

Trends within the adsorption energy of alcohols over rutile $\text{TiO}_2(1\ 1\ 0)$ and $(0\ 1\ 1)$ clusters

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Abstract

The non-dissociative adsorption energy of a series of alcohols over a rutile $\text{Ti}_8\text{O}_{29}\text{H}_{26}$ cluster, representing the $\text{TiO}_2(0\ 1\ 1)$ surface, as well as over a rutile $\text{Ti}_{11}\text{O}_{42}\text{H}_{40}$ cluster, representing the $\text{TiO}_2(1\ 1\ 0)$ surface, was computed by means of a semi-empirical PM3 method. Over $\text{TiO}_2(0\ 1\ 1)$ surface the non-dissociative adsorption energy of methanol, ethanol, *n*-propanol and *i*-propanol were 1.29, 1.46, 2.08, and 2.40 eV, respectively. This trend can reasonably be explained by gas phase acidity, as measured by their relative (to methanol) polarizability. On the other hand, the same series investigated over $\text{TiO}_2(1\ 1\ 0)$ gave the following adsorption energy values: 1.49, 1.60, 1.96, and 1.94 eV, respectively. The relatively low adsorption energy for *i*-propanol, shows a deviation from the expected correlation. The reason for that is most likely structural. While $\text{TiO}_2(1\ 1\ 0)$ surface contains Ti^{4+} cations five- and six-fold coordinated to oxygen, $\text{TiO}_2(0\ 1\ 1)$ surface contains Ti^{4+} all in a five-fold coordination environment. Thus, it appears that the alternating rows of bridging oxygen anions of the $(1\ 1\ 0)$ surface exert a repulsive interaction over the two-methyl groups of *i*-propanol decreasing its adsorption energy.

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Keywords: Adsorption energy; Rutile; Adsorbates

1. Introduction

Metal oxides are of great technological importance for several processes such as catalysis, corrosion, gas sensing and thin film growth for dielectrics and superconductors. All these processes depend on the structure and the bonding configuration of atoms at oxide surfaces [1–3]. Unlike metals, oxides have generally no direct metal–metal bonds. Metal cations in oxides are surrounded by a coordination sphere of oxygen anions. This results in formation of cation–anion centers, $\text{M}^{x+}-\text{O}^{2-}$. These centers may be viewed as pairs of Lewis acid–base sites on the surface of the oxides. The distribution and nature of these sites depend on

the surface structure and intrinsic characteristics of the oxides. For example, O^{2-} in MgO are six-fold coordinated to Mg^{2+} in the bulk (rock salt structure). They become five-fold coordinated on the surface (terraces), four-fold coordinated on the steps and three-fold coordinated on the edges. Consequently, the stability of these O^{2-} ions will change accordingly and this will affect their adsorption and reaction behaviors [4–6].

TiO_2 is one of the most studied transition metal oxides. First principle calculations were used to investigate the energy of adsorption of H_2O , CH_3OH , H_2O_2 , and HCOOH on a $\text{TiO}_2(1\ 1\ 0)$ surface [7]. The adsorption energy for the most favorable molecular mode of adsorption is very close to that for dissociative adsorption in the cases of H_2O , CH_3OH , and H_2O_2 . In general, the surface structure plays a crucial role in

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determining the conformations of the most stable geometries for adsorbed species. Equally important is the hydrogen bonding between adsorbed species [7]. The actual surface structure will differ, a little, from that produced by a simple cleaving of the bulk structure. Due to relaxation, the top several layers move in or out to minimize the surface energy.

