Formaldehyde Adsorption and Decomposition on Rutile

(110): A First-Principles Study

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Abstract

We investigated the adsorption and decomposition of formaldehyde (HCHO) molecule on stoichiometric rutile TiO₂ (110) surface using first principles calculations. By comparing the adsorption energy of one bidentate and two monodentate configurations, we found the bidentate configuration is the most stable one because of an additional C-O bond formation. The monodentate configuration can change into the bidentate configuration by overcoming a small barrier less than 0.1 eV. Then we investigated the decomposition of HCHO which involves two deprotonation processes starting from different adsorption structures. The energy barrier of the first deprotonation is 1.3 eV and 1.1 eV for bidentate and monodentate configurations. After the first deprotonation, an adsorbed formate HCOO specie is formed. The second deprotonation needs 1.74 eV and 1.64 eV for bidentate and monodentate configurations respectively. After that, an adsorbed CO₂ is formed. It can desorb from the surface after overcoming a small barrier of 0.12 eV. In principle, it is also possible to obtain a CO molecule from the surface. Yet a large energy barrier higher than 1.74 eV needs to be overcome. By analyzing the energy level alignment of molecular orbitals with TiO₂ energy band edges, we discussed the photocatalytic activity of the reactants and intermediates during the decomposition process. Our results give a clear description to the adsorption structure and thermal decomposition process of HCHO on rutile TiO₂ (110) surface. The discussion of photocatalytic reactivity based on energy level alignment provides valuable insights to understand the combined photocatalytic and thermally catalytic reactions.

Keyword: DFT, formaldehyde decomposition, photocatalytic reactivity

1. Introduction

TiO₂ surfaces have important applications in photovoltaics, heterogeneous catalysis and photocatalysis due to their chemical stability, high photoelectric conversion efficiency, non-toxicity and low cost.[1-6] A good understanding of intrinsic physical and chemical processes on pristine TiO₂ surfaces is thus essential for the development of these applications.[7-13] J. T. Yates, among others, has contributed significantly to the fundamental surface science studies on TiO₂. [14-18]

Formaldehyde (HCHO), as the simplest aldehydes, is a common toxic pollutant that can lead to severe healthy issues; besides, it is an important precursor for organic synthesis. Heterogeneous photocatalytic oxidation using TiO_2 is becoming an attractive technique for the degradation of airborne contaminants such as formaldehyde.[19] Formaldehyde is known as the product of methanol oxidation on TiO_2 surface.[20-22] Recent thermal desorption spectroscopy (TPD) and X-ray photoelectron spectroscopy (XPS) investigations by W. Huang et.al. and X. Yang et.al. showed that during photocatalytic and thermal catalytic surface reactions, HCHO produce C_2H_4 , CO, CO_2 and CH_3OH on rutile $\text{TiO}_2(110)$ at different temperature. The adsorbed formate (HCOO) and HCO are important intermediates in the reaction.[21, 23, 24] C. M. Friend et.al. discovered that transient HCO is generated photochemically from formaldehyde and then it couples with residual methoxy on the surface to yield methyl formate.[25] Z. Zhang et.al. studied the adsorption and diffusion of HCHO on TiO_2 surface using atomic resolved scanning tunneling microscopy (STM).[26-28] There are also several theoretical works on HCHO adsorption on TiO_2 . [29-31] For example, Kieu et. al. proposed an adsorption model of HCHO on TiO_2 (110) and (001) surfaces based on density functional theory (DFT) calculations. Chemical monodentate adsorption structures by forming O-Ti bond with oxygen of HCHO and five-fold-coordinated titanium (Ti_{5c}) of substrate have adsorption energies about -0.68 eV.[29] Haubrich et. al. proposed a new bidentate adsorption configuration with oxygen of HCHO bonded to Ti_{5c} and carbon of HCHO bonded to a neighboring bridge bonded oxygen (O_b).[30] The adsorption energy of bidentate configuration is about 0.6 eV lower than monodentate configurations proposed by Kieu et. al. A new bidentate adsorption configuration with oxygen of HCHO bonded to Ti_{5c} and carbon of HCHO bonded to surface-in-plane oxygen of TiO_2 substrate proposed by Liu et. al. yet has the adsorption energy close to monodentate adsorption configuration.[31] Zhang et.al. and Haubrich et.al. studied the effects of oxygen vacancy on the adsorption.[28, 30, 32] The diffusion barrier of HCHO on TiO_2 is also studied by DFT.[32]

