

Modelling of the adsorption of formic acid and formaldehyde over rutile $\text{TiO}_2(1\ 1\ 0)$ and $\text{TiO}_2(0\ 1\ 1)$ clusters

L. Kieu, P. Boyd, H. Idriss*

Department of Chemistry, The University of Auckland, Private Bag 92019, Auckland, New Zealand

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Abstract

While several computational works have addressed the energetics of adsorption over $\text{TiO}_2(1\ 1\ 0)$ surface no work has, so far, addressed the adsorption energy of any molecule over $\text{TiO}_2(0\ 1\ 1)$ surface. Yet, the $(0\ 1\ 1)$ surface, also known as phase I of reconstructed $\text{TiO}_2(0\ 0\ 1)$, is extremely active towards simple oxygenates as shown for over a decade. In this work, the adsorption of formaldehyde and formic acid has been studied using the molecular orbital semi-empirical method PM3 over a rutile $\text{Ti}_8\text{O}_{29}\text{H}_{26}$ cluster representing $\text{TiO}_2(0\ 1\ 1)$ surface. A study over a rutile $\text{Ti}_{11}\text{O}_{42}\text{H}_{40}$ cluster representing $\text{TiO}_2(1\ 1\ 0)$ surface has been made for comparison. The adsorption energy of formaldehyde was found smaller than that of formic acid over both surfaces. However, while the adsorption energy of formaldehyde was comparable over both TiO_2 surfaces, that of formic acid was dramatically larger over $\text{TiO}_2(0\ 1\ 1)$ surface (the one containing all Ti^{4+} cations five-fold-coordinated to oxygen anions, Ti_{5c}^{4+}) than that over $\text{TiO}_2(1\ 1\ 0)$ surface (the one containing alternating rows of Ti_{5c}^{4+} and Ti_{6c}^{4+}). This adsorption energy was computed equal to 1.6 and 1.1 eV, respectively. Repulsive interaction between bridging oxygen anions, in the case of the $(1\ 1\ 0)$ surface is most likely the reason for the relatively smaller energy of adsorption. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Adsorption; Formic acid; Formaldehyde

1. Introduction

TiO_2 is one of the most thoroughly studied transition metal oxides. The reasons for that are numerous: catalysis, pigments, dielectric, ceramics, biological application, etc. Several reviews have treated the chemical pathways over TiO_2 single crystals and powders [1–3]. Several single crystals of rutile TiO_2 were investigated including $\text{TiO}_2(1\ 1\ 0)$, $\text{TiO}_2(1\ 0\ 0)$ and $\text{TiO}_2(0\ 0\ 1)$. A major contribution to the stability of a surface of an oxide is the degree of coordinative unsaturation of the surface-layer cations, with greater unsaturation giving less stability. The $(1\ 1\ 0)$ face is the one most commonly found in both na-

ture and synthetic rutile crystals because it gives the maximum coordination of the surface titanium ions — half remain six-coordinate, and half become five-coordinate. Surface X-ray diffraction [4], ion scattering [5], and theoretical calculations [6] have shown a small relaxation of the surface. The surface five-fold-coordinated Ti cations move in toward the bulk [6] (slightly out of the plane of the four oxygen atoms) as do the bridging oxygen atoms. Several STM investigations [7–10] have enabled near-atomic level visualisation of the surface, further confirming the structure. Reconstruction by high-temperature annealing to (1×2) has also been observed [11]. On the bulk-terminated $(0\ 0\ 1)$ structure, all surface Ti atoms are only four-fold-coordinated — thus, this surface is quite unstable. Ab initio calculated surface energies

* Corresponding author.

for rutile and anatase TiO_2 were given by other workers [6].

The formation of a low-temperature “phase I” and a subsequent high-temperature “phase II” structure of $\text{TiO}_2(001)$ upon annealing was observed and characterised with LEED, AES, EELS, and UPS [12,13] in the late 1970s. Comparison of theoretically calculated LEED patterns for different structures with those observed allowed the determination of the facets present [13]. Annealing to 750–800 K produced the $\{011\}$ -faceted structure (phase I), in which all surface Ti atoms are five-fold-coordinated, reducing the free energy of the surface. Relaxation of the (011) surface has been modelled [6], with the results indicating a movement of the surface oxygen and Ti atoms 0.02 and 0.01 Å out of the surface, respectively, while the second-layer oxygen move 0.01 Å inward.

The reactions of a variety of molecules on the surfaces of stoichiometric and defect-containing $\text{TiO}_2(110)$ single crystals have been investigated, although the reactivity of the stoichiometric surface is rather low. The low reactivity is partly due the presence of out-of-plane bridging oxygen anions and the fact that 50% of Ti^{4+} ions are six-fold-coordinated and are thus, in principle, unreactive. The alternating rows of these six-fold-coordinated cations force the reaction to occur along the five-fold-coordinated cation rows, unless the molecule is large enough to cross the six-fold-coordinated barrier row (such as the case of bi-isonicotinic acid [14]). Several reactants were studied over this surface, see [3] for a review of this work.