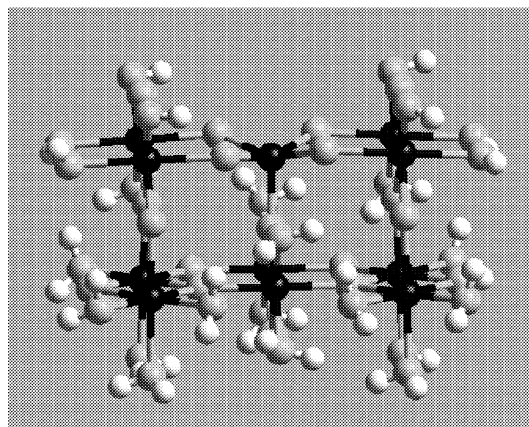
The (1 1 0), (1 0 0) and (0 0 1) rutile TiO_2 surfaces have been the subject of numerous experimental and theoretical investigations [1–3,8,9]. For example, the (1 0 0) surface exhibits a series of (1 × 3), (1 × 5) and (1 × 7) reconstructions upon annealing at 600, 800 and 1200 °C, respectively [1,8,10]. The (0 0 1) plane is the least stable of all the low index planes of TiO_2 . The ideal termination of the bulk structure exposes all surface titanium atoms in a four-fold coordination environment [1]. Several experiments were conducted, by AES [11], EELS [11], UPS [11], LEED [12], XPS [13], AFM [14], NEXAFS [15], and STM [16,17] techniques, to investigate the surface and electronic structure of $\text{TiO}_2(0 0 1)$ single crystal. Results suggested that faceting with different crystallographic orientation terminates the surface. Comparison of theoretically calculated LEED pattern to the experimental data allowed the determination of these facets [11]. The low temperature phase, produced by annealing up to ~750 K, is the {0 1 1}-faceted structure, in which all surface titanium atoms are five-fold coordinated to oxygen anions. A few experimental studies have considered the interaction of alcohol molecules with this {0 1 1}-faceted $\text{TiO}_2(0 0 1)$ surface. The alcohols that have been investigated include CH_3OH , $\text{C}_2\text{H}_5\text{OH}$, $n\text{-C}_3\text{H}_7\text{OH}$ and $i\text{-C}_3\text{H}_7\text{OH}$. These alcohols dissociatively adsorb at room temperature [18,19] to form surface bound alkoxy (–OR) and hydroxyl (–OH) groups. XPS analyses of the C 1s of the functional group over $\text{TiO}_2(0 1 1)$ surface have shown no major differences in the binding energy of these alkoxides; XPS C 1s were 286.8 [17], 286.5 and 286.9 [18] eV for $\text{CH}_3\text{O(a)}$, $\text{CH}_3\text{CH}_2\text{O(a)}$, and $(\text{CH}_3)_2\text{CHO(a)}$, respectively ((a) for adsorbed). This indicates that once the dissociative adsorption has occurred, the effect of the alkyl chain on the binding energy of the alkoxide is negligible. Moreover, temperature programmed desorption (TDP) also shows no difference in the first desorption peak temperature between these alcohols [17,18]; although studies of sub-monolayer coverages at low temperatures were not conducted.

On the contrary, alcohols do not dissociate on $\text{TiO}_2(1 1 0)$ surface [20,21]. The adsorption energies of methanol on rutile $\text{TiO}_2(1 1 0)$ and $\text{SnO}_2(1 1 0)$ surfaces have been computed by DFT [7,20]. Over $\text{TiO}_2(1 1 0)$ surface, at both full- and half-coverage, the adsorption energies of molecular and dissociated modes are very close in energy, with the latter slightly more stable (by ~20 kJ/mol) at half coverage [7]. Similarly, the half-coverage adsorption energies are larger, then those at full coverage in the case of $\text{SnO}_2(1 1 0)$ surface [20]. However, the dissociated mode of adsorption is clearly more favored than the non-dissociated mode over $\text{SnO}_2(1 1 0)$.

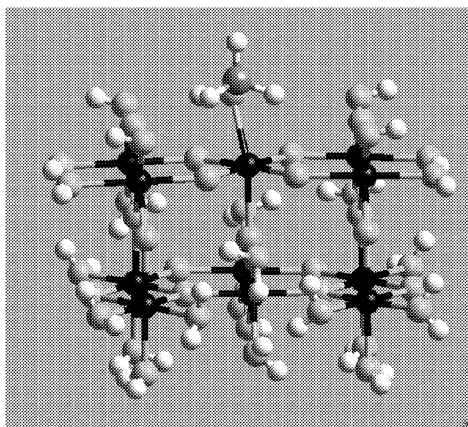
To date, no theoretical work has addressed the adsorption energy of any alcohol on the surface of rutile $\text{TiO}_2(0 0 1)$ or on any of its stable faceted surfaces: the {0 1 1}- and the {1 1 4}-faceted. This work aim to calculating the non-dissociative adsorption energy of simple alcohols on the surface of the first thermodynamically stable structure of $\text{TiO}_2(0 0 1)$; the {0 1 1}-faceted surface. A comparison with $\text{TiO}_2(1 1 0)$ surface is also included. The work does also attempt to relate the observed trend of adsorption energy on these surfaces with known physical properties of the adsorbates such as: their ionization potential, electron affinity (EA), inductive effect and polarizability due to changing the nature of the alkyl chain.

