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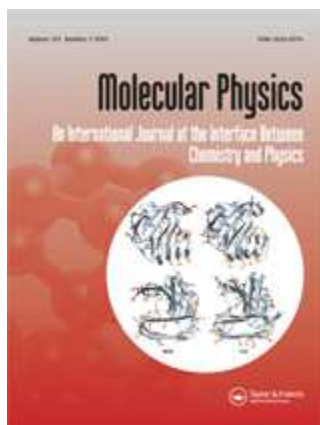
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Influence of the OH groups of hydroxylated rutile (110) surface on the Lewis acidity: an investigation of CO adsorption by quantum-mechanical simulations

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8 surface on the Lewis acidity: an investigation of CO
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12 adsorption by quantum-mechanical simulations.
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ABSTRACT

The adsorption of carbon monoxide on the clean and hydroxylated rutile (110) surface has been investigated by a periodic approach at DFT/B3LYP level. The hydroxylated surface has been modelled by considering both terminal and bridging OH groups. The variation of the electrophilicity of the Lewis acid site near these groups has been evaluated by taking into account the adsorbate-substrate distance, the magnitude of the interaction energy and the blue-shift of the adsorbed CO stretching frequency. The obtained results suggest that the electrophilicity increases in proximity of OH terminal groups, while decreases near the OH bridging ones.

KEYWORDS

Adsorption; Carbon monoxide; Hydroxylated rutile (110); Lewis acidity; Density functional calculations.

MANUSCRIPT TEXT

Introduction

Titanium dioxide (TiO_2) represents one of the most interesting metal oxides as it is widely employed in the industrial field [1]. Like the other metal oxides, TiO_2 adsorbs water when exposed at the atmosphere: the H_2O molecule can be adsorbed molecularly or dissociatively. For this reason, in the field of the heterogeneous catalysis it is necessary to pre-treat the surface before performing the adsorption of the reagents. However, the pre-treated surface usually presents some isolated hydroxyl groups which can not be easily removed [2]. Since the presence of these OH groups may affect the adsorption due to a possible modification of the surface acidity, an investigation on the electrophilicity of the Lewis acid site of the hydroxylated surface becomes interesting. Among the possible techniques to study the surface Lewis acidity, IR spectroscopy on the adsorption of carbon monoxide (CO) represents one of the most widely employed ones [3]. The way in which this molecule adsorbs on the surface of a metal oxide is well-known: the interaction with a metal cation which has no d electrons, e.g. Ti^{4+} , occurs by a σ -bond. As consequence of this interaction, the CO stretching frequency shifts toward higher wavenumbers with respect to the gas-phase (i.e. 2143 cm^{-1}); the greater is the electrophilicity of the surface Lewis acid site, the higher is the IR stretching frequency of the adsorbed CO [4].

The aim of this work is to perform a quantum-mechanical investigation on the adsorption of CO on the clean and hydroxylated rutile (110) representing the most stable surface of TiO_2 . In particular, the attention is focused on the variations of the electrophilicity which arise from the presence of an OH group next to a surface Lewis acid site corresponding to the Ti^{4+} ion. From the theoretical point of view, the adsorption of H_2O on the considered surface has been widely studied and one of the most discussed questions concerns the way in which the molecule adsorbs, i.e. molecularly or dissociatively [e.g. 5-13 and references quoted therein]: according to the obtained results, the dissociative adsorption seems to be favoured with respect to the molecular one, mainly when a low surface coverage is considered. A lot of theoretical investigations on the CO on the clean surface are reported in the literature and the calculated blue-shift of the adsorbed CO stretching frequency moves in the range $28\text{-}140 \text{ cm}^{-1}$ [e.g. 14-20]. One of

1 the most important common results is that the adsorption through the C atom is energetically much more
2 favourable than that through the O one [14, 17-19]. To our best knowledge, no theoretical works
3 concerning the CO adsorbed on the hydroxylated surface have been carried out.
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10 Computational details