Formaldehyde adsorption and reaction [15] has been investigated over a $\text{TiO}_2(001)$ single crystal by TPD and XPS techniques. On oxygen defected surface a large part of formaldehyde is reduced to methanol with a methanol to formaldehyde ratio of 0.47; both peaks desorbed at ca. 370 K. The remaining is decomposed to CO and CO_2 at higher temperatures. Healing surface defects produced the $\{011\}$ -faceted surface where the ratio methanol to formaldehyde decreased by almost half when compared to oxygen defected surfaces. Theoretical as well spectroscopic results have indicated that the most favourable configuration for HCHO adsorption over stoichiometric oxides is normal to the surface with the oxygen bound to the metal cation [16,17].

No theoretical work has addressed the adsorption energy of HCHO over $\text{TiO}_2(110)$ or any of the

faceted structure of $\text{TiO}_2(001)$ single crystal. However, first principle calculations based on DFT and the pseudo potential method were used to investigate the energy of adsorption of HCOOH on a $\text{TiO}_2(110)$ surface [18]. The adsorption energy varied from 0.61 to 1.95 eV depending on the coverage and conformation. There are no reports of calculated adsorption energy of HCOOH over the $\{011\}$ -faceted TiO_2 single crystal.

Although cluster calculations may not be an accurate representation of an extended surface they nevertheless, provide an important guide. Moreover, they may be of considerable importance when considering the surface reactions of nanocrystals of oxides.

2. Methodology

A TiO_2 rutile unit cell was generated using the Cerius 2 program (Molecular Simulation Inc.) [19]. This was then cleaved along the (110) or the (011) directions. It was necessary to select a cluster large enough to be a reasonable representation of the surface, but not too large in order to conduct the work in a reasonable time with our computational resources. Several trial runs were conducted to gauge variations of the computation results as a function of cluster dimension. A cluster with a depth of two unit cells and a surface area of 3×2 units for the (110) was considered sufficient. This cluster contained 11 Ti cations (see below). This is in line with recent work based on DFT treating the adsorption of CO and H_2O over $\text{TiO}_2(110)$ surfaces where a cluster of seven Ti cations was found an adequate representation of the surface Lewis acid sites [41]. This structure was obtained after moving the (110) plane down to half a unit cell and cutting all three, four and five titanium cations at the bottom and sides of the cluster. This cluster is not charge neutral. In order to make it neutral, protons were added to neutralise the excess negative charge. After addition of the required number of protons, the $\text{Ti}_{11}\text{O}_{42}\text{H}_{40}$ cluster is obtained, Fig. 1a. This cluster was used for all calculations. Similar treatment was conducted for the (011) cluster and the resulting charge neutral cluster is shown in Fig. 1b ($\text{Ti}_8\text{O}_{29}\text{H}_{26}$).

Both the $\text{Ti}_{11}\text{O}_{42}\text{H}_{40}$ and the ($\text{Ti}_8\text{O}_{29}\text{H}_{26}$) were used for the calculation of the adsorption energy of