2. Methodology

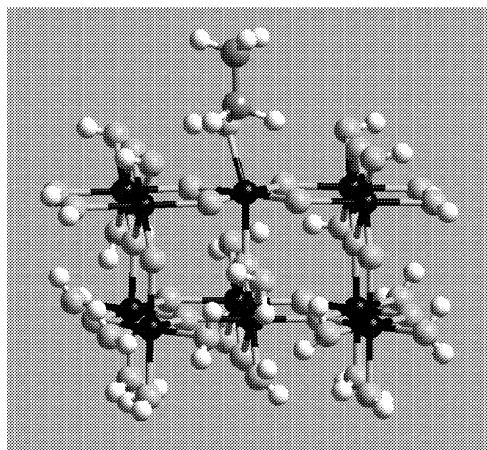
A TiO_2 rutile unit cell is generated using a Cerius 2 program (Molecular Simulation Inc.). It is then cleaved along the (1 1 0) or the (0 1 1) directions. It was necessary to select a cluster large enough to be of reasonable representation of the surface, but not too large because of computation time. We have conducted several runs to compute the adsorption energy of methanol (as an example of an adsorbate) as a function of the cluster size for both types of clusters ((0 1 1) and the (1 1 0)). Clusters with 11 Ti atoms for the (1 1 0) and of eight Ti atoms for the (0 1 1) were judged adequate for conducting the runs. The size of the cluster is consistent with results of other workers [22]. The as-obtained cluster is not charge neutral. The excess negative charge (due to non-bonded oxygen atoms) was neutralized by adding protons to



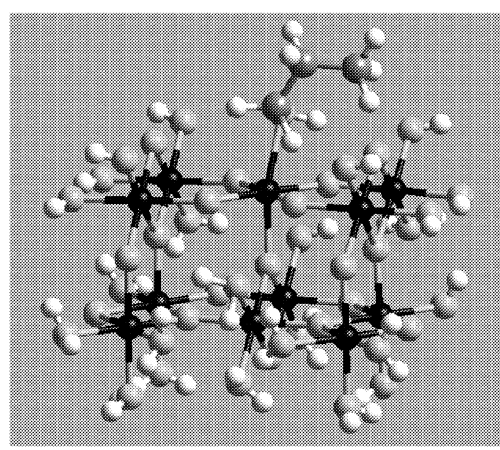
a



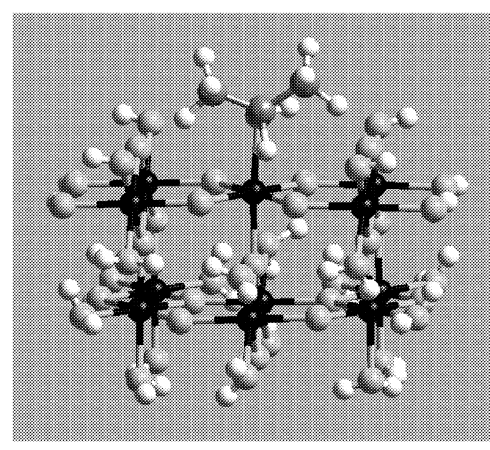
b



c



d



e

Fig. 1. (a) $\text{Ti}_{11}\text{O}_{42}\text{H}_40$ charge neutral cluster, black, gray and white correspond to Ti^{4+} , O^{2-} and H^+ , respectively. (b) $\text{Ti}_{11}\text{O}_{42}\text{H}_40$ (representing rutile $\text{TiO}_2(110)$ surface) + methanol. Black, light grey, dark grey and white correspond to Ti^{4+} , O^{2-} , C and H^+ , respectively. (c) $\text{Ti}_{11}\text{O}_{42}\text{H}_40$ (representing rutile $\text{TiO}_2(110)$ surface) + ethanol. Black, light grey, dark grey and white correspond to Ti^{4+} , O^{2-} , C and H^+ , respectively. (d) $\text{Ti}_{11}\text{O}_{42}\text{H}_40$ (representing rutile $\text{TiO}_2(110)$ surface) + *n*-propanol. Black, light grey, dark grey and white correspond to Ti^{4+} , O^{2-} , C and H^+ , respectively. (e) $\text{Ti}_{11}\text{O}_{42}\text{H}_40$ (representing rutile $\text{TiO}_2(110)$ surface) + *i*-propanol. Black, light grey, dark grey and white correspond to Ti^{4+} , O^{2-} , C and H^+ , respectively.

the cluster. The resulting clusters, $\text{Ti}_{11}\text{O}_{42}\text{H}_{40}$ and $\text{Ti}_8\text{O}_{29}\text{H}_{26}$ representing the (110) and the (011) surfaces of TiO_2 , respectively can be found in Fig. 1 of [21]. For each cluster, two types of surfaces were considered. One as obtained and the other after geometry optimization using a force field calculation (universal force field [31]). The force field is a molecular mechanics model composed of a four-component picture of the intra- and inter-molecular forces within a given system. These are: (i) interactions between pairs of atoms, (ii) summation over all valence angles in the lattice, (iii) torsion, (iv) Coulomb potential for electrostatic and Lennard–Jones for van der Waals interactions. More details can be found in [21,30,31].