11 The calculations have been performed at DFT level using the CRYSTAL06 software package [21],
12 based on the expansion of the crystalline orbitals as a linear combination of a basis set consisting of
13 atom centred Gaussian orbitals.
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18 The titanium and oxygen atoms have been described by a 86-51G* and a 8-411G contraction,
19 respectively [22]; the most diffuse sp exponents are $\alpha^{\text{Ti}} = 0.598$ and $\alpha^{\text{O}} = 0.184 \text{ bohr}^{-2}$. The carbon
20 monoxide has been described using the standard 6-311G* contraction [23].
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26 The B3LYP hybrid functional [24] has been adopted. The exchange-correlation functional has been
27 integrated numerically on a grid of points; integration over radial and angular coordinates has been
28 performed by using Gauss-Legendre and Lebedev schemes, respectively. A pruned grid consisting of
29 75 radial points and 5 sub-intervals with (50,146,194,434,194) angular points has been adopted for all
30 calculations. The default truncation thresholds of 10^{-6} , 10^{-6} , 10^{-6} , 10^{-6} and 10^{-12} for the Coulomb and
31 exchange series [25] have been used. A Monkhorst-Pack shrinking factor equal to 4, corresponding to 9
32 symmetry unique k -points in the adsorbate-substrate system, has been used. A tolerance in the total
33 energy of $1 \cdot 10^{-8}$ Hartree per unit cell has been considered for convergence in the self consistent field
34 procedure.
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47 The internal coordinates have been determined by minimizing the total energy within an iterative
48 procedure based on the total energy gradient calculated analytically with respect to the nuclear
49 coordinates. Convergence has been determined from the absolute value and the root-mean-square
50 (RMS) of the largest component of both gradients and nuclear displacements. The thresholds for the
51 maximum forces and atomic displacements have been set to 0.00045 and 0.00180 a.u., respectively
52 while the value for the RMS forces and atomic displacements have been set to 0.00030 and 0.00120 a.u.,
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1 respectively. Geometry optimization has been terminated when all the four conditions were
2 simultaneously satisfied [26-27].
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4 The vibrational frequencies have been calculated from the dynamical matrix which is obtained from
5 numerical differentiation of the analytical gradient of the energy with respect to the atomic positions
6 using a displacement of 0.001 Å in a two-point sampling [28-29].
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11 Results and discussion