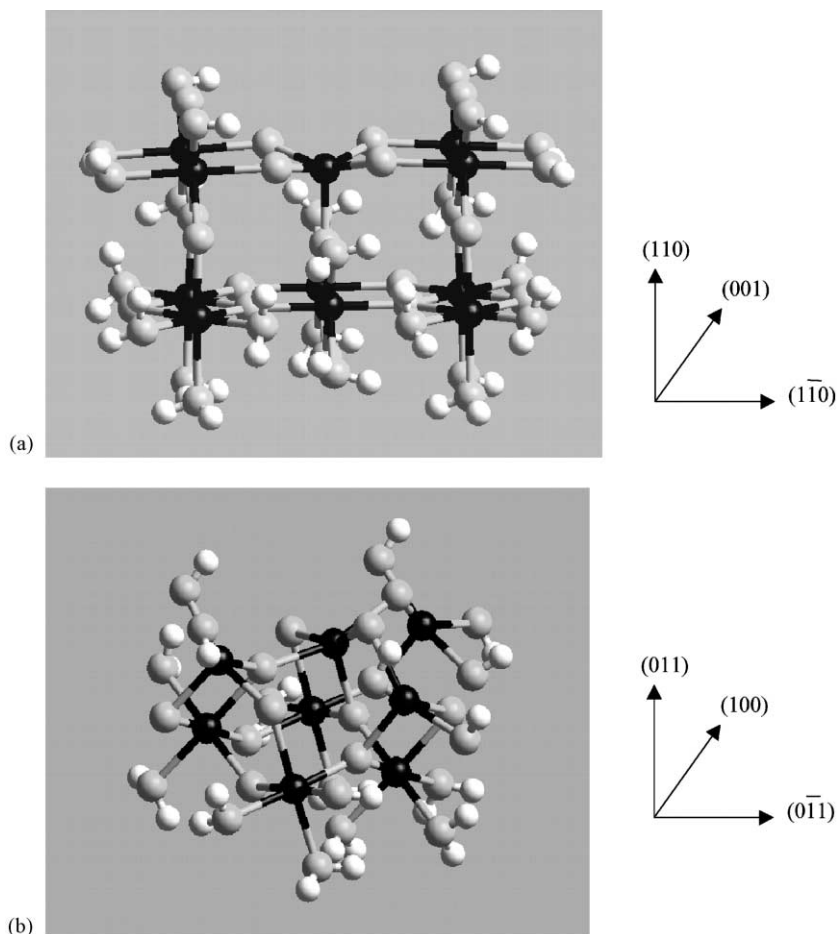


Fig. 1. Optimised surfaces of (a) rutile $\text{Ti}_{11}\text{O}_{42}\text{H}_{40}$ cluster representing $\text{TiO}_2(1\ 1\ 0)$ surface and (b) rutile $\text{Ti}_8\text{O}_{29}\text{H}_{26}$ cluster representing $\text{TiO}_2(0\ 1\ 1)$ surface. Black balls: Ti atoms; grey balls: oxygen atoms; small white balls: hydrogen atoms.

formic acid and formaldehyde as a representation of $\text{TiO}_2(1\ 1\ 0)$ and $\text{TiO}_2(0\ 1\ 1)$ surfaces, respectively. For each cluster two types of surfaces were considered. One used the cluster generated from the crystal coordinates of TiO_2 rutile as described above. The other used this cluster after geometry optimisation using a force field calculation (Universal Force Field) [20]).

The adsorption geometry of formaldehyde was considered based on spectroscopic data. Numerous infra red spectroscopy (IR) and electron energy loss spectroscopy (EELS) have shown that aldehydes such as formaldehyde are adsorbed in an η^1 mode (a) over metal oxides and oxidised metals. On the other hand, they are adsorbed in an $\eta^2(\text{C}, \text{O})$ mode (b)

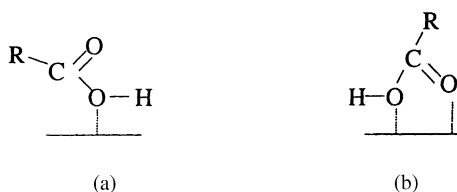
on metals as well as oxygen defected metal oxides [34–36].



R = H for formaldehyde and the surface is represented by the solid line.

Since we are not investigating the effect of surface defects (such as oxygen anion vacancies) only

structure (a) is considered. In structure (a), the oxygen of formaldehyde is adsorbed on one of five-fold Ti cations (designated Ti_{5c}). In the case of formic acid, both spectroscopic and theoretical studies [18,29–33,37,38] have indicated that several adsorption modes may exist and co-exist depending on the nature of the material and its prior treatment. The more nucleophilic oxygen in the molecule is that of the hydroxyl and numerous spectroscopic works have shown that the presence of the uni-dentate mode [37–40]. Although one may consider the adsorption mode the bi-dentate (d) only the mono-dentate mode was studied in this work.



R = H for formic acid

The adsorption energy on $TiO_2(110)$ surface was calculated as follows:

1. The oxygen atom of the carbonyl group is bonded to the five-fold titanium cation on the surface.
2. The energy of the resulting cluster + molecule was then calculated using the semi-empirical molecular orbital method PM3(d) [21].
3. Calculations were carried out on both the non-optimised and optimised clusters. In both cases, the surface Ti_{5c} bonded to the adsorbate, as well as the adsorbate (formaldehyde or formic acid) were allowed to move freely. Calculations allowing both Ti_{5c} and the surrounding lattice oxygen to move leads to highly distorted surface structures. Accordingly only the adsorbate and the Ti_{5c} were allowed to move.
4. The adsorption energies were calculated using the following formula:

$$E_{\text{ads}} = E_{\text{model}} - (E_{\text{bare}} + E_{\text{molecule}})$$

where E_{model} is the energy of the adsorption model, E_{bare} the energy of bare surface, and E_{molecule} the energy of molecules (i.e. formic acid or formaldehyde).