The adsorption energy was calculated as follows:

- The oxygen atom of the alcohol molecule is bonded to the five-fold titanium cation on the surface, Ti_{5c}^{4+} (Fig. 1b, for example).
- The resulting $\text{Ti}_{11}\text{O}_{42}\text{H}_{40}$ cluster + the alcohol molecule is transferred to the Spartan program (Wavefunction Inc., CA) in order to perform a semi-empirical calculation of the heat of formation for this cluster.
- All calculations were performed using semi-empirical PM3 (d) method. The PM3 is a self-consistent field (SCF) method, it takes into account electrostatic repulsion and exchange stabilization. It uses a restricted basic set of one s orbital and three p orbitals (p_x , p_y and p_z) per atom and ignores overlap integrals in the secular equation. It is based on MNDO (a modified neglect of diatomic differential overlap (NNDO) method: NNDO means neglected differential overlap between atomic orbitals on different atoms). The name, PM3 derives from the fact that it is the third parameterization of MNDO, AM1 (Austin model 1) is the second.
- The surface Ti_{5c}^{4+} bonded to the adsorbate and the latter (methanol to *i*-propanol) was allowed to move freely. Calculations allowing both Ti_{5c}^{4+} and the surrounding lattice oxygen to move leads to highly distorted surface structures. Accordingly, only the adsorbate and the Ti_{5c}^{4+} were allowed to move. 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. methanol, ethanol, *n*-propanol, or *i*-propanol).

3. Results

3.1. Effects of changing the size of alcohols on the heat of adsorption over $\text{TiO}_2(110)$ surface

We have previously investigated the non-dissociative adsorption energy of formic acid and formaldehyde on the surfaces of $\text{TiO}_2(110)$ and $\text{TiO}_2(011)$ represented by $\text{Ti}_{11}\text{O}_{42}\text{H}_{40}$ and $\text{Ti}_8\text{O}_{29}\text{H}_{26}$ clusters, respectively. In these calculations, the oxygen of formaldehyde as well as the oxygen of the hydroxyl group of formic acid were allowed to interact with the five-fold Ti_{5c}^{4+} center (the most highly charged ion exposed on the surface) of both the (110) and (011) surfaces [21]. In this work, we have followed the same method [21], where the O atoms of ROH molecules are put in contact with these Ti centers. This results in additional interactions of surface oxygen ions (O_{2c}^{2-} and O_{3c}^{2-}) with hydrogen atoms of ROH adsorbates; the acidic H atoms (RO–H) and, the H atoms of the alkyl group (H–CHR'OH).

All calculations were conducted on a $\text{Ti}_{11}\text{O}_{42}\text{H}_{40}$ cluster. Results of these adsorption energies as well as the corresponding structural parameters are presented in Table 1. The molecular adsorbates are denoted by m, the hydroxyl oxygen of the alcohols by O_m , and in plane oxygen atoms (O_{3c}^{2-}) by O_{in} .

The adsorption energies after energy minimization are about 0.5 eV less when compared to the as-obtained structure. A simple explanation might be as follows. Upon energy minimization, the in plane oxygen atoms move out of the surface resulting in a slight increase of the repulsive force between the adsorbed molecules and the surface. For both structures, the adsorption energies increase with increasing the adsorbate size. In the case of *i*-propanol, the steric repulsion between the two methyl groups and the bridging oxygen anions on the surface might be the reason for the decreasing of the bond energy (Section 4). The bond distance between Ti_{5c}^{4+} and the hydroxyl oxygen of the alcohols does not follow a linear trend (a decrease) as the energy increases.

Table 1

Adsorption energies and parameters of alcohols on the $\text{Ti}_{11}\text{O}_{42}\text{H}_{40}$ cluster representing the rutile $\text{TiO}_2(110)$ surface (before) and after geometry optimization

Molecules (m)	E_{ads} (eV)	$r(\text{O}_m\text{-Ti})$ (Å)	$r(\text{C-O})$ (Å)	$r(\text{O-H})_m$ (Å)	$\angle(\text{O}_m\text{-Ti-O}_m)$ (°)
Methanol	(2.08) 1.49	(2.323) 2.180	(1.435) 1.438	(0.972) 0.996	(78.02) 62.80
Ethanol	(2.42) 1.60	(2.199) 2.143	(1.450) 1.448	(0.971) 0.994	(78.38) 62.10
<i>n</i> -Propanol	(2.69) 1.96	(2.100) 2.259	(1.452) 1.436	(0.971) 1.003	(61.48) 66.96
<i>i</i> -Propanol	(2.49) 1.94	(2.245) 2.148	(1.451) 1.473	(1.001) 0.972	(72.95) 78.57

This might be due to two possible reasons: (i) steric effect between the alkyl groups and surface oxygen atoms, (ii) secondary interactions occurring between hydrogens of the alkyl groups and surface bridging oxygen. Indeed, the alkyl hydrogens tend to approach more closely to the O_{2c}^{2-} surface than the hydroxyl proton: attracted by the higher negative charge of oxygen anions (when compared to O_{3c}^{2-} anions) of the surface (see Fig. 1e for the case of *i*-propanol).