12 The rutile phase belongs to the $P4_2/mnm$ (D_{4h}^{14}) tetragonal space group and the unit cell is defined by
13 the two lattice vectors **a** and **c** and by the fractional coordinate *u*. The rutile (110) surface has been cut
14 from the bulk whose parameters have been previously optimized [30] and is depicted in Fig. 1a: it
15 consists of fivefold and sixfold coordinated titanium atoms (indicated as Ti(5f) and Ti(6f)) and twofold
16 and threefold coordinated oxygen atoms (indicated as O(2f) and O(3f)). The Ti(5f) and O(2f) correspond
17 to the surface Lewis acid and basic sites, respectively. The dissociation of the H₂O molecules involves
18 these two sites; in fact, the hydroxyl group adsorbs on the Ti(5f) and the proton on the O(2f).
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33 The calculations has been performed by using a periodicity equal to (3 × 3), in order to avoid the
34 interaction between the two hydroxyl groups; the surface has then been modelled by periodically
35 repeating the Ti₃₆O₇₂ unit corresponding to a 6-atomic layers slab. The hydroxylated surface has been
36 obtained from the full optimisation of the system which is represented in Fig. 1b. The hydroxyl group
37 corresponding to the adsorption of an OH group on the Ti(5f) is usually indicated as terminal OH group
38 while that resulting from the adsorption of a H atom on the O(2f) is defined as bridging one. The
39 optimised O-H bond lengths are 0.961 Å for the former and 0.967 Å for the latter; the corresponding OH
40 stretching frequencies occur at 3732 and 3650 cm⁻¹, respectively.
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52 As it has been mentioned in the introduction, this work mainly aims in evaluating separately the
53 effects arising from the interaction between one of the two kinds of OH groups and the nearest surface
54 Lewis acid site. For this purpose, in order to avoid the reciprocal influence between the two hydroxyl
55 groups, it has been necessary to isolate as more as possible the two OH groups considering a slab having
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1 a large surface area and allowing to keep the two groups at the major possible distance. Then, the
2 considered surface represents a good model for obtaining the isolation of the two hydroxyl groups.
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5 The adsorption on the clean surface has been obtained by adsorbing the CO molecule in an initial
6 geometry perpendicular to the surface with the carbon atom above the Ti(5f) of the relaxed surface. In
7 the case of the hydroxylated surface, the molecule has been placed above the Ti(5f) nearest to one of the
8 two OH groups: for clearness, the system obtained by the CO adsorption near the terminal OH group is
9 indicated as Structure (I) while that resulting from the adsorption near to the bridging OH group is
10 indicated as Structure (II). In all the three cases (clean surface and Structures I and II), the geometry
11 optimization has been performed by relaxing all the atoms of the system.
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15 The calculated CO bond length in the isolated optimized molecule is equal to 1.127 Å and the value is
16 in good agreement with the experimental one corresponding to 1.128 Å [31]. The most important
17 structural parameters of the systems related to the adsorption of CO on the clean and the hydroxylated
18 surface are reported in Table 1. The most important feature consists in the decrease of the CO bond
19 length with respect to the isolated molecule. As it can be seen, the adsorption on the hydroxylated
20 surface gives rise to an increase of the O-H bond length of the terminal OH group in the case of the
21 Structure (I) while no variations occur for the Structure (II).
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25 Focusing on the C-Ti distance, the value concerning the adsorption on the clean surface (2.505 Å) is
26 bigger than that referring to the Structure (I) (2.444 Å), while it results smaller than the value associated
27 to the Structure (II) (2.534 Å). This means that the molecule adsorbed on the clean surface interacts
28 with the Ti(5f) ion in a weaker way with respect to the Structure (I) and in a stronger manner with
29 respect to the Structure (II).
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33 In Table 1, the Mulliken overlap populations (OP) for both the C-O bond and the C-Ti distance are
34 also given: the values referring to the molecule adsorbed on the clean surface are very close to those
35 obtained by Reinhardt et al. [16]. Concerning the CO bond, the OP behaviour is consistent with the
36 variation of the C-O length: in fact, the molecule adsorbed on the clean surface has the same OP of the
37 Structure (I) and a bigger value with respect to the Structure (II). Also the behaviour of the OP related
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1 to the C-Ti distance is in agreement with the changes of the structural parameter: the value associated to
2 the molecule adsorbed on the clean surface is smaller than that referring to the Structure (I) and bigger
3 than that related to the Structure (II).
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7 It is important to notice that the interaction between the CO molecule and the surface is not
8 represented by only a σ -bond: in fact, even if the Ti ion under investigation is formally a Ti^{4+} one, it has
9 also d electrons which can interact with the molecule through a π back-donation. This can be easily seen
10 from the Density of States (DOS) projected on the CO basis functions which are depicted in Fig. 3: the
11 most important feature consists in a broadening due to the adsorption of both the 5σ and $2\pi^*$ orbitals of
12 the CO molecule. Besides, the reported DOS show that the orbitals of the adsorbed CO shift towards
13 lower energy with respect to the free CO and this means that the interaction with the surface leads to a
14 stabilizing effect for the molecule; in particular, the largest shift is observed for the 5σ orbital. The DOS
15 of the CO adsorbed on the hydroxylated surface do not present appreciable differences with respect to
16 the DOS of the molecule interacting with the clean surface and then they were not reported.
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31 In Table 2, the interaction energy (E_{int}) is reported. E_{int} , which measures the strength of the adsorbate-
32 substrate interaction, has been corrected for the basis set superposition error (BSSE) employing the
33 Counterpoise (CP) method [32]; a negative value of E_{int} means that there is attraction between the
34 adsorbate and the substrate while a positive value indicates a repulsion between them. As it can be seen,
35 the value of E_{int} reproduces the behaviour observed for the C-Ti distance. In fact, its absolute value
36 associated with the adsorption on the clean surface ($18.10 \text{ kJ}\cdot\text{mol}^{-1}$) is smaller than those referring to the
37 Structure (I) ($25.13 \text{ kJ}\cdot\text{mol}^{-1}$) and bigger than those related to the Structure (II) ($12.20 \text{ kJ}\cdot\text{mol}^{-1}$). This
38 confirms that the interaction between the CO molecule and the clean surface is weaker than that
39 associated to the Structure (I) and stronger than that referring to the Structure (II).
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52 In Table 2, the adsorbed CO stretching frequency (ν_{CO}) is also reported. The calculated ν_{CO} , whose
53 blue-shift is correlated to the electrophilicity of the adsorption site, has been scaled by using a scaling
54 factor equal to 0.966 [33]; the value referring to the isolated optimized molecule is 2135 cm^{-1} and this is
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comparable with the experimental one (2143 cm^{-1} [31]). Again, the behaviour of ν_{CO} is in agreement with those observed for both the C-Ti distance and E_{int} . In fact, the $\Delta\nu_{\text{CO}}$ resulting from the adsorption on the clean surface (62 cm^{-1}) is smaller than that related to the Structure (I) (66 cm^{-1}) and bigger than that associated to the Structure (II) (51 cm^{-1}). Then, it can be inferred that the Ti(5f) of the clean surface is less electrophilic than that referring to the Structure (I) and more electrophilic than that corresponding to the Structure (II).