3. Results and discussion

3.1. Energetics of formic acid (HCOOH) and formaldehyde (CH_2O) adsorption on $TiO_2(011)$

In order to investigate the adsorption energy of an organic molecule, one first needs to identify the adsorption geometry. One is guided in this by both theoretical insights as well as experimental data. The most highly charged ion exposed on the surface is the five-fold coordination titanium cations Ti_{5c} . Numerous works have shown that it is indeed the Ti_{5c} that is involved in the adsorption and we expect this to coordinate with the negative O atom of the adsorbate [18,32,33]. We assume that the O of the carbonyl is bound to Ti_{5c} , in the case of formaldehyde, and the oxygen of the hydroxyl is bound to Ti_{5c} , in the case of formic acid (see Section 2 for more details). A further complication occurs in the undissociated adsorption, it is related to the hydrogen bonding of the acidic H (HCOOH), in the case of formic acid, or one of the two H of formaldehyde. As will be indicated below these hydrogen atoms become closer to the surface due to electrostatic interaction with bridging (110) or in-plane (011) oxygen anions. Figs. 2 and 3 present formic acid and formaldehyde adsorption on $Ti_8O_{29}H_{26}$ cluster representing $TiO_2(011)$ -faceted of $TiO_2(001)$ single crystal. Both surfaces are charge neutral, but one has its surface atomic position optimised by force field. They are called thereafter, surfaces I (non-optimised) and II (optimised). The computed data are given in Tables 1 and 2 for both structures. We note that the adsorption energy of CH_2O is less than that of HCOOH for both structures I and II. In effect, CH_2O is less polarisable than HCOOH (polarisability is 2.8×10^{-24} and $3.4 \times 10^{-24} \text{ cm}^{-3}$ for CH_2O and HCOOH, respectively [22]) and as such it is not unexpected to find that the adsorption energy follows the same trend, provided that no major repulsive interaction with the surface occurs. In both structures I and II, there is a considerable energy difference. It is 1.24 eV in the case of CH_2O and 0.77 eV for HCOOH. The hydrogen atoms of formaldehyde are denoted H(1) and H(2) while that of HCOOH is denoted H(2). The bond distance C–H(2) is observed longer than the C–H(1) in the case of CH_2O probably because the attractive interactions between H(2) and in-plane oxygen

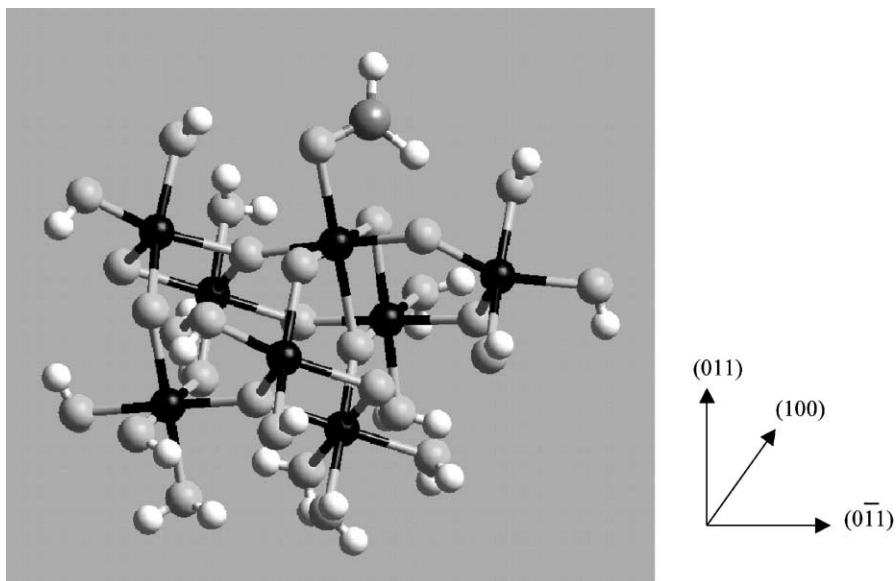


Fig. 2. $\text{Ti}_8\text{O}_{29}\text{H}_{26}$ cluster representing rutile $\text{TiO}_2(011)$ surface + HCOOH . Black balls: Ti atoms; light grey balls: oxygen atoms; dark grey: carbon atoms; small white balls: hydrogen atoms; C=O is represented by a single bond.