It is worth comparing our cluster calculations to those of other workers. A variety of spectroscopic measurements and theoretical models have been used to investigate the nature of bound methanol to TiO_2 surfaces. Since this work is addressing the adsorption energy over clusters of TiO_2 , a comparison with results on other clusters seems appropriate. Ferris and Wang have used ab initio electronic structure method to calculate the adsorption energy of methanol on model structures of ideal (110) and (100) rutile TiO_2 surfaces [22]. The difference between our work and that of Ferris and Wang [22] is in the cluster size. In [22], the authors have used a one layer $\text{Ti}_7\text{O}_{15}\text{H}_{26}$ cluster representing the (110) surface of TiO_2 . The (110) cluster of this work is a two-layer cluster (five and six Ti atoms for the first and second layer, respectively). Ferris and Wang work also conducted a force optimization on their cluster (see methodology in [22]). They found a binding energy of 1.94 eV for the non-dissociatively adsorbed mode of methanol. This is in reasonable agreement with our results (Table 2). The optimum Ti– O_m distance (m stands for methanol) was found at 2.06 Å in the case of methanol– $\text{Ti}_7\text{O}_{15}\text{H}_{26}$ [22] and it is found 2.18 Å in the case of methanol– $\text{Ti}_{11}\text{O}_{42}\text{H}_{40}$ (Table 1). The slight difference in equilibrium distance might explain the difference in adsorption energy. Their data (as well as those of others) and ours are presented in Table 2.

3.2. Effects of changing the size of alcohols on their heat of adsorption over $\text{TiO}_2(011)$ surface

All calculations were conducted on a $\text{Ti}_8\text{O}_{29}\text{H}_{26}$ cluster. Hydroxyl oxygen atom of the alcohols was allowed to bind to one of the Ti_{5c}^{4+} on the (011) surface. It is important to indicate that the surface does not contain bridging oxygen anions (unlike the (110) surface) (Fig. 2a). In the optimized structure, the angles between Ti_{5c}^{4+} and the co-planar oxygen anions of the surface are slightly smaller than those of the as-obtained structure. For example, they are 121.4 and 128.7° for the optimized and as obtained conformations, respectively. As in the case of the (110) relaxed structure, the co-planar oxygen anions move slightly out of the surface to minimize its energy. Table 3 shows the results of the calculated binding energies as well as the structural parameters for the same series of alcohols on the (011) surface. As in the case of the (110) surface, a large difference in the adsorption energy exists between the as-prepared and the optimized structures. Optimizing the structure prior to adsorption decreases the energy of adsorption by about 1 eV

Table 2

Computed energies of molecularly adsorbed methanol over TiO_2 and SnO_2 surfaces

Oxide	E_{ads} (eV) methanol	Method	Reference
$\text{TiO}_2(110)$	1.05 ($\theta = 0.5$)	DFT, GGA	[7]
$\text{SnO}_2(110)$	2.42 ($\theta = 0.5$)	DFT, GGA	[19]
$\text{Ti}_7\text{O}_{15}\text{H}_{26}\text{TiO}_2$ (110)	1.94	Ab initio, 3-21 G* basis set	[22]
$\text{Ti}_6\text{O}_{15}\text{H}_{20}\text{TiO}_2$ (100)	0.63	Ab initio, 3-21 G* basis set	[22]
$\text{Ti}_{11}\text{O}_{42}\text{H}_{40}\text{TiO}_2$ (110)	1.49	PM3	This work
$\text{Ti}_8\text{O}_{29}\text{H}_{26}\text{TiO}_2$ (011)	1.29	PM3	This work