In Table 2, the OH stretching frequency (ν_{OH}) for both the terminal and the bridging OH groups is also given. As it can be seen, its behaviour is in agreement with the variation of the O-H bond lengths: in fact, a red-shift of the frequency associated to the terminal OH group is obtained in the case of the Structure (I) while no appreciable variations occur for the Structure (II).

In conclusion, by considering the adsorbate-substrate distance, the interaction energy and the CO adsorbed frequency it can be concluded that surface Lewis acidity of the site of the clean surface is smaller than that of the site near to a terminal OH group and bigger than that of the site near to a bridging OH group.

It is important to notice that the quantum-mechanical investigation performed in the current work allows to obtain important information which cannot be deduced from the experiments. In fact, the experimental adsorption of CO is generally performed on a surface having residual OH groups and results in a blue-shift of about 45 cm^{-1} [34] which is comparable with the present values. However, from the experimental point of view, it is very difficult to determine if the Ti ion involved in the adsorption is far or near to a terminal or a bridging OH group.

Conclusions

This work reports the main results obtained from a quantum-mechanical study of the adsorption of CO on the clean and hydroxylated rutile (110) surface. The study referring to the hydroxylated surface has been carried out for the first time. This surface has been modeled by considering two different kinds of hydroxyl groups, i.e. a terminal and a bridging OH one. According to the calculated adsorbate-substrate

1 distance, the interaction energy and the adsorbed CO stretching frequency, it can be deduced that the
2 presence of the terminal OH group gives rise to an increase of the electrophilicity of the near surface
3 Lewis acid site. By contrast, this site becomes less electrophilic when it is near to the bridging OH
4 group.
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Table 1. Optimized parameters for the CO-rutile (110) system.^a

	Clean surface	Hydroxylated surface ^b	
		Structure I	Structure II
C–O	1.121	1.121	1.123
$\Delta(\text{C-O})^c$	-0.006	-0.006	-0.004
C–Ti	2.505	2.444	2.534
O–C–Ti	180.0	177.2	179.3
O–H(I) ^d	--	0.963	0.961
O–H(II) ^d	--	0.967	0.967
OP (C–O) ^e	0.659	0.659	0.646
OP (C–Ti) ^e	0.018	0.021	0.016

^a lengths and angles are reported in angstroms and degrees, respectively.