Most of the existing theoretical works focus on the adsorption structure of HCHO on rutile TiO_2 (110) surface.[29-31] However, the thermal catalytic and photocatalytic reaction mechanism of HCHO on this surface is still unclear. In this work, we first confirmed the adsorption structures of HCHO on stoichiometric rutile $\text{TiO}_2(110)$ surface. One bidentate and two monodentate configurations are studied. Then we investigated the thermal reaction pathways of HCHO decomposition to CO_2 and CO starting from different adsorption structures. Our study shows that the energy barrier of the deprotonation of the first H is 1.3 eV and 1.1 eV for bidentate and monodentate configurations. After that, an adsorbed formate HCOO_b specie is formed. The deprotonation of the second H needs 1.74 eV and 1.64 eV for bidentate and monodentate configurations. A CO_2 can be separated from the surface by overcoming a small barrier of 0.12 eV afterwards. In contrast, to separate a CO from the surface, an energy barrier around 1.8 eV needs to be overcome. By analyzing the energy level alignment of molecular orbitals with TiO_2 energy band edges, we discussed the photocatalytic activity of the reactants and intermediates during the decomposition process. Our results give a clear description to the adsorption structures and thermal decomposition process of HCHO on rutile TiO_2 (110) surface. The photocatalytic reactivity discussion based on energy level alignment provides valuable insights to understand the combined photocatalytic and thermal catalytic reactions.

2. Calculation details

We performed periodic DFT calculations by using the Vienna Ab-initio Simulation Package (VASP).[33, 34] The generalized gradient approximation (GGA) functional was adopted with the Perdew-Burke-Ernzerhof (PBE) exchange-correlation description.[35, 36] The energy cutoff of 400 eV for plane-wave basis sets was used to expand the valence electronic wave function with valence configuration of C-2s²2p², H-1s¹, O-2s²2p⁴ and Ti-4s²3d². The projector augmented wave (PAW) method was used to describe the electron-ion interaction.[37, 38] Dipole moment corrections were adopted to cancel the interactions between the slab and its periodic images for all calculations. The structure was optimized until the force on each atom is smaller than 0.02 eV/Å. A slab containing 3 Ti-O-Ti tri-layer was applied. The atoms in the bottom Ti-O-Ti tri-layer were fixed to the positions within bulk TiO₂ during the structure optimization. To avoid the interlayer interaction, we added a vacuum of 15 Å between the slabs. 5×2 surface super cell was used to investigate HCHO reaction pathway. Nudged elastic band (NEB)[39] method was adopted to search reaction paths of HCHO decomposing to CO or CO₂. During the optimization and NEB calculations, only Gamma point was used. For the electronic structure and total energy calculations, 8×4×1, 4×3×1 and 3×3×1 k-point mesh sets were used for 2×2, 3×2 and 5×2 unit cell respectively. To compare the stability of various adsorption structures, we defined the adsorption energy as:

$$E_{ads} = E_{HCHO+TiO_2} - E_{HCHO} - E_{TiO_2} \quad (1)$$

3 Results and discussion

3.1 Adsorption configurations

We first studied the adsorption structure of HCHO on TiO₂. HCHO is a planar molecule with C_{2v} symmetry and partially polarized. Oxygen atom of HCHO molecule (O_m) could bind to Ti_{5c} from substrate by forming bond via the hybridization of O_{2p} and Ti_{3d} orbitals. Hydrogen bonds could further stabilize the structure since both O_b and three-fold-coordinated oxygen in plane (O_p) could have dispersive interaction with molecular hydrogen atoms. Besides the Ti_{5c}-O_m bond, the three-fold-coordinated molecular carbon (C_m) could also bind to O_b accompanied by the hybridization of C_m changing from sp² to sp³.

