A Hybrid Density Functional Study of Water Adsorption on Rutile TiO$_2$(110) for Applications in Solar Hydrogen Production.

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ABSTRACT

The adsorption of water on the TiO$_2$(110) surface has been investigated using hybrid exchange periodic density functional calculations. Both the dissociative and non-dissociative adsorption modes have been considered, as well as the coverage dependence of the binding energy. Our results for the adsorption of one molecule per surface unit cell suggest that, in this case, dissociative water adsorption is more favorable than non-dissociative adsorption at all levels of coverage.

Keywords: rutile titanium dioxide, (110) surface, water adsorption, coverage dependence.

1 INTRODUCTION

A large amount of research effort is being devoted to one of the greatest challenges of our time: the production and use of energy without compromising our environment. Global warming, ozone layer depletion, and climate change in general are amongst the many major environmental impacts caused by the increasing use of non-renewable sources as fuel for human activity. Renewable energy sources such as solar, wind, tidal and geothermal provide energy production alternatives. However, the combination of high costs and low efficiencies of these systems is currently a serious problem [1–3].

Some of the most significant applications of nanomaterials science lie within the energy sector, the solar and hydrogen economies in particular. Due to important advances in this area, the dye-sensitized (Grätzel) solar cell [4] is close to large-scale commercialization. Current challenges in the hydrogen economy include the storage/transport of hydrogen, as well as the efficient conversion of hydrogen into electrical energy in fuel cells. One of the major problems with fuel cell technology [5] is the high manufacturing cost [3]. In addition, the production of hydrogen via water splitting has become one of the most significant challenges within this area [6].

The artificial photosynthesis system uses sunlight to drive a thermodynamically uphill reaction. The process leads to the production of oxygen from water, alongside a reduced fuel such as hydrogen [2], and provides a carbon-free renewable route to hydrogen production. Photocatalytic water splitting over semiconductor materials, such as titanium dioxide (TiO$_2$), is being studied to a large extent. Despite years of research in this field, the required solar-to-fuel efficiencies have been unattainable at a reasonable cost [7]. There is a need for the efficiency of the process to be improved, and it is hoped that a fundamental understanding of the photocatalysis will facilitate the design of more efficient systems.

TiO$_2$ is a typical transition metal oxide which presents itself in a variety of crystal structures, three of which are well known: rutile, anatase and brookite. Rutile TiO$_2$(110) has been widely studied as a quintessential model oxide; the rutile phase is the most thermodynamically stable structure and its (110) surface has the lowest surface formation energy. A number of processes have been reported to occur on the TiO$_2$(110) surface. It has received considerable attention, particularly for its use in photochemical reactions [8], heterogeneous catalysis [9], sorbent technology [10], gas sensors [11], and finally, photoelectrochemical solar energy conversion for the production of hydrogen [12], as well as electricity [13]. This broad range of applications reflects the importance of studying meticulously the surface chemistry of TiO$_2$.

A wide range of fundamental studies of chemical processes on TiO$_2$, using model low Miller index surfaces, can be found in the literature. Although the adsorption of atoms and molecules, particularly H$_2$O, is one of the most extensive areas of study in TiO$_2$ surface science [14], it is well known that discrepancies and unresolved contradictions are present to this date. There is substantial disagreement on the adsorption mechanism and the interactions involved, and there still remains a lack of understanding of the fundamental processes that occur at these surfaces.

There are two important adsorption mechanisms by which a water molecule is able to bind to a surface: dissociative and non-dissociative adsorption. The former involves deprotonation of the water molecule and the formation of surface hydroxyls; the latter entails direct interaction of the molecule with the surface [15]. An ongoing issue that has attracted much attention is the question of whether the water molecule is adsorbed molecularly or dissociatively, and the conditions under which each mode of adsorption takes place. The debate lies especially between theoretical and experimental investigations. The majority of experimental studies agree that water dissociates only at oxygen vacancy sites [16–21]. In contrast, a substantial number of theoretical studies indicate that the dissociation of water is energetically favoured on

the stoichiometric non-defective TiO$_2$(110) surface [22–27]. There have been, however, some studies that disagree with the general view described above [28–31]. Breakthroughs in the area have resulted in a variation of the theoretical understanding of the adsorption process [32, 33], and specifically the important role of intermolecular interactions.

The purpose of this study is to enhance the current understanding of the interaction of H$_2$O with the rutile TiO$_2$(110) surface by using a highly accurate modelling approach, based on density functional theory. The structure and composition of the TiO$_2$ surface and its interaction with surface species has been simulated as a function of the coverage, with a single molecule adsorbed per surface unit cell on the defect-free surface. Both the dissociative and non-dissociative cases have been considered, and the relative stability of different configurations of atoms has been determined.

This paper is organised as follows. Section 2 contains technical details of the calculations. In Section 3, the results of the water adsorption calculations are presented and discussed. The main conclusions of this study are summarised in Section 4.

