HO _b	2.07	-2.2	2.18	-2.55
b + HO _b + Vo	2.11	-1.78	2.19	-1.85
b	2.04	-1.98	2.16	-2.25
b + Vo	2.06	-3.73	2.17	-3.08
c + HO _b + Vo	2.13/2.27	-2.29	2.25/2.36	-2.13
c + Vo	2.13/2.26	-3.85	2.28/2.31	-3.34
d + HO _b + Vo	2.15/2.16	-1.93	2.30/2.22	-1.3
d + Vo	2.09/2.11	-3.29	2.17/2.17	-3.01

Sn-O bond length than Ti-O.

3.1.3 Adsorption of formate

In addition to be treated as a product of formic acid dissociation, formate can be examined independently for its adsorption on the surface as it is an important intermediate that links different reaction pathways, including the oxidation of formaldehyde and the dissociation of formic acid. On the stoichiometric TiO_2 and SnO_2 surfaces, the formate species prefers to bind at the five-coordinated Sn or Ti sites. On the stoichiometric TiO_2 surface, the adsorption of formate results in two stable adsorption configurations (Figure 4(a) and 4(b)). The formate adsorption structure of Figure 4(a) is similar to the formate portion of the dissociatively adsorbed formic acid (Figure 3(b)), i.e. a bridge-bonded bidentate formate species (Figure 4(a)). The Ti-O distance is 2.04 Å and Sn-O 2.16 Å. In Figure 4b, two oxygen atoms bind the same

Figure 4. Optimized adsorption configurations of HCOO on stoichiometric TiO_2 (SnO_2) surface. Light grey sphere represent Ti (Sn) atoms, dark grey C, white H and red O.

five-coordinated Ti atom with a Ti-O distance 2.16 Å, forming a bidentate chelate structure. In contrast, our calculation showed that only the bridging bidentate structure is stable on SnO_2 . The chelate structure shown in Figure 4b is not stable on SnO_2 (110). On the V_O defective surfaces, adsorption of formate resulted in three similar adsorption configurations to those shown in Figure 3(b)-(d). These configurations may be intermediates in the dehydration and dehydrogenation processes of formic acid.[26, 27] The relative stability of the three adsorbed

formate species shown in Figure 3 has an order of 3(d) < 3(b) < 3(c) on both TiO₂(110) and SnO₂(110). The Sn-O distances are also longer than the Ti-O distances in the corresponding configurations. The adsorbed formate configuration in Figure 3(b) is stable on the both stoichiometric and defective TiO₂ and SnO₂ surfaces. As shown in Table 2, introducing oxygen vacancy stabilizes the adsorbed formate species on both surfaces.

Comparing all the adsorbed configurations of formic acid and formate on the two stoichiometric surfaces, we find that SnO₂ shows stronger binding toward the adsorbates than TiO₂ (Figure 3(a), 3(b) and 4(a)). However, the adsorption energies of the similar adsorption configurations on TiO₂ in the oxygen vacancy site (Figure 3(c) and (d)) are larger than those on SnO₂. These differences in binding strength can be attributed to the more localized electrons near the oxygen vacancy on TiO₂.

3.2 Effect of oxygen vacancy on surface chemistries

The conversion of the adsorbed species transformation on the surface is important to catalysis and often holds keys to understand the catalytic mechanism and optimize catalytic performance. The reactive O_b and Vo on both SnO₂(110) and TiO₂(110) play important roles in catalysis and sensors, often through the Mars-van Krevelan mechanism. In this mechanism O_b reacts with the adspecies, creating Vo on the surface. Therefore, the generation and diffusion as well as the replenish of the Vo sites directly impact the reaction on these surfaces. We previously studied the diffusion of Vo on TiO₂(110) as well as their reactivity toward a range of molecules both experimentally and theoretically. Herein, we examined water formation and conversion between formic acid and formaldehyde on SnO₂(110) and TiO₂(110) to evaluate factors that contribute to the difference of the surface reactivity. In particular, we started by examining Vo formation as both reactions involve O_b and Vo [4, 28].

The direct formation of Vo can be viewed as formation and desorption of molecular oxygen, i.e.

The formation energy can be calculated by taking the difference of the stoichiometric slab and the slab with one Vo plus half of an oxygen molecule, i.e. $E_{\text{ad}}(\text{direct}) = E(\text{de-TiO}_2/\text{SnO}_2) + 1/2E(\text{O}_2) - E(\text{TiO}_2/\text{SnO}_2)$, $E(\text{O}_2)$ is the total energy of an isolate O_2 molecule in gas phase. Applying this equation to the clean surfaces, we obtained $E_{\text{ad}}(\text{direct}) = 2.31\text{eV}$ for $\text{TiO}_2(110)$ and 2.37eV for $\text{SnO}_2(110)$. As reported previously, the formation energy of oxygen vacancy in a metal oxide depends on the chosen model and functionals used in the calculation. For TiO_2 system, the formation energy for one Vo ranges from 2.6 to 4 eV.[8] For example, Cantele et al. reported a value of 2.8 eV [29]. The formation energy of oxygen vacancy on SnO_2 also spreads in a range of 2.0 to 3.5 eV.[30] For example, Adachi's calculation produced a value of 2.41eV.[31]