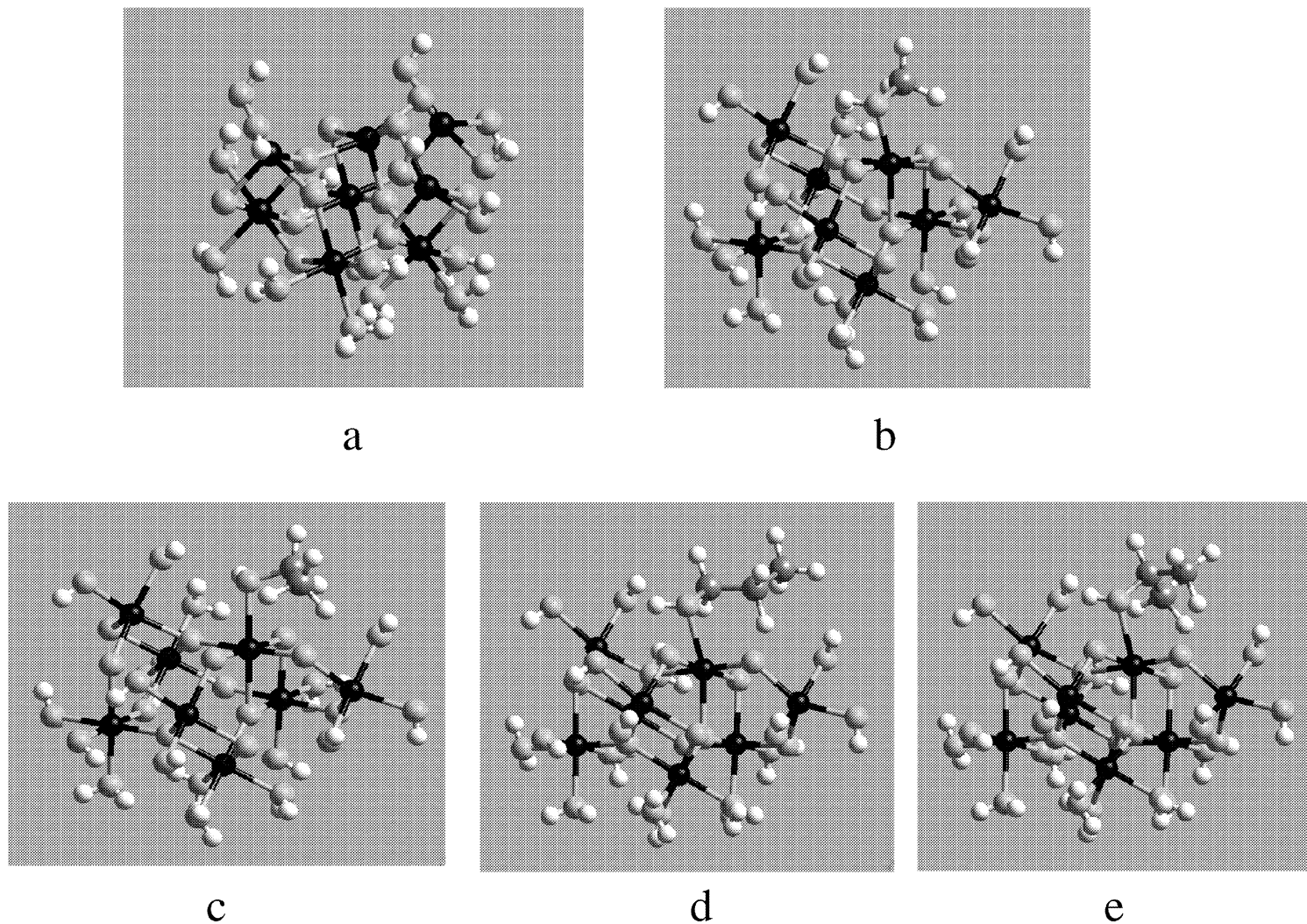


Fig. 2. (a) $\text{Ti}_8\text{O}_{29}\text{H}_{26}$ charge neutral cluster, black, grey and white correspond to Ti^{4+} , O^{2-} and H^+ , respectively. (b) $\text{Ti}_8\text{O}_{29}\text{H}_{26}$ (representing rutile $\text{TiO}_2(011)$ surface) + methanol. Black, light grey, dark grey and white correspond to Ti^{4+} , O^{2-} , C and H^+ , respectively. (c) $\text{Ti}_8\text{O}_{29}\text{H}_{26}$ (representing rutile $\text{TiO}_2(110)$ surface) + ethanol. Black, light grey, dark grey and white correspond to Ti^{4+} , O^{2-} , C and H^+ , respectively. (d) $\text{Ti}_8\text{O}_{29}\text{H}_{26}$ (representing rutile $\text{TiO}_2(110)$ surface) + *n*-propanol. Black, light grey, dark grey and white correspond to Ti^{4+} , O^{2-} , C and H^+ , respectively. (e) $\text{Ti}_8\text{O}_{29}\text{H}_{26}$ (representing rutile $\text{TiO}_2(110)$ surface) + *i*-propanol. Black, light grey, dark grey and white correspond to Ti^{4+} , O^{2-} , C and H^+ , respectively.

Table 3

Adsorption energies and parameters of alcohols on the $\text{Ti}_8\text{O}_{29}\text{H}_{26}$ cluster representing the rutile $\text{TiO}_2(011)$ surface (before) and after geometry optimization

Molecules (m)	E_{ads} (eV)	$r(\text{O}_m\text{-Ti})$ (Å)	$r(\text{C-O})$ (Å)	$r(\text{O-H})_m$ (Å)	$\angle(\text{O}_m\text{-Ti-O}_{\text{co}})$ (°)
Methanol	(2.25) 1.29	(2.195) 2.177	(1.426) 1.443	(0.993) 0.982	(82.21) 81.92
Ethanol	(2.48) 1.46	(2.148) 2.153	(1.443) 1.442	(0.964) 0.977	(62.48) 82.21
<i>n</i> -Propanol	(2.58) 2.08	(2.225) 2.163	(1.445) 1.451	(0.992) 0.988	(64.62) 61.08
<i>i</i> -Propanol	(2.42) 2.40	(2.240) 2.197	(1.434) 1.450	(0.996) 0.980	(70.58) 57.82

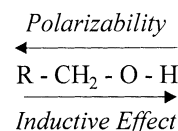
for methanol and ethanol. The effect appeared to decrease with increasing the size (and structure) of the molecule, 0.5 eV for *n*-propanol (and no change for *i*-propanol).