Based on those bond formation analyses, we proposed three adsorption configurations of HCHO on pristine rutile TiO₂ (110) as shown in Figure 1. First, HCHO molecule could adsorb on TiO₂ substrate maintaining its planar configuration by forming Ti_{5c}-O_m bond and a hydrogen bond with O_b or O_p, forming namely monodentate configurations. The two kinds of monodentate configurations can be labeled as η¹-O_b and η¹-O_p respectively. (Figure 1 (a) (d) and (b) (e)) The two monodentate configurations are almost degenerate in energy as shown in Table 1. The Ti_{5c}-O_m bond length is around 2.2 Å. Then, the bidentate configuration can be formed by forming two chemical bonds: Ti_{5c}-O_m bond and C_m-O_b bond. It is labeled as η² as shown in Figure 1(c) and (f). This configuration has a shorter Ti_{5c}-O_m bond (1.82 Å) and an additional C_m-O_b bond (1.42 Å), resulting the decrease of *E_{ads}* compared to two monodentate adsorption configurations. (Table 1) By forming this bidentate structure, the molecular carbon becomes tetrahedrally coordinated accompanied by the transition of carbon orbital hybridization from sp² to sp³. Our calculation results agree with C. M. Friend's study.[30]

Figure 1. Adsorption configurations of HCHO on stoichiometric TiO₂ (110) surface. (a-c) and (d-f) show the side and top views of monodentate adsorption structure $\eta^1\text{-O}_b$, $\eta^1\text{-O}_p$ and bidentate adsorption structure η^2 .

Table 1. Adsorption energies and Ti_{5c}-O_m bond lengths of HCHO adsorption on stoichiometric TiO₂ (110) surface.

Adsorption configurations	E_{ads} (eV) (2×2)	E_{ads} (eV) (3×2)	E_{ads} (eV) (5×2)	Ti _{5c} -O _m (Å) (2×2)	Ti _{5c} -O _m (Å) (3×2)	Ti _{5c} -O _m (Å) (5×2)
$\eta^1\text{-O}_b$	-0.58	-0.73	-0.73	2.244	2.205	2.198
$\eta^1\text{-O}_p$	-0.61	-0.76	-0.77	2.237	2.192	2.190
η^2	-1.25	-1.76	-1.81	1.824	1.820	1.818

In the XPS, TPD and STM measurements both of the monodentate and bidentate configurations have been observed.[23, 27] And the monodentate configuration has been observed to be the dominate adsorption.[23] However, in our calculations the energy difference between the monodentate and bidentate configuration is as large as 1.1 eV for (5×2) supercell (Table 1). Trying to understand this, we checked the influence of HCHO coverage on its adsorption stability. Besides the (5×2) super cell (0.1 ML), two more different super cells of 3×2 (0.17 ML) and 2×2 (0.25 ML) were adopted. Here 1 ML refers to one HCHO adsorbed on each Ti_{5c} atom. The E_{ads} with different coverage is presented in Table 1. The structures of the three configurations do not change much. And the order of relevant stability also keeps. Yet we found that the bidentate η^2 is more sensitive to the adsorption coverage. The E_{ads} increases a little bit from -1.81 eV to -1.76 eV when then coverage increases from 0.1 ML to 0.17 ML. Then it increases distinctly to -1.25 eV when the coverage reaches 0.25 ML. In contrast, the two monodentate configurations are less sensitive to the coverage. The increasing of E_{ads} along with the coverage is less than 0.2

eV. With a coverage of 0.25 ML, the energy difference of bidentate η^2 with monodentate $\eta^1\text{-O}_b$ and $\eta^1\text{-O}_p$ is only about 0.6 eV. This can be easily understood from the steric effects aroused by two reasons: i. The bidentate η^2 configuration has the tetrahedral configuration instead of planar configuration. ii. The stronger $\text{Ti}_{5c}\text{-O}_m$ bond in η^2 configuration pulls the Ti_{5c} out of the surface. The large distortion of TiO_2 surface also induces steric effects.

Figure 2. The reaction pathways and corresponding structures of adsorption configuration conversion from bidentate η^2 to monodentate $\eta^1\text{-O}_p$ then monodentate $\eta^1\text{-O}_b$ of HCHO on stoichiometric $\text{TiO}_2(110)$ surface. The results of (5x2) and (2x2) super cells are shown using the black and green bars.