3.2.1 The conversion between formaldehyde and formic acid

Dissociation of formic acid on the oxide surfaces resulted in formaldehyde as the major product with water being produced simultaneously.[32] The formation of water can also be viewed as a result of coupling two surface bridging hydroxyl groups on the neighboring O_b sites from the dissociative adsorption of formic acid. The pathway is believed to involve the following steps [33]:

and one Vo is produced as a result of water formation and desorption. This reaction mechanism provided us another way to define Vo through the water formation and desorption. In this case, the formation energy can be calculated through $E = E(\text{H}_2\text{O}) + E(\text{de-sur}) - E(\text{sur-2OH})$. According to this definition, the formation energy of Vo is the reaction energy of reaction (2) shown above. This definition resulted in a Vo formation energy of 1.44 eV on $\text{TiO}_2(110)$ and 2.01 eV on $\text{SnO}_2(110)$. Experimentally, water formation on TiO_2 has been observed in a temperature range of 350 to 490K,[33] and $\sim 400\text{K}$ on SnO_2 [19]. The potential energy profile that compares

Figure 5. Potential energy profile diagram of H₂O formation on TiO₂ and SnO₂.

water formation on TiO₂(110) and SnO₂(110) was plotted in Figure 5. According to this result, creation of Vo on TiO₂(110) is easier than on SnO₂(110) from the surface with hydroxyls since it costs less energy.

Experimental results also indicated that the vacancies formed due to water formation may be healed at a higher temperature by the decomposition of the adsorbed formate species. The decomposition produces HCO_{ads} with the other oxygen atom filling the Vo site.[34] This pathway connects the adsorbed formaldehyde species and the surface formate species, as illustrated in the following process:

with HCOO_v indicating one of the oxygen atoms occupying the Vo site. Next we examined the oxidation process from the adsorbed formaldehyde. The oxidation of formaldehyde on the metal oxides is likely to involve the surface oxygen atom, resulting in the creation of Vo. The

consensus is that formaldehyde is first oxidized to dioxymethylene, and then dehydrogenates to CO₂ through the surface formate species.[15] Herein, we can use the calculated stable adsorption configurations on TiO₂(110) and SnO₂(110) to build the oxidation process of formaldehyde to formic acid. The reaction pathway can be expressed as:

We can use the Ti-formaldehyde as the starting configuration to illustrate the process. A rotation of the adsorbed H₂CO species and the formation of C-O_b with the bridging oxygen resulted in the Ti-dioxymethylene species. This step has a small barrier of ~0.2 eV, as we reported previously.[13] The Ti-dioxymethylene species binds the surface through its oxygen atom and the O_b atom in a bidentate fashion, similar to the V_o-bidentate formate species. Further dehydrogenation of the Ti-dioxymethylene species resulted in the V_o-bidentate formate species and one H adatom on a neighboring O_b site, i.e. a surface hydroxyl. The proton of the surface

Figure 6 Potential energy profile of formaldehyde and formate conversion on TiO₂ and SnO₂.

hydroxyl can protonate the Vo-bidentate formate species, resulting in the adsorbed formic acid and return O_b to its original state. The potential energy diagram linking formic acid and formaldehyde on both surfaces was plotted in Figure 6. As shown in Figure 6, the formate species is the most stable species along the reaction pathway and are expected to be the most commonly detected species on the surfaces. Also shown in the Figure is that protonation of the surface formate species to formic acid is not energetically favorable than its reduction to formaldehyde. We note that the intermediates on $SnO_2(110)$ are less energetically favorable than the corresponding intermediates on $TiO_2(110)$, indicating that $TiO_2(110)$ has a higher reactivity for the surface reactions. These results may be a reflection of the different electronic structures of the two oxides, primarily the two metals.

4. Conclusion

The adsorption of formaldehyde, formic acid, and formate on the stoichiometric and defective (110) surfaces of TiO_2 and SnO_2 has been investigated using DFT-based first principles method. SnO_2 has a similar Vo formation energy to TiO_2 via the direct route but is 0.57 eV higher than TiO_2 if Vo is considered as a product of water formation from the surface hydroxyls. The adsorption configurations reported in our previous studies on $TiO_2(110)$ were found also stable on $SnO_2(110)$. A comparison of the adsorption energies showed that the stoichiometric SnO_2 exhibits a stronger binding toward the adsorbates than TiO_2 , while adsorption strengths reversed on the surfaces with one Vo. In addition, we found that the oxygen vacancy stabilizes the adsorbed formate species.

The stable adsorption configurations were built into the pathway of formaldehyde oxidation to formic acid. Our results showed the Vo-bidentate formate species is the key intermediate in the oxidation of formaldehyde to formic acid and TiO_2 has a higher activity for the reactions.

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Graphics Abstract