4. Discussion

4.1. Correlation with physical properties of the adsorbates

Several factors may affect the adsorption step. Polarizability and inductive effects are known to have dramatic effects on the extent of acidity of alcohols. They may have opposite effects depending on the nature of the side chain and the physical environment. The decrease of the alcohols acidity from methanol to the higher analogues in solution is due to the electron-releasing ability of the alkyl chain: inductive effect. However, it is well known since the pioneering work by Brauman and Blair [23,24], that the acidity-scale of alcohols chain is inverted in the gas phase. Table 4 shows the polarizability (*P*) [25], the inductive effect (*I*) [25] as well as the HOMO and LUMO energy positions for the series of alcohols

considered in this work. Actually, the polarizability effect is negligible in solution [25]. This is because the charge on the oxygen atom of the alkoxy anion disperses in the solvent via hydrogen bonding. More explanation can be found in Catalán's work [25].



As a consequence, the polarizability may become very important in the gas phase. The opposing effects of *P* and *I* will thus influence the interaction of an incoming molecule in the gas phase with the surface of an ionic oxide. A plot of the non-dissociative adsorption energy for the series of alcohols, investigated in this work as a function of the difference between *P* and *I*, relative to methanol is shown in Fig. 3. As expected the adsorption energy increases with increasing *P*–*I*. The trend is however different for both surfaces, while the (0 1 1) shows a smooth increase, the (1 1 0) shows in fact a decrease in ΔE_{ads} (defined as, E_{ads} of a given alcohol – E_{ads} of methanol) from *n*-propanol to *i*-propanol. The inductive effect doubles for a

Table 4

Comparison between the desorption energy of a series of alcohols over Pt(1 1 1) and Ag(1 1 0) single crystals and their physical properties

Alcohol	<i>I</i> (eV)	<i>P</i> (eV)	LUMO (eV)	HOMO (eV)	E_{des}^a Ag(1 1 0) [27] (eV)	E_{des} Pt(1 1 1) [28] (eV)
Methanol	0	0	3.51	–10.85	0.38	0.47
Ethanol	0.05	0.17	3.33	–10.45	0.46	0.49
<i>n</i> -propanol	0.05	0.22	3.25	–10.22	0.50	0.57
<i>i</i> -propanol	0.10	0.31	3.28	–10.12	–	0.52
<i>n</i> -Butanol	0.06	0.25	–	–10.06	0.55	0.60

I: inductive effect [25]; *P*: polarizability [25]; HOMO: highest occupied molecular orbital; calculated using the semi-empirical PM3. The negative sign is to indicate that energy is required to remove one electron. LUMO: lowest unoccupied molecular orbital; calculated using the semi-empirical PM3.

^a Computed from T_{max} (maximum desorption of the TPD peak) with $\beta = 5 \text{ K s}^{-1}$ and assuming $n = 10^{13} \text{ s}^{-1}$; $\ln(b/n)RT = E_{\text{des}}$.

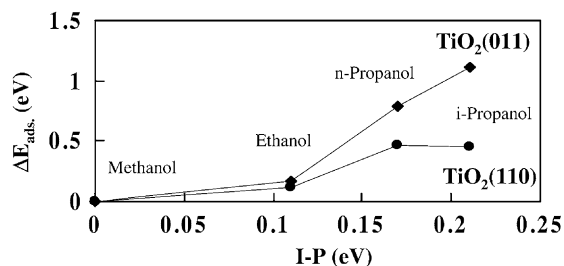


Fig. 3. ΔE_{ads} as a function of inductive effect, I , polarizability, P over $\text{TiO}_2(110)$ and $\text{TiO}_2(011)$, $\Delta E_{\text{ads}} = E_{\text{ads}}$ of a given alcohol $- E_{\text{ads}}$ of methanol. Both I and P are relative to methanol. The lines are guide to the eyes.

branched molecule (such as the two CH_3 - groups in the case of *i*-PrOH), but there is a modest change when an extra CH_3 - group is added to a linear chain), see Table 4. The increase in P is large enough to partially offset I , however. It appears that electron–electron repulsion between the bridging oxygen anions, O_{2c}^{2-} , (out of plane) of the surface of $\text{TiO}_2(110)$ with the two methyl groups of *i*-PrOH is important enough to weaken the adsorption and break the trend.