It is possible for the bidentate and monodentate configurations to convert to each other. We calculated the structure conversion energy barriers using (5x2) (0.1 ML) and (2x2) (0.25 ML) as shown in Figure 2. One can see that for both cases, the energy barrier between $\eta^1\text{-O}_b$ and $\eta^1\text{-O}_p$ is very small, which is less than 50 meV. Yet the energy barrier between $\eta^1\text{-O}_p$ and η^2 is more sensitive to the coverage. For 0.1 ML, it is as small as 30 meV. For 0.25 ML, the barrier reaches 0.1 eV. The large energy difference and small conversion barrier between bidentate and monodentate configurations could not explain the dominate adsorption of monodentate configuration.[23] Z. Zhang and Q. Ge et.al. also discussed the present DFT results are at odds with the experimental observation. [26] We believe that a deeper theoretical investigation, including the effects of oxygen vacancy and Ti interstitial is further needed.

3.2 Thermal decomposition reaction pathway

After we confirmed the adsorption structures, we studied the decomposition energy barrier of HCHO on rutile $\text{TiO}_2(110)$ surface from different adsorption structures. We use (5x2) super cell

to investigate the decomposition reaction pathway. The decomposition of HCHO to CO or CO₂ essentially is a two-step deprotonation process. The protons transfer from HCHO to TiO₂ surface to form surface hydroxyls (OH_b) with O_b. First we studied the decomposition reaction pathway of the most stable η^2 structure. Figure 3 shows the reaction pathways and corresponding structures. Figure 3(a)-(c) shows the process of the first deprotonation. The proton transfer from HCHO to a neighboring O_b forming an OH_b. After that, an intermediate formate HCOO_b is formed. During this process, the sp³ hybridization in η^2 changes to the sp² hybridization in adsorbed HCOO. The energy barrier for the first deprotonation step is 1.3 eV and the adsorbed HCOO_b is 1.4 eV more stable than HCHO adsorbed on TiO₂ (110) surface, namely the first deprotonation is an exothermic reaction. The reverse reaction from HCOO_b to HCHO needs to overcome a large energy barrier of 2.7 eV.

Figure 3. The reaction pathway and corresponding structures of bidentate η^2 HCHO decomposition to CO₂ and CO. structure (c), (e) and (g) corresponds to intermediates of HCOO_b, HCOO_b' and the adsorbed CO₂.

The second deprotonation process first involves breaking of Ti-O_m bond (Figure 3(d)). After that, by forming two H bonds with the neighboring OH_b and O_b, another intermediate formate HCOO_b' is formed, which is 0.22 eV less stable than the intermediate HCOO_b (Figure 3(e)). The energy barrier of this process is 0.49 eV. Then the HCOO_b' is deprotonated by transferring a proton to the other neighboring O_b and forming another OH_b (Figure 3(e-g)). During this

deprotonation process, the O_b where HCO adsorbed is pulled out of the surface with the Ti- O_b bond increasing from 2.17 Å in Figure 3(e) to 2.81 Å forming an adsorbed CO_2 in oxygen vacancy on TiO_2 (Figure 3(g)). The reactant (HCO) and product (CO_2) of this step have almost degenerate energy and the energy barrier is around 1.74 eV. By overcoming a small energy barrier of 20 meV, the CO_2 molecule can desorb easily from the surface (Figure 3(g), (j) and (k)). In principle it is also possible to reduce CO_2 to a CO molecule. However, our calculations show that a large barrier of 1.95 eV needs to be overcome to separate CO from the surface (Figure 3(g)-(i)). The decomposition of HCHO to CO_2 is an exothermic reaction. The energy difference between the product and the reactant is 1.14 eV.

Figure 4. The reaction pathway and corresponding structure of monodentate η^1-O_b HCHO decomposition to CO_2 and CO. (c) and (e) corresponds to the intermediate $HCOO_b$ and the adsorbed CO_2 .

