Hybrid density-functional calculations of formic acid on anatase TiO₂ (101) surfaces

L. Kou, E. N. Lima, A. L. da Rosa*, and Th. Frauenheim

Universidade Federal de Goiás, Campus Samambaia, Instituto de Física, CEP 74690-900, Goiânia, Goiás

*andreialuisa@ufg.br

Keywords: titanium dioxide, formic acid, first-principles calculations

Abstract

Recent experimental observations suggested that the presence of oxygen vacancies on TiO₂ surfaces affects the adsorption mode of formic acid. We use density-functional theory and the hybrid density-functional HSE06 form for the exchange-correlation functional to determine the structural properties and the band structure of single molecules on TiO₂ (101) surfaces. We show that formic acid adsorbs dissociatively on both perfect and defective surfaces with no overlap between oxygen defect and molecular states, leading to no change in the adsorption mode. We propose that both relaxation experienced by the surface atoms due to the presence of vacancies and molecule adsorption are responsible for the stabilization of the monodentate mode.

Introduction

There is a considerable technological interest in combining organic and inorganic semi-conductor materials in order to obtain hybrid materials with novel properties. One of the crucial aspects for the realization of these hybrid systems is the understanding of the semi-conductor/organic interface. Molecules containing carboxyl groups (-COOH) are frequently used as anchor groups on rutile and anatase TiO₂ surfaces. The role of this anchor group is to assist charge transfer at the interface, help to stabilize the oxide surface and provide a strategy for further immobilization of dyes and biomolecules. Adsorption of formic acid on rutile TiO₂ surfaces has been explored in several previous work. Quantum-mechanical molecular dynamics simulations showed that the adsorption of a formic acid molecule (H-COOH) on a partially reduced rutile TiO₂-(110) leads to a quick dissociation into a formate ion and a proton.⁽¹⁾ Infrared reflection-absorption spectroscopy (IRRAS) and spin-polarized density functional theory (DFT) including Hubbard U corrections reported that bridging bidentate formate species are formed, binding preferentially far from oxygen vacancy sites.^[2] The role of oxygen vacancies on anatase TiO₂ surfaces on the adsorption of molecules containing -COOH groups is more controversial. At low coverages, scanning transmission microscopy of formic acid (CH₂COOH) on anatase (101)

surfaces showed that this molecule has a dissociative bidentate binding geometry.

A density functional tight binding study of acetic acid on TiO₂ on anatase (101), rutile (110), and brookite (001) identified a bidentate configuration⁽⁴⁾ on all polymorphs. First-principles calculations using DFT+U show a molecular monodentate geometry of formic acid on TiO₂,^(5, 6) while standard GGA calculations^(7, 8) and tight-binding⁽⁹⁾ predicted a bidentate geometry.

Contrary to the rutile phase, it is well-known that anatase (101) surfaces are not easily reducible, as has been reported in several experimental and theoretical investigations.^(3, 10-12) On these surfaces, the barrier for surface diffusion toward the deeper layers is small and oxygen vacancies should reside at subsurface sites.^(11, 12) Recent vibrational spectroscopy investigations have suggested that formic acid adsorbs in a bidentate configuration in the presence of oxygen vacancies,⁽¹³⁾ whereas a monodentate mode was found on perfect anatase TiO₂(101) surfaces.⁽¹³⁾

In this work, DFT calculations using the Heyd-Scuseria-Ernzenhof form (HSE06) for the exchange-correlation functional has been employed to clarify the microscopic nature of the interaction of formic acid with perfect and defective TiO₂(101) surfaces at low coverages. We demonstrate that acetic acid adsorbs in a monodentate mode on both perfect and defective surfaces. The

presence of oxygen vacancies affects the adsorption geometry but not the adsorption mode of such molecules because no overlap exists between defect levels and molecular levels.

Methods and Results

The $\text{TiO}_2(101)$ anatase surfaces have been modeled using a slab with 216 atoms containing a surface with (3×3) periodicity and separated by a 10 Å vacuum region to avoid spurious interactions among molecules in neighboring cells. A single molecule was adsorbed on the surface starting from several possible geometries. Our calculations have been performed using the VASP package (14) within the HSE06 approximation (15,16, 17,18) for the exchange-correlation potential to obtain the geometry and the electronic structure. We used a plane wave cutoff of 300 eV and only the Γ point for all calculations. All atomic positions were relaxed until the interatomic forces were smaller than 0.01 eV/Å.