One may also present the trend by the change in the ionization potential (IP) of the adsorbates. Or more accurately, by the difference between IP and the EA since the adsorbate is donating (IP) charges to Ti_{5c}^{4+}

and is poised to accept (EA) charges from lattice O_{2c}^{2-} . IP can accurately be given by the HOMO position while the EA can be approximated by the LUMO position. The adsorption energy of the four alcohols as a function of the difference between the LUMO and the HOMO energy positions is shown in Fig. 4. The HOMO values determined by PM3 were similar to those of the IP values taken from [26]. High LUMO–HOMO (EA–IP) values mean that less energy is consumed during the adsorption process and might thus be translated by stronger bonding. Again, for $\text{TiO}_2(110)$ cluster, *i*-propanol deviates from the trend.

Similar experimental works on metal single crystals have also shown such a finding. The energy of desorbing molecules during TPD of linear alcohols over $\text{Ag}(110)$ increases with increasing the side chain [27]; *i*-PrOH was not investigated. Over $\text{Pt}(111)$ [28], the same series of alcohols that has been conducted in this work, was experimentally studied by TPD. The results are summarized in Table 4. It is unfortunate that no set of experimental data on reversible adsorption of alcohols over well-defined oxide surfaces is available and one cannot compare the results reported here to experimental works on an oxide surface. Nevertheless, the results show certain trend that can reasonably be explained by simple physical properties. Both polarizability/inductive effect and ionization

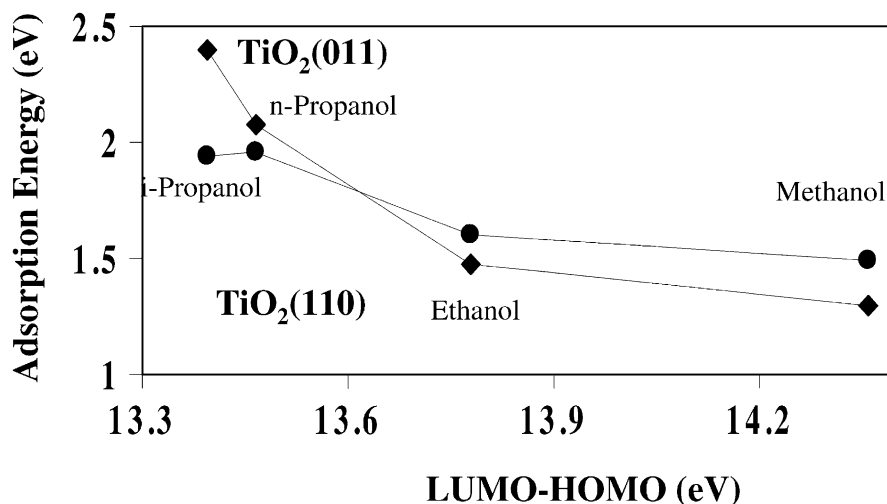


Fig. 4. E_{ads} for a series of alcohols as a function of LUMO–HOMO energy positions over $\text{TiO}_2(110)$ and $\text{TiO}_2(011)$ surfaces. The lines are guide to the eyes.

potential (HOMO)/electron affinity (LUMO) of the adsorbates seem appropriate in describing the extent of solid–gas interactions on the surface of TiO₂.

4.2. More general trends

The surface of the {011}-faceted TiO₂(001) single crystal has been shown active for the adsorption and reaction of formaldehyde [13], methanol [17] and formic acid [29]. Both TPD and XPS C 1s results did show that the surface uptake (at saturation) is in the following order: formic acid > methanol > formaldehyde. The adsorption energy computed in this work and from [20] show the same trend: formic acid (1.62 eV) > methanol (1.29 eV) > formaldehyde (0.68 eV). This is actually consistent with the picture of two pair interactions (for RO–H and RC(O)O–H molecules) were both the oxygen of the adsorbate and the oxygen of the surface are interacting with their counter ions. Thus, formic acid (more acidic) has a higher adsorption energy than methanol (less acidic). Moreover, both have higher adsorption energy than formaldehyde since the latter is occurring only via one pair interaction (O of the HCHO with the under-coordinated Ti ions, Ti_{5c}⁴⁺).

5. Conclusions

The non-dissociative adsorption energy of a series of alcohols over the surfaces of TiO₂(110) and TiO₂(011) has been computed by a semi-empirical PM3 method. The TiO₂(110) was represented by a Ti₁₁O₄₂H₄₀ cluster while the TiO₂(011), the first stable reconstruction of TiO₂(001) single crystal, was represented by a Ti₈O₂₉H₂₆ cluster. The adsorption energy increased with increasing the alcohol size, with the exception of *i*-propanol over TiO₂(110). The acidity, as determined by the polarizability/inductive effect, or the ionization potential (HOMO)/electron affinity (LUMO) of the adsorbates could reasonably describe the trend. The deviation of *i*-propanol from the trend over TiO₂(110) is most likely due to repulsive interaction between bridging surface oxygen anions and the two methyl groups of *i*-propanol.

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