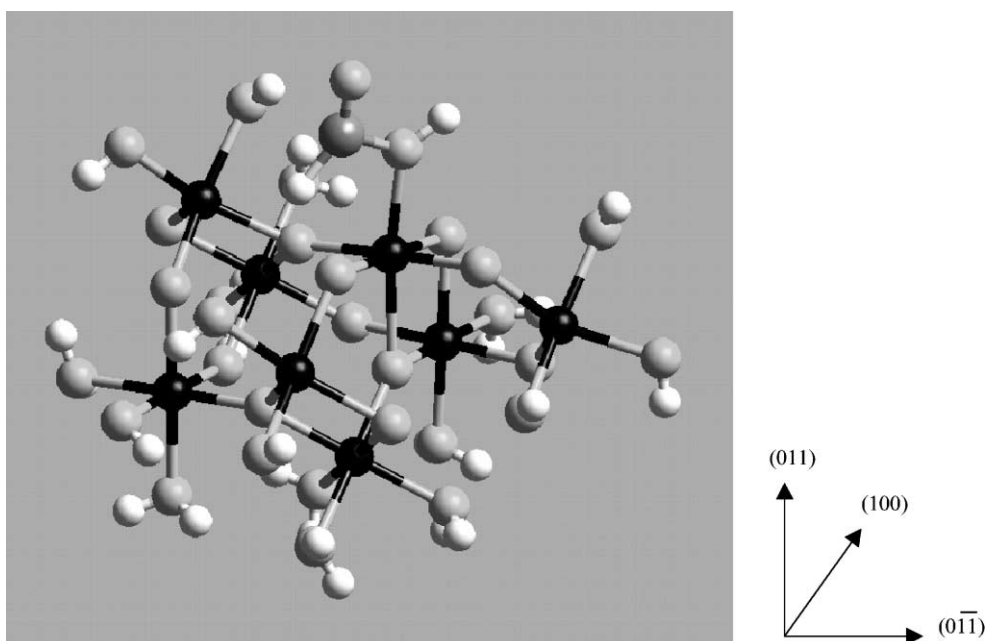


Fig. 3. $\text{Ti}_8\text{O}_{29}\text{H}_{26}$ cluster representing rutile $\text{TiO}_2(011)$ surface + HCHO . Black balls: Ti atoms; light grey balls: oxygen atoms; dark grey: carbon atoms; small white balls: hydrogen atoms; C=O is represented by a single bond.

Table 1
Theoretical energies, from [6]^a, of rutile TiO₂ surfaces^b

Surface	Surface Ti coordination	Unrelaxed surface energy (J m ⁻²)	Relaxed surface energy (J m ⁻²)
(1 1 0)	5, 6	2.05	1.78
(1 0 0)	5	2.40	2.08
(0 0 1)	4	2.81	2.40
(0 1 1), equivalent to phase I of reconstructed TiO ₂ (0 0 1)	5	2.06	1.78
(1 1 1a)	O–Ti–O-terminated	3.95	2.91
(1 1 1b)	O-terminated	3.95	2.60

^a In [6], the tables are inverted, that of anatase should be that of rutile and vice versa.

^b Although shown the coordination number of surface Ti cations. (1 1 1a): asymmetric surface; (1 1 1b): asymmetric inverse of the asymmetric surface.

(denoted O_{in}) on the surface. Moreover, O_m–Ti distance is consistently smaller for HCOOH adsorption than for CH₂O adsorption. The C=O in the case of HCHO has not been elongated when compared to the gas phase molecule (see data in Table 3 for gas phase HCHO and HCOOH) showing that it has not lost part of its double bonds character after the adsorption.

3.2. Energetics of formic acid (HCOOH) and formaldehyde (CH₂O) adsorption on TiO₂(1 1 0)

Figs. 4 and 5 show results of HCHO and HCOOH adsorption over Ti₁₁O₄₂H₄₀ cluster representing the TiO₂(1 1 0) surface. Similar trends are observed on this surface. Again, the adsorption energy of CH₂O is smaller than that of HCOOH on both structures I and II (Table 3), although the difference is less remarkable particularly on the optimised (I) surface when compared to the (0 1 1) surface. Again, the bond distance

C–H(2) is longer than the C–H(1) in the case of CH₂O because the attractive interactions between H(2) and bridging oxygen on the surface.

HCOOH is far more stable on the (0 1 1) surface than on the (1 1 0) surface, by ca. 0.5 eV, on the optimised surface. This is not surprising, it was very early recognised that the {0 1 1}-faceted TiO₂(0 0 1) single crystal is far more active towards organic adsorbates than TiO₂(1 1 0) [23]. The reason may as well be due to the presence of bridging oxygen creating an electrostatic repulsion layer that the incoming molecules are required to break before adsorption.

Table 4 presents the computed adsorption energy of formic acid over several oxides by several theoretical methods. It is not a simple task to compare the values to those of experimental works. Unlike metals, oxides tend to dissociate the adsorbates because of several factors including polarisability and dipole–dipole interactions [24]. Moreover, despite the important progress in surface science of oxides observed in recent years. Important data are still missing. For example, it is clear from the table that increasing the surface coverage does decrease the adsorption energy of formic acid (adsorbate–adsorbate repulsive interactions), yet we have no experimental data investigating this point. In addition, data of submonolayer adsorption at very low-temperatures (to prevent the dissociation) over oxides are scarce. Nevertheless, over the {0 1 1}-faceted TiO₂(0 0 1) single crystal formaldehyde desorbs at slightly lower temperature than formic acid by 15–20 K [15,25] during TPD (both reactants were dosed at room temperature); thus, the order qualitatively agrees with the computed adsorption energy. It is, however, not possible to make