Discussion

In order to understand the role of oxygen vacancies on the adsorption of formic acid on titania surfaces, it is primordial to describe the oxygen defect formation energies and band structure properly. In Figure 1, the positions for the oxygen vacancies are shown in brown. Vacancy positions are denoted as V_{On} , with $n = 1-5$ ($n = 1$ means the surface top layer, and $n = 5$ means the fifth layer below the surface). A general trend is that oxygen atoms located around the oxygen vacancy relax toward the vacancy position, in an attempt to heal the oxygen vacancy. It is interesting to note that this happens independent of where the vacancy is located. In our model favors stabilization of the oxygen vacancy at the outermost site (V_{O1}). This configuration is more stable by 0.33 eV than a vacancy in the subsurface site V_{O5} . Previous calculations by Yadong Li and Yi Gao (22) using GGA/PBE and a (1×4) supercell with 144 atoms found an energy difference of 0.18 eV between both sites (the subsurface site is more stable). The work of Selloni (12,24) was carried out using also GGA/PBE, reporting a stability of 0.5 eV for a 216 atom supercell favoring the subsurface site. In ref (24) additional DFT+U calculations with 96

and 144 atoms in the supercell report that DFT+U could stabilize the top layer site by 0.3 eV for large values of U. Spin-polarized hybrid PBE0 calculations with 144 atoms in the supercell and constant-current STM measurements reported in ref 21 found that the subsurface oxygen vacancy is 0.61 eV more stable than the vacancy at the surface. Therefore, the conclusion regarding the energy necessary to stabilize the vacancy site seems to be dependent on two basic parameters, that is, the size of the supercell and the form of the potential used to treat the exchange-correlation.

Figure 1. Schematic representation of a slab model for the clean anatase (101) TiO_2 surface. The positions of the vacancies on each layer (V_O) are indicated with the brown color.

We discuss next what happens if a molecule like formic acid is adsorbed on both perfect and defective surfaces. The geometry of formic acid on the perfect anatase (101) surface is shown in Figure 1Ia. The bidentate and monodentate adsorption energies differ by less than 0.2 eV, the monodentate mode being more stable. The bidentate mode (not shown) leads to surface titanium atoms (Ti_{surf}) binding to molecule oxygen atoms (O_{mol}) with bond lengths of 2.03 and 2.10 Å. For the monodentate mode, the bond lengths are 2.01 and 2.40 Å. Previous investigations on carboxylic acid molecules ($\text{CH}_3\text{-COOH}$) showed that the bidentate and monodentate geometries also have similar adsorption energies.(4) This corroborates our results because we do not expect a significant difference in the reactivity for these two molecules. On defective surfaces, the molecule adsorbs in a dissociative monodentate mode regardless of the oxygen vacancy position. Starting from a bidentate mode or nondissociative monodentate mode always leads to a configuration with higher energy. The structure containing an oxygen vacancy on the first layer, denoted as V_{O1} , shows relaxation of the oxygen atom in the

fourth layer of the slab toward the vacancy in the first layer.

This leads to a shortening of the bond length between this oxygen atom and the Ti in the first layer, which decreases to 1.81 Å. The other bond lengths between the oxygen in the fourth layer and first neighbor Ti atoms are 2.07 Å. The bond length between the oxygen of the molecule that binds to the titanium atom of the surface is 1.92 Å.

Figure II: Optimized atomic geometries of formic acid on the anatase (101) TiO_2 surface: (a) perfect surface and defective surfaces with an oxygen vacancy in the (b) first layer, (c) second layer, (d) third layer, (e) fourth layer, and (f) fifth layer.

The structure with an oxygen vacancy in the second layer, V_{O2} , is shown in Figure IIc. Relaxation of the oxygen atom in the third layer of the slab toward the missing oxygen atom in the second layer by 0.30 Å is seen. The relaxed oxygen atom now has two nearest-neighbor Ti atoms with bond lengths of 1.82 and 1.86 Å. The distance between the formic acid oxygen and the titanium surface atom is 1.93 Å.