^b structure **I** and **II** refer to the adsorption on the Ti(5f) near to the terminal and the bridging OH groups, respectively (see text).

^c variation of the CO bond length with respect to the isolated optimized molecule (1.127 Å).

^d I and II indicate the terminal and the bridging OH groups, respectively (see text).

^e OP means the Mulliken overlap population.

Table 2. Interaction energy, CO and OH stretching frequency for the CO-rutile (110) system.^a

	Clean surface	Hydroxylated surface ^b	
		Structure I	Structure II
E_{int}	-18.10	-25.13	-12.20
ν_{CO}	2197	2201	2186
$\Delta\nu_{\text{CO}}^{\text{c}}$	62	66	51
$\nu_{\text{OH(I)}}^{\text{d}}$	--	3698	3729
$\nu_{\text{OH(II)}}^{\text{d}}$	--	3650	3650

^a E_{int} and ν_{CO} are given in $\text{kJ}\cdot\text{mol}^{-1}$ and cm^{-1} , respectively.

^b structure **I** and **II** refer to the adsorption on the Ti(5f) near to the terminal and the bridging OH groups, respectively (see text).

^c variation of the CO stretching frequency with respect to the isolated optimized molecule (2135 cm^{-1}).

^d I and II indicate the terminal and the bridging OH groups, respectively (see text).

FIGURE CAPTIONS

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7 **Figure 1.** (a) Model of the rutile (110) surface: Ti(5f) and Ti(6f) correspond to fivefold and sixfold
8 coordinated titanium cations while O(2f) and O(3f) indicate twofold and threefold coordinated oxygen
9 anions. (b) Model of the hydroxylated rutile (110) surface: OH (I) represents the terminal OH group
10 while OH (II) corresponds to bridging one. (a) and (b) have been obtained by using the XCRYSDEN
11 program [35].
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18 **Figure 2.** (a) Model of the CO-rutile (110) system obtained from the adsorption on the clean surface; (b)
19 model of the CO-rutile (110) system resulting from the adsorption of CO on the Ti(5f) near to the
20 terminal OH group; (c) model of the CO-rutile (110) system corresponding to the adsorption of CO on
21 the Ti(5f) near to the bridging OH group. In (a), (b) and (c) only the outermost surface ions are depicted;
22 the dashed lines represent the bonds between CO and TiO₂. (a), (b) and (c) have been obtained by using
23 the XCRYSDEN program [35].
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32 **Figure 3.** Density of States (DOS) (arbitrary units) projected on the CO basis functions. Continuous line
33 is for the CO-rutile (110) system; dotted line is for the free CO slab.
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Figure 1