Table 2
Adsorption energy and parameters of CH₂O and HCOOH on both the optimised (I) and non-optimised (II) TiO₂(0 1 1) surfaces

Parameter	I		II	
	CH ₂ O	HCOOH	CH ₂ O	HCOOH
R(O _m –Ti) (Å)	2.15	2.08	2.16	2.06
r(C=O) (Å)	1.24	1.20	1.23	1.19
r(C–O) (Å)	–	1.42	–	1.43
r(C–H(1)) (Å)	1.09	–	1.09	–
r(C–H(2)) (Å)	1.18	1.39	1.18	1.28
r(O–H) (Å)	–	0.95	–	0.96
∠(O _m –Ti–O _{co}) (°)	82.86	83.26	79.65	79.96
E _{ads} (eV)	1.92	2.39	0.68	1.62

Table 3
Adsorption energy and parameters of CH₂O and HCOOH of both the optimised and non-optimised TiO₂(1 1 0) surfaces

Parameter	I		II		Other works
	CH ₂ O	HCOOH	CH ₂ O	HCOOH	
$r(\text{O-Ti})$ (Å)	2.17	2.11	2.14	2.24	2.1 ± 0.1 [26] HCOOH/TiO ₂ (1 1 0)
$r(\text{C=O})$ (Å)	1.23	1.20	1.24	1.20	HCHO 1.23 INDO [27] 1.2078 exp. [28] HCOOH 1.24 INDO [27] 1.213 DFT [18]
$r(\text{C-O})$ (Å)	–	1.39	–	1.42	1.202 exp. [28] 1.29 INDO [27] 1.354 DFT [18] 1.343 exp. [28]
$r(\text{C-H}(1))$ (Å)	1.09	–	1.09	–	1.05 INDO [27] 1.116 exp. [28]
$r(\text{C-H}(2))$ (Å)	1.18	1.24	1.18	1.22	
$r(\text{O-H})$ (Å)	–	0.97	–	1.01	0.97 INDO [27] 0.986 DFT [18] 0.972 exp. [28]
$\angle(\text{O}_m\text{-Ti-O}_{in})$ (°)	87.12	86.06	86.73	74.45	
$\text{O}_{in}\text{-H}(2)$	1.82	1.77	1.80	1.77	
E_{ads} (eV)	1.21	2.06	0.66	1.11	

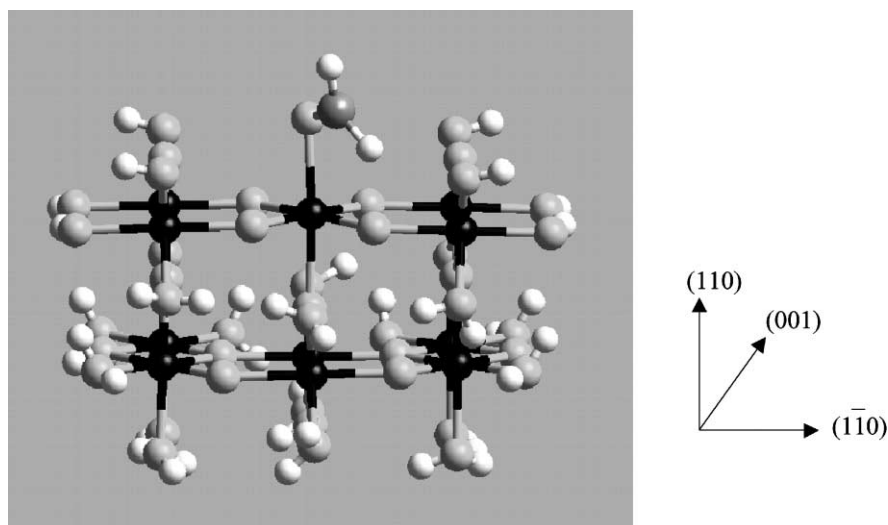


Fig. 4. Ti₁₁O₄₂H₄₀ cluster representing rutile TiO₂(1 1 0) surface + HCOOH. Black balls: Ti atoms; light grey balls: oxygen atoms; dark grey: carbon atoms; small white balls: hydrogen atoms; C=O is represented by a single bond.