Then we study the decomposition HCHO starting from monodentate structures. Since η^1-O_p and η^1-O_b are almost degenerate in energy and the energy barrier between them is very small, we only study the decomposition reaction pathway starting from η^1-O_b as shown in Figure 4. The first deprotonation process is a proton transfer to a neighboring O_b through the hydrogen bond and forming an OH_b (Figure 4(a-c)). After that an intermediate $HCOO_b$ is formed with O_b in adjacent row which is 2.4 eV lower in energy (Figure 4(c)). The energy barrier of this process is 1.11 eV. The second deprotonation is a little bit different with the decomposition from η^2 structure. Here we did not find the formation of stable intermediate $HCOO_b'$. This is because the absent of a neighboring OH_b and the hydrogen bond between intermediate $HCOO_b'$ and OH_b could not be formed. The intermediate $HCOO_b$ is directly deprotonated into an adsorbed CO_2

(Figure 4(e)) by overcoming an energy barrier of 1.64 eV. Similarly, the energy barrier to reduce CO₂ to CO is as large as 1.74 eV. (Figure 4 (e)-(g)) Since $\eta^1\text{-O}_b$ is less stable than η^2 , obviously the decomposition from η^2 to CO₂ is also an exothermic reaction. The energy difference between the product and the reactant is 2.31 eV. The reverse reaction process contains an energy barrier of 3.51 eV from HCOO_b to HCHO.

Our results show that the adsorbed formate HCOO_b and HCOO_{b'} are two stable intermediates during the decomposition. These results are in agreement with some of the experimental observation.[23-25] Our results also prove that the decomposition of toxic HCHO to non-toxic CO₂ is an exothermic reaction, suggesting that stoichiometric rutile TiO₂ (110) surface could be used to decompose HCHO. In contrast, the decomposition to CO is much more difficult.

3.3 Photocatalytic reactivity

Since TiO₂ is a widely used photocatalytic material, it is also very important to understand the photocatalytic reactivity on it. The thermal catalytic reactions and photocatalytic reactions are often combined together in the experimental measurements and practical applications.[23-25]

Photocatalytic activity depends on the optimal alignment of electronic levels at the molecule-semiconductor interface.[40-43] When an adsorbed molecule has the highest occupied molecular orbital (HOMO) or lowest unoccupied molecular orbital (LUMO) in the band gap or at least close to valance band maximum (VBM) or conduction band minimum (CBM) of TiO₂, it has high photocatalytic reactivity. Therefore, we investigate the energy level alignment based on the calculations of total and partial density of states (DOS) for the stable reactant (HCHO), intermediates (HCOO_b and HCOO_{b'}) and product (CO₂) in the decomposition of HCHO on rutile TiO₂(110) surface. The bottom Ti-O-Ti tri-layer contains unsaturated two-coordinated O (O_{2c}) and Ti_{5c} with bulk-like structure which contributes artificial DOS.[44] Therefore in the calculations of total DOS, we subtract the contribution of the bottom Ti-O-Ti tri-layer. In this report the electronic structure is calculated at the DFT level using PBE functional. It is well known that DFT underestimates the band gap due to the lack of self-interaction correction. However, based on our previous energy level alignment investigations of H₂O and CH₃OH on TiO₂, we found that although DFT-PBE does not give the correct band gap, it provides the energy level alignment agrees qualitatively with many-body quasiparticle GW results.[40-43] Therefore, in this report we use DFT with PBE functional to investigate the energy level alignment.

The total and partial DOS is shown in Figure 5. To make the partial DOS contributed by the adsorbate more visible, it is expanded by 5 times. The VBM and CBM is marked using dotted lines. First, as shown in Figure 5, the LUMOs of the adsorbates all have energies more than 1.5 eV higher than CBM, meaning that the photo-reduction induced by excited electrons is difficult. In contrast, two of the adsorbed structures have HOMOs very close to VBM, suggesting a good reactivity for photo-oxidation. Figure 5 (a)-(c) give the total and partial DOS of HCHO on rutile TiO₂ (110) surface with monodentate and bidentate configurations. One can see that the HOMO of monodentate $\eta^1\text{-O}_b$ and $\eta^1\text{-O}_p$ is at around -1.5 eV below VBM. In contrast bidentate η^2 has its HOMO only 0.1 eV below VBM. This suggests that bidentate η^2 configuration is a possible hole trapping site. Comparing with CH₃OH, HCHO with η^2 structure has better hole scavenger properties.[40] In the inset of Figure 5 (c) we plot out the orbital distribution of the HOMO of HCHO as the hole acceptor level. We found that it is the π^* orbital hybridized by the 2p orbitals from C_m, O_m and O_b. The Ti_{3d} orbital also has small contribution. Trapping an excited hole may