The oxygen vacancy in the third layer of the slab, V_{O3} (Figure IId), leads to relaxation of the oxygen atom sitting in the second layer of the slab toward the vacancy site. The bond length between this oxygen and neighboring Ti atoms is 1.81 Å. The surface titanium atom

and the oxygen molecule atom have a bond length of 1.93 Å. The other bond lengths between the surface titanium atom and oxygen first neighbors are 1.92, 1.96, and 2.14 Å. The dissociated hydrogen binds to a surface oxygen atom with a bond length of 0.96 Å.

As the oxygen vacancy sits in the fourth layer, V_{O4} (Figure IIe), a strong relaxation of the top TiO_2 surface layer occurs, meaning that the molecule adsorption strongly affects the relaxation of surface atoms. The oxygen surface again relaxes toward the bulk region of the slab where the oxygen vacancy lies. The distances between the surface titanium atom bonded to the formic acid oxygen is 1.91 Å. The oxygen in the first layer relaxes now to the inner region of the slab by 0.5 Å. Its bond lengths with surrounding Ti atoms are shortened to 1.80–1.82 Å. However, STM experiments and DFT calculations (11,12) suggested that vacancies diffusing toward the surface have a smaller diffusion barrier than vacancies diffusing toward the bulk region. Upon adsorption, a possible scenario is that the surface electrostatic potential has now changed due to molecule adsorption, affecting the oxygen diffusion barrier.

For an oxygen vacancy in the fifth layer, V_{O5} (Figure IIff), again formic acid adsorption leads to a large relaxation of the top TiO_2 surface atoms. Oxygen atoms sitting at the fourth subsurface layer almost fill up the vacancy in the fifth layer. The surface titanium and oxygen molecule bond length is now 1.90 Å. The surface oxygen atoms form a bond with the hydrogen molecule with a bond length of 0.97 Å.

One can therefore conclude that acetic acid adsorbs on a monodentate mode on both perfect surfaces and defective surfaces. This is in agreement with recent experimental observations that the presence of oxygen vacancies affects the adsorption of formic acid on TiO_2 surfaces.(13) However, the adsorption mode does not change. The difference in relaxation experienced by the atoms due to both vacancy and molecule adsorption affects the electronic structure of

the surface, leading to stabilization of the monodentate mode.

Finally, we investigate the electronic structure of the molecule on the perfect and defective anatase (110) TiO_2 surfaces, shown in Figure III. In transition metal oxides, the correct description of band gaps and defect levels is primordial to predict or confirm the electronic structure of this material. Methods that can correct the electron self-interaction error of standard DFT, such as DFT+U and hybrid functionals and even screened exchange, should give a more reliable description of charge localization of these defects, as has been discussed in refs 10, 19, and 20.

Figure III. Electronic band structures of perfect and oxygen-deficient TiO_2 surfaces upon adsorption of H-COOH .

The vacancy states as seen from Figure IIIa are 0.85, 1.02, 0.94, 0.90, and 0.99 eV below the TiO_2 conduction band for the $\text{V}_{\text{O}1}$, $\text{V}_{\text{O}2}$, $\text{V}_{\text{O}3}$, $\text{V}_{\text{O}4}$, and $\text{V}_{\text{O}5}$, respectively. This gives origin to a localized state in the gap as the electron localizes around Ti atoms. Previous results report HSE values of 0.6 eV for bulk and 0.5 eV for a slab containing oxygen vacancies at subsurface sites. (10) Experimental values from photoemission spectroscopy reported 2.3 eV above the TiO_2 valence band, (23) which agrees with our HSE results. Little overlap is found among molecular and vacancy states. While the molecular state is closer to the top of the valence band, the defect level is right below the conduction band. For the perfect surface

and surfaces containing vacancies in the first, fourth, and fifth layers, the molecular state lies close to the TiO_2 valence band top. On the other hand, for the system where the oxygen vacancy relaxes in order to heal the vacancy, as in the case of $\text{V}_{\text{O}2}$ and $\text{V}_{\text{O}3}$, the molecular level in the gap is similar to the adsorption on the perfect surface. We propose that the absence of overlap between molecular and defect states explains why no change in the adsorption mode is found.