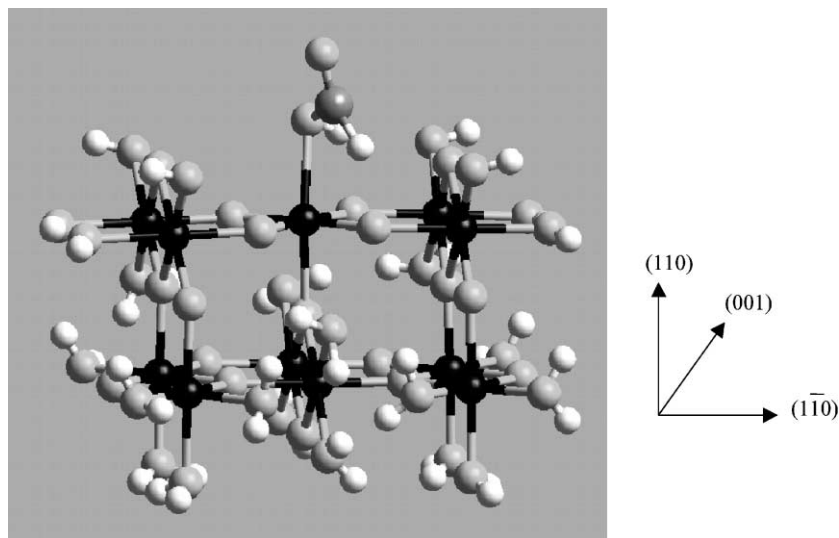


Fig. 5. $\text{Ti}_{11}\text{O}_{42}\text{H}_{40}$ cluster representing rutile $\text{TiO}_2(110)$ surface + HCHO. Black balls: Ti atoms; light grey balls: oxygen atoms; dark grey: carbon atoms; small white balls: hydrogen atoms; C=O is represented by a single bond.

Table 4
Computed adsorption energies of formic acid over several oxide surfaces^a

Oxide	E_{ads} (eV)	Method	Conformation	References
$\text{TiO}_2(110)$	0.65 ($\theta = 0.5$)	DFT, GGA	M, uni-dentate	[18]
Periodic	0.61 ($\theta = 1$)			
	0.79 ($\theta = 0.5$)		D, uni-dentate	[18]
	0.71 ($\theta = 1$)			
$\text{TiO}_2(110)$	2.50 ($\theta = 0.5$)	Ab initio Hartree–Fock	M, uni-dentate through OH	[32]
Slab	2.11 ($\theta = 1$)	(CRYSTAL)		
$\text{TiO}_2(110)$	1.72 p(2×1)	DFT, GGA	D	[33]
Periodic	1.70 c(2×2)			
$\text{Ti}_{11}\text{O}_{42}\text{H}_{40}$	1.11	PM3	M	This work
$\text{TiO}_2(110)$				
$\text{Ti}_8\text{O}_{29}\text{H}_{26}$	1.62	PM3	M	This work
$\text{TiO}_2(011)$				
$\text{ZnO}(10\bar{1}0)$	2.1	Ab initio	D, uni-dentate	[29]
Periodic		Hartree–Fock		
Zn_9O_9	1.64	MINDO/3	D, uni-dentate	[30]
$\text{ZnO}(10\bar{1}0)$				
$\text{MgO}(100)$	0.51	DFT, GGA	M	[31]
Periodic	0.88	DFT, GGA	D, bi-dentate	

^a D: dissociated, M: molecular.

a general remark from such a table, there are as much differences between periodic and cluster calculations for one oxide as it is between cluster calculations between two oxides.

One can see from Tables 2 and 3 that the adsorption energies are smaller on the non-optimised surface (I)

than on the optimised one (II). This is mainly due to the fact that the Ti cation at the surface moves slightly into the bulk while the lattice O atoms move outside. This results in a stronger repulsion (Pauli) and destabilisation of the adsorbate-surface system. Similar observation has been made by other workers

treating the adsorption of CO₂ over SnO₂(1 1 0) slab surfaces [42].

In summary, this work presents the first calculation of the adsorption energy of formaldehyde and formic acid over the {0 1 1}-faceted TiO₂(0 0 1) single crystal. While formaldehyde is relatively weakly adsorbed (0.68 eV) formic acid is strongly adsorbed, $E_{\text{ads}} = 1.62$ eV. Cluster calculations in this work have shown that formaldehyde adsorption energy over TiO₂(1 1 0) is very similar to that over TiO₂(0 1 1), 0.66 and 0.68 eV, respectively. On the other hand, formic acid adsorption was far more stable, by upto 0.5 eV, on the (0 1 1) face than on (1 1 0) in qualitative agreement with experimental results.