2 COMPUTATIONAL DETAILS

All calculations have been carried out using the CRYSTAL09 [34] code, based on the linear combination of atomic orbitals (LCAO). The hybrid-exchange density functional theory has been adopted by using the B3LYP functional [35, 36], which has been reported to be highly accurate for the calculation of electronic properties of materials [37–39].

The TiO$_2$(110) surface has been simulated using the slab approach, consisting of 9 atomic layers (see Figure 1). In order to investigate the coverage dependence of H$_2$O adsorption, supercell of different sizes and shapes were used (see Figure 2).
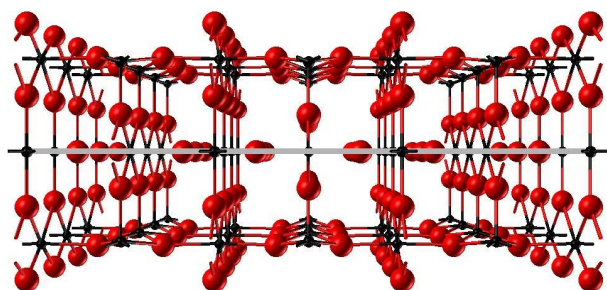

Figure 1: Side view of a 9 atomic layer slab used to simulate the TiO$_2$(110) surface. Atom colours: Red - O, Black - Ti.

Geometry optimization of the clean surface and adsorbate-substrate system was carried out by minimizing the energy with respect to the atomic positions. Two cases have been analyzed: firstly only the 3 outermost atomic layers and the adsorbate were allowed to relax, and secondly all atomic coordinates were included in the geometry optimization.

3 RESULTS AND DISCUSSION

Table 1 shows the corrected binding energies (BE) of the substrate-adsorbate system with respect to the clean surface and the isolated molecule [40]. The binding energies for both the dissociative and non-dissociative adsorption of water are given as a function of the coverage, Θ. Supercell size and shape both affect intermolecular interactions. Since one molecule is adsorbed per simulation cell, these theoretical calculations do not allow for non-periodic molecular behaviour.

In both the dissociative and non-dissociative mode, the adsorption occurs at the surface pentacoordinated Ti sites. In Table 1, for all considered cases the binding energy is negative, therefore all are favorable. Dissociative adsorption is more stable than the corresponding non-dissociated state, independently of the coverage. In the dissociative case, a H atom detaches from the H$_2$O molecule, and bonds to the nearest bridging O atom. The stability of this state can be rationalized by the formation of hydrogen bonding interactions between the bridging and terminal hydroxyls [41].

When increasing the size of the cell along the [0 0 1] direction (corresponding to **a**$_{slab}$) and decreasing the coverage, the adsorption sequentially becomes more favorable due to the decrease of the repulsion between adsorbates. The extension of the cell in the [1 $\overline{1}$ 0] direction (**b**$_{slab}$) gives similar results, but for the non-dissociative case the change in energy is negligible (< 0.03eV).

The effect of the distance between adsorbates can be analyzed further. It is evident that in the 1x1 periodicity there is a stronger repulsion between adsorbates along the [0 0 1] direction (with **a**$_{slab}$ = 2.979 Å) than along the [1 $\overline{1}$ 0] direction (with **b**$_{slab}$ = 6.561Å). In fact, both dissociative and non-dissociative modes are more favorable in the 2x1 case than the 1x2 ($\Theta = 1/2$), and in the 2x2 case than the 4x1 ($\Theta = 1/4$).

In Table 1 an interesting trend can be seen: the difference between BE for dissociative and non-dissociative adsorption, ΔBE, increases with decreasing coverage. This entails that the dissociated state becomes more stabilized when adsorbates are further apart in both directions. The observed trend is in agreement with Ref. [41], in which the increase of BE as a function of the coverage was less significant.

Finally, the effect of atomic relaxation in the slab has been considered. When the atomic coordinates of all atoms are optimized, compared to the case where only the 3 outermost atomic layers and adsorbate are relaxed, the binding energies are reduced by less that 0.5 eV. This indicates that the perturbation of the surface due to the adsorbed molecule in the bulk-like region may be significant. Therefore, it could be interesting to explore the effect of slab thickness.