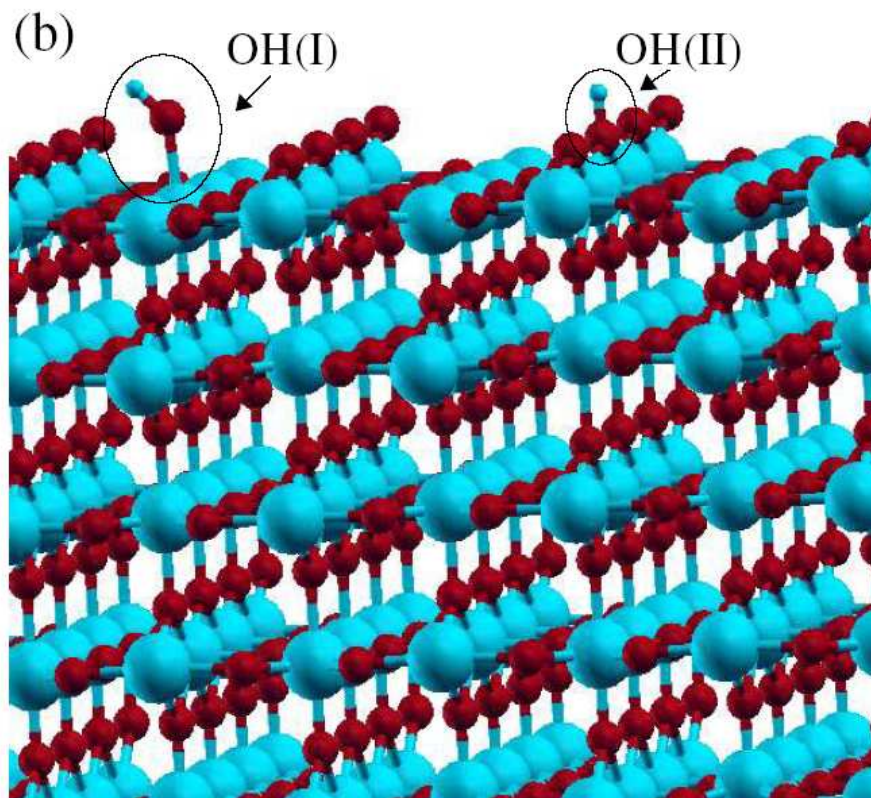
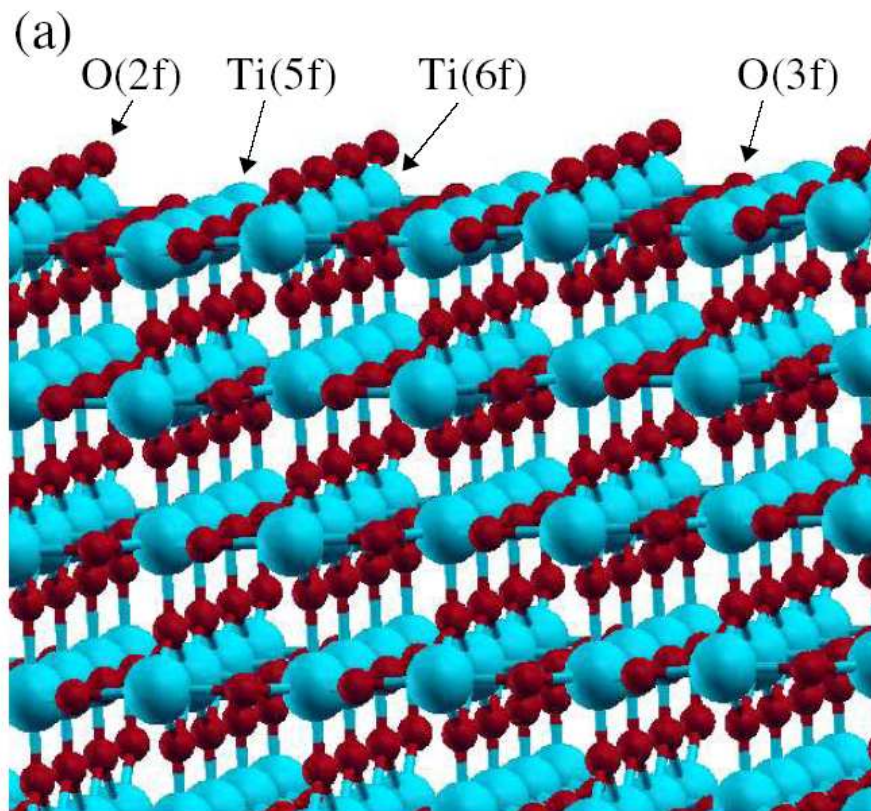