References

- [1] M.A. Barteau, Chem. Rev. 96 (1996) 1413.
- [2] A.L. Linsebigler, G. Lu, J.T. Yates Jr., Chem. Rev. 3 (1995) 735.
- [3] H. Idriss, M.A. Barterau, Adv. Catal. 45 (2000) 261.
- [4] G. Charlton, P.B. Howes, C.L. Nicklin, P. Steadman, J.S.C. Taylor, C.A. Muryn, S.P. Harte, J. Mercer, R. McGrath, D. Norman, T.S. Turner, G. Thornton, Phys. Rev. Lett. 78 (1997) 495.
- [5] B. Hird, R.A. Armstrong, Surf. Sci. 385 (1997) L1023.
- [6] P.M. Oliver, G.W. Watson, E.T. Kelsey, S.C. Parker, J. Mater. Chem. 7 (1997) 563.
- [7] Q. Zhong, J.M. Vohs, D.A. Bonnell, Surf. Sci. 274 (1992) 35.
- [8] I. Cocks, D.Q. Quo, E.M. Williams, Surf. Sci. 390 (1997) 119.
- [9] P.W. Murray, N.G. Condon, G. Thornton, Phys. Rev. B 51 (1995) 10989.
- [10] H. Onishi, Y. Iwasawa, Phys. Rev. Lett. 76 (1996) 791.
- [11] P.J. Möller, M.C. Wu, Surf. Sci. 224 (1989) 265.
- [12] R.H. Tait, R.V. Kasowski, Phys. Rev. B 20 (1979) 5178.
- [13] L.E. Firment, Surf. Sci. 116 (1982) 205.
- [14] L. Patthey, H. Rensmo, P. Person, K. Westmark, L. Vayssieres, A. Stahans, A. Petersson, P.A. Brühwiler, H. Siegbahn, S. Lunell, N. Mårtensson, J. Chem. Phys. 110 (1999) 5913.
- [15] H. Idriss, K.S. Kim, M.A. Barteau, Surf. Sci. 262 (1992) 113.
- [16] S.R. Cain, F. Emmi, Surf. Sci. 232 (1990) 209.
- [17] G. Busca, J. Lamotte, J.C. Lavalley, V. Lorenzelli, J. Am. Chem. Soc. 109 (1987) 5197.
- [18] S.P. Bates, G. Kresse, M.J. Gillan, Surf. Sci. 409 (1998) 336.
- [19] Cerius 2, Version 3.5, Molecular Simulation, San Diego, CA, 1997.
- [20] Universal Force Field, Version 1.02, A.K. Rappé, C.J. Casewit, K.S. Colwell, W.A. Goddard, W.M. Skiff, J. Am. Chem. Soc. 114 (1992) 10024.
- [21] Spartan, Version 5.0, Wavefunction, Inc., Irvine, CA.
- [22] D.R. Lide, Hand Book of Chemistry and Physics, 75th Edition, CRC Press, Boca Raton, FL, 1994.
- [23] V.E. Henrich, P.A. Cox, The Surface Science of Metal Oxides, Cambridge University Press, Cambridge, 1994.
- [24] R.I. Masel, Principles of Adsorption and Reaction on Solid Surfaces, Wiley, New York, 1994.
- [25] K.S. Kim, M.A. Barteau, Langmuir 6 (1990) 1485.
- [26] S. Thevuthansan, G.S. Herman, Y.J. Kim, S.A. Chambers, C.H.F. Peden, Z. Wang, R.X. Ynzunza, E.D. Tober, J. Morais, C. S. Fadley, Surf. Sci. 401 (1998) 261.
- [27] P. Persson, A. Stashans, R. Bergström, S. Lunell, Int. J. Quatum Chem. 70 (1998) 1055.
- [28] K.-H. Hellwege, A.M. Hellwege (Eds.), Landolt–Börnstein Numerical Data and Functional Relationship in Science and Technology, Vol. 7, Structural Data of Free Polyatomic Molecules, Springer, Berlin, 1976.
- [29] P. Persson, L. Ojamäe, Chem. Phys. Lett. 321 (2000) 302.
- [30] N.U. Zhanpeisov, H. Nakatsuiji, M. Hada, M. Yoshimoto, J. Mol. Catal. A: Chem. 118 (1997) 69.
- [31] M.A. Szymański, M.J. Gillan, Surf. Sci. 367 (1996) 135.
- [32] J. Ahdjoudi Jr, C. Minot, Catal. Lett. 46 (1997) 83.
- [33] P. Käckell, K. Terakura, Appl. Surf. Sci. 166 (2000) 370.
- [34] D.A. Chen, C.M. Friend, Langmuir 14 (1998) 1451.
- [35] C.J. Houtman, M.A. Barteau, J. Catal. 130 (1991) 528.
- [36] K.T. Queeney, C.R. Arumainayagam, A. Balaji, C. M Friend, Surf. Sci. 418 (1998) L31.
- [37] G.B. Deacon, R.J. Phillips, Coordin. Chem. Rev. 33 (1980) 227.
- [38] A. Yee, S.J. Morrison, H. Idriss, J. Catal. 279 (1999) 186.
- [39] B.E. Hayden, A. King, M.A. Newton, J. Phys. Chem. B 103 (1999) 103.
- [40] J.L. Davis, M.A. Barteau, J. Am. Chem. Soc. 1782 (1989) 111.
- [41] M. Casarin, C. Maccato, A. Vittadini, Appl. Surf. Sci. 142 (1999) 196.
- [42] M. Melle-Franco, G. Pacchioni, A.V. Chadwick, Surf. Sci. 478 (2001) 25.