4 CONCLUSIONS

This work explores single molecule adsorption on a model surface, and shows that water adsorption on TiO$_2$(110) is dependent on coverage. Our results show that if the molecules
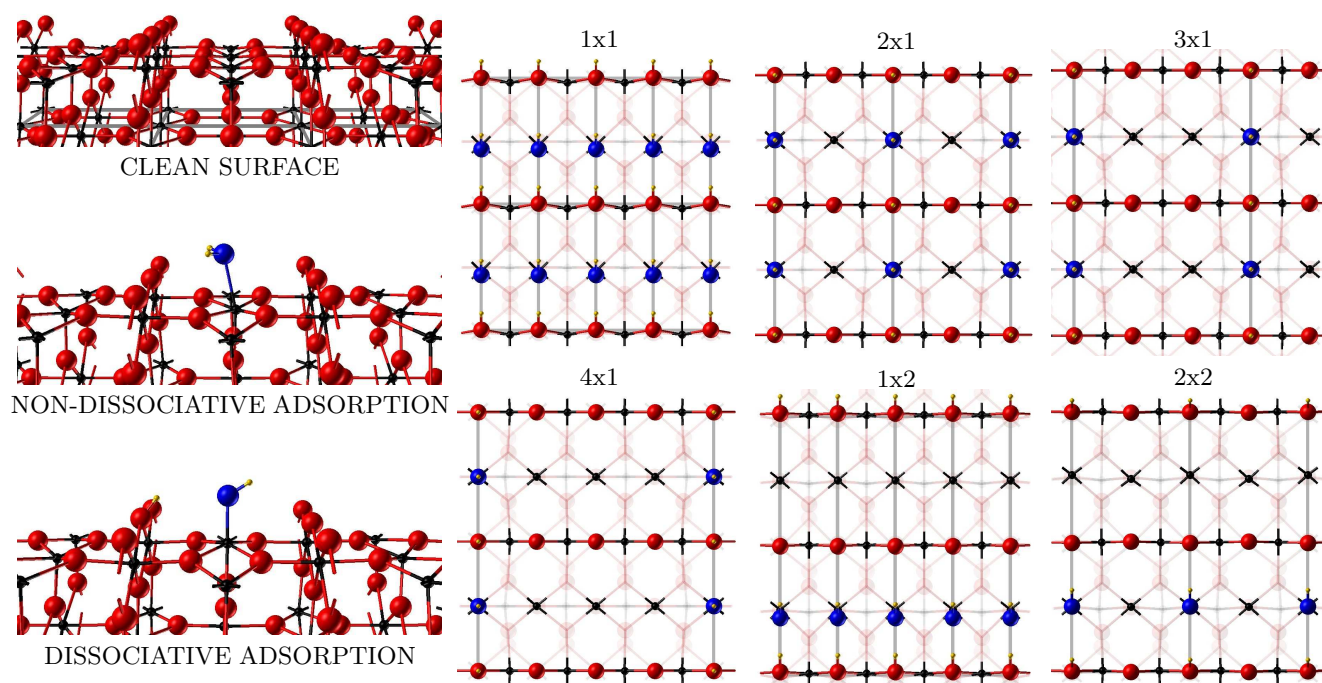
Figure 2: 3D representations of the clean rutile (110) surface, adsorbate-substrate system, and top views illustrating various levels of coverage of the dissociated state. Atom colours: Red - substrate O, Black - substrate Ti, Blue - adsorbate O, Yellow - adsorbate H.

Table 1: The corrected binding energies (BE) of the substrate-adsorbate system with respect to the clean surface and the isolated molecule [40] are shown for two different cases where A) all atomic coordinates have been optimized, and B) coordinates of the outermost three atomic layers and adsorbates have been optimized. Binding energies for both the dissociative and non-dissociative adsorption modes are shown.

		A) All atomic coordinates optimised			B) Surface and adsorbate atomic coordinates optimised		
		BE / eV			BE / eV		
Supercell size	Coverage, Θ	Dissociative	Non-dissociative	Δ BE / eV	Dissociative	Non-dissociative	Δ BE / eV
1x1	1	-0.59	-0.24	0.35	-0.45	-0.20	0.25
2x1	1/2	-0.87	-0.47	0.40	-0.49	-0.44	0.05
3x1	1/3	-1.19	-0.55	0.64	-0.78	-0.51	0.26
4x1	1/4	-1.29	-0.58	0.71	-0.85	-0.54	0.31
1x2	1/2	-0.65	-0.21	0.45	-0.46	-0.20	0.27
2x2	1/4	-1.33	-0.85	0.48	-0.85	-0.68	0.17

are constrained to be periodic with one molecule per surface unit cell, then dissociative adsorption is favored. It has been shown that decreasing the coverage from $\Theta = 1$ to $\Theta = 1/4$ consequently stabilizes the adsorbate-substrate system, since when $\Theta = 1$ there is a stronger repulsion between adsorbates along the $[0\,0\,1]$ direction (with $\mathbf{a}_{slab} = 2.979$ Å) than along the $[1\,\bar{1}\,0]$ direction (with $\mathbf{b}_{slab} = 6.561$Å).

It has previously been shown that intermolecular hydrogen bonding largely determines the adsorption state [33]. In-

teradsorbate interactions must be considered, as well as the interaction of water with the surface. Further investigation will involve studying mixed dissociative and non-dissociative adsorption states, which become accessible when the constraint of monomolecular periodicity is lifted by adsorbing two independent molecules of water per surface unit cell. The coverage dependence will be analyzed in order to explore interadsorbate interactions further.

5 ACKNOWLEDGMENTS

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