Figure 2

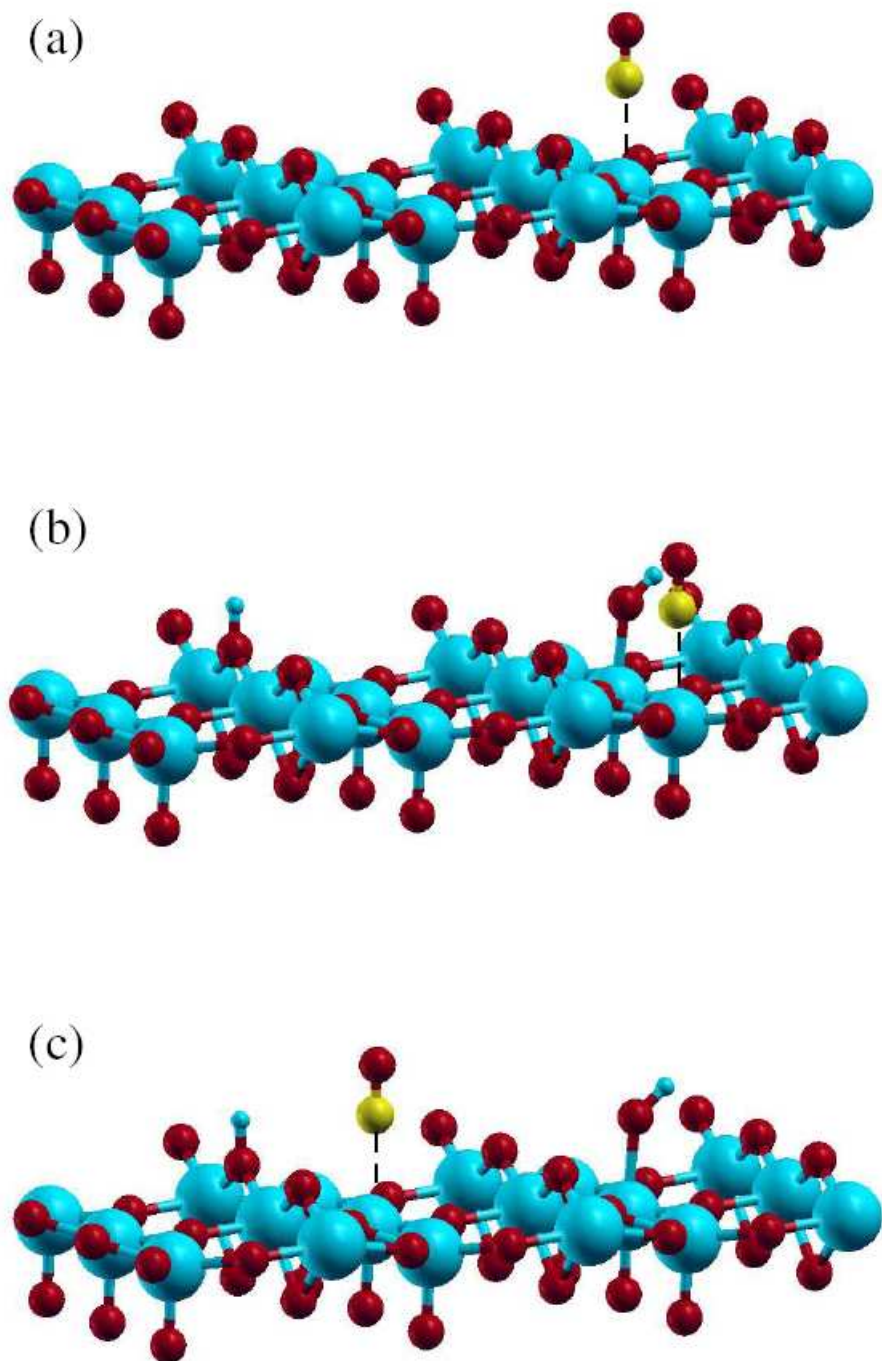


Figure 3