In this work, we have performed DFT calculations using the HSE06 exchange-correlation functional in order to clarify the microscopic nature of the interaction of formic acid with perfect and defective anatase $\text{TiO}_2(101)$ surfaces. We demonstrate that acetic acid adsorbs in a monodentate mode on both perfect and defective surfaces and that oxygen vacancies affect the adsorption geometry but not the adsorption mode.

Acknowledgments

A.L.R. and Th.F. would like to thank the German Science Foundation (DFG) under the program FOR1616 for financial support. A.L.R. would like to thank P. Deak for fruitful discussions. Adapted with permission from (10.1021/acs.jpcc.7b06957). Copyright (2017) American Chemical Society.

References below

1. Mattsson, A.; Hu, S.; Hermansson, K.; Österlund, L. *J. Chem. Phys.* **2014**, 140, 034705
2. Mattsson, A.; Osterlund, L. *J. Phys. Chem. C* **2010**, 114, 14121
3. Grinter, D. C.; Nicotra, M.; Thornton, G. *J. Phys. Chem. C* **2012**, 116, 11643
4. Manzhos, S.; Giorgi, G.; Yamashita, K. *Molecules* **2015**, 20, 3371
5. Miller, K. L.; Musgrave, C. B.; Falconer, J. L.; Medlin, J. W. *J. Phys. Chem. C* **2011**, 115, 2738
6. Vittadini, A.; Selloni, A.; Rotzinger, F. P.; Grätzel, M. *J. Phys. Chem. B* **2000**, 104, 1300
7. Raghunath, P.; Lin, M. C. *J. Phys. Chem. C* **2008**, 112, 8276
8. Martsinovich, N.; Jones, D. R.; Troisi, A. *J. Phys. Chem. C* **2010**, 114, 22659
9. Luschtinetz, R.; Gemming, S.; Seifert, G. *Eur. Phys. J. Plus* **2011**, 126, 98
10. Deak, P.; Aradi, B.; Frauenheim, T. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2012**, 86, 195206
11. He, Y.; Dulub, O.; Cheng, H.; Selloni, A.; Diebold, U. *Phys. Rev. Lett.* **2009**, 102, 106105
12. Cheng, H.; Selloni, A. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2009**, 79, 092101
13. Xu, M.; Noei, H.; Buchholz, M.; Muhler, M.; Wöll, C.; Wang, Y. *Catal. Today* **2012**, 182, 12
14. Kresse, G.; Furthmüller, J. *Comput. Mater. Sci.* **1996**, 6, 15

15. Heyd, J.; Scuseria, G. E.; Ernzerhof, M. J.
Chem. Phys. **2006**, 124, 219906

16. Landmann, M.; Rauls, E.; Schmidt, W. G. J. Phys.: Condens. Matter
2012, 24, 195503

17. Janotti, A.; van de Walle, C. G. Phys. Rev. B **2007**, 76, 165202

18. Tang, H.; Lévy, F.; Berger, H.; Schmid, P. E. Phys. Rev. B **1995**, 52,
7771

19. Ha, M.-A.; Alexandrova, A. N. J. Chem. Theory Comput. **2016**, 12,
2889

20. Li, H.; Guo, Y.; Robertson, J. J. Phys. Chem. C **2015**, 119, 18160

21. Scheiber, P.; Fidler, M.; Dulub, O.; Schmid, M.; Diebold, U.; Hou,
W.; Aschauer, U.; Selloni, A. Phys. Rev. Lett. **2012**, 109, 136103

22. Li, Y.; Gao, Y. Phys. Rev. Lett. **2014**, 112, 206101

23. Jackman, M. J.; Deak, P.; Syres, K. L.; Adell, J.; Balasubramanian
Thiagarajand, A. L.; Thomas, A. G. ArXiv; 2014;
<https://arxiv.org/ftp/arxiv/papers/1406/1406.3385.pdf>.

24. Cheng, H.; Selloni, A. J. Chem. Phys. **2009**, 131, 054703