lower the breaking-bond energy barriers of C_m-O_m , C_m-O_b or $Ti_{5c}-O_m$ bonds. We propose that by breaking the C_m-O_m and C_m-O_b bonds simultaneously, an intermediate CH_2 can be generated from the surface. If there are two neighboring $HCHO$, C_2H_4 could be produced. This qualitatively explains the observation of C_2H_4 in the XPS and TPD experiments.[23, 24] The hole trapping may also help the transition from the bidentate η^2 configuration to monodentate η^1 configuration by breaking the C_m-O_b bond. Because of the contribution of Ti_{3d} orbital, for η^2 configuration, $Ti-O_m$ bond break, e.g., the transition from $HCHO$ to $HCOO_b$ could also be easier.

Figure 5. Total (black) and partial (red) DOS of the reactants ($HCHO$), intermediates ($HCOO_b$ and HCO) and product (CO_2) on rutile $TiO_2(110)$ surface. For those systems which have high photocatalytic reactivity ((c) and (e)), the orbital spatial distribution of adsorbate HOMO is presented in the inset.

Figure 5(d)-(f) show the total and partial DOS of adsorbed $HCOO_b$, $HCOO_b'$ and CO_2 . One can see that HOMO of CO_2 is as low as -3.7 eV below VBM, suggesting a very low photocatalytic reactivity. The HOMO of $HCOO_b$ is also at -1.2 eV below VBM. In contrast, the $HCOO_b'$ intermediate has its HOMO just at VBM, implying it to be a hole scavenger. In the inset of Figure 5 (e), we plot the orbital distribution of $HCOO_b'$ HOMO. It is also mainly the π^* orbital hybridized by the $2p$ orbitals of C_m and O_m . The H and O_b atoms also have small contribution. Trapping an excited hole may help to break the C_m-O_m , C_m-O_b or C_m-H bonds. It could induce the desorption of HCO from the surface and help the second deprotonation to generate CO_2 .

4 Conclusions

Trying to understand the thermal catalytic and photocatalytic properties of HCHO on TiO_2 , we performed a systematic study based on first principles calculations. First, we investigated the adsorption structures of HCHO on stoichiometric rutile TiO_2 (110) surface. We confirmed three different adsorption structures containing one bidentate and two monodentate configurations. The two monodentate configurations are almost degenerate in energy. The bidentate configuration is the most stable one because of one additional $\text{C}_\text{m}\text{-O}_\text{b}$ bond formation and the orbital hybridization changing from sp^2 to sp^3 . The energy difference and conversion energy barrier between the bidentate and monodentate configurations depend on the adsorption coverage. Second, we studied the thermal decomposition of HCHO to CO_2 from different adsorption structure on stoichiometric rutile TiO_2 (110) surface. The decomposition includes two deprotonation processes. The energy barrier of the first deprotonation is 1.3 eV and 1.1 eV for bidentate and monodentate configurations. After the first deprotonation, an adsorbed formate HCOO_b specie is formed. The second deprotonation needs 1.74 eV and 1.64 eV for bidentate and monodentate configurations. An intermediate HCOO_b' can be generated from bidentate configuration. After that, an adsorbed CO_2 is formed. It can desorb from the surface after overcoming a small barrier of 0.12 eV. In principle, it is also possible to obtain a CO molecule from the surface. Yet a large energy barrier around 1.8 eV needs to be overcome. Third, by analyzing the energy alignment of molecular orbitals with TiO_2 energy band edges, we discussed the photocatalytic activity of the reactants and intermediates during the decomposition process. We found that the adsorbed HCHO with bidentate configuration and the intermediate HCOO_b' have high photocatalytic reactivity. Trapping the excited holes may help the conversion between the bidentate and monodentate configurations and the generation of C_2H_4 . Our results apply a clear description to the adsorption structure and thermal decomposition process of HCHO on rutile TiO_2 (110) surface. The band alignment discussion provides valuable insights to understand the combined photocatalytic and thermally catalytic reactions of HCHO on rutile TiO_2 (110) surface.

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