Structure and Energetics of Water Adsorbed at TiO_2 Anatase (101) and (001) Surfaces

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We present density functional calculations of H_2O interacting with the (101) and (001) surfaces of TiO_2 anatase at various coverages θ. On the (101) surface, nondissociative molecular adsorption at fivefold coordinated Ti sites is favored at both low and monolayer coverage. On the (001) surface, for $\theta \leq 0.5$, H_2O is adsorbed dissociatively, with an adsorption energy $\Delta H_{\mathrm{H,OH}} \sim 1.6$ eV. At $\theta = 1$, H_2O can be adsorbed molecularly ($\Delta H_{\mathrm{H_2O}} = 0.82$ eV/molecule), but a state with half of the H_2O adsorbed dissociatively and the other half H bonded in a "second layer" is energetically more favorable. These results are discussed in the context of the available experimental information. [S0031-9007(98)07231-7]

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The interaction of water with TiO_2 surfaces has been the subject of intensive research for many years, motivated by its central role in many applications of this material, e.g., in catalysis, photochemistry, and electrochemistry [1,2]. The majority of these studies, in particular, theoretical calculations, deal with the rutile (110) surface, which is the most stable surface of TiO_2 rutile, that is, in turn, the most stable polymorph of titanium dioxide. However, it is anatase, another polymorph of TiO_2, which is more efficient and more widely used in catalysis and (photo)electrochemistry [3,4]. Anatase is about 1.2–2.8 kcal/mol less stable than rutile and transforms to rutile in the temperature range of 700–1000 °C. As rutile, anatase crystallizes in a tetragonal lattice, and its structure can be described in terms of chains of TiO_6 octahedra. These octahedra are significantly more distorted in anatase than in rutile, and they are also connected in a different way [2].

Because of difficulties in growing large single crystals, most of the available experimental information on the surface chemistry of anatase is based on studies of disperse samples. Moreover, the use of different preparation techniques has led to samples of different morphologies and impurity contents, which may be responsible for the fact that different and sometimes conflicting experimental results have been reported in the literature, even on fundamental issues such as the character—molecular versus dissociative—of the adsorption of water. In fact, while some authors found that on anatase both dissociated and molecular water occurs [5], others report that most of the water is adsorbed molecularly and that different molecular states are present [6]. Also the number of residual hydroxyl groups present after heating is not well established, even though many authors agree on the existence of two kinds of residual hydroxyls, which produce ir bands at $\sim$3720 and $\sim$3670 cm^{-1} [3,7].

On the basis of this experimental information, different models of the anatase surface and of water adsorption at this surface have been proposed, but no clear picture has emerged yet [3]. So far, theoretical studies have been very few, have used simplified models and/or methods, and have considered only anatase (001), for which H_2O dissociative adsorption has been predicted to be favored [8,9]. However, it is known that for most samples the (001) is only a minority surface, while natural anatase samples expose mainly the (101) surface. In particular, we are here interested in real anatase samples used for solar cell devices [10,11]. It has been found that in typical preparations [12] these contain mainly two surfaces: the (101) and the (100)/(010) ones at approximately equal amounts, together with some (001). The latter is at the top and bottom of the (100)/(010) rods, and is also found in (101) particles with truncated tops.

In this paper we study the interaction of water with the (101) and (001) anatase surfaces by means of first-principles density functional calculations for different H_2O coverages (we define the coverage θ as the ratio between the number of adsorbed H_2O molecules and the number of surface fivefold coordinated Ti sites). Knowing the structure of the hydrated surfaces is important not only because water is almost always present on the surfaces of anatase, but also because this should help understanding—and therefore controlling—the catalytic and (photo)electrochemical properties of this material. For water on anatase (101), we find that molecular adsorption is favored, irrespective of coverage. The adsorption energy for the undissociated molecule, $\Delta H_{\mathrm{H_2O}} \sim 0.7$ eV, is $\sim$0.4 eV larger than that for the dissociated case. The greater stability of the molecular state can be related to the presence of two H bonds between the hydrogens of the adsorbed molecule and two bridging surface oxygens. For the (001) surface, instead, the character and energetics of the adsorption vary with θ. For $\theta \leq 0.5$, H_2O molecules are found to dissociate spontaneously (i.e., without barrier), and the adsorption energy is quite large, $\Delta H_{\mathrm{H,OH}} \sim 1.6$ eV. For $\theta > 0.5$, a state is favored, where H_2O molecules up to half monolayer are adsorbed dissociatively, while the remaining ones form H bonds with the terminal OH and the bridging O groups. For this mixed state $\Delta H_{\mathrm{mix}} \sim 1$ eV/molecule is found.

To model the surface, we used periodically repeated slabs separated by a vacuum of $\sim$11 Å width. For the (101) surface, our supercell comprises two surface cells along [010], while for the (001) surface four surface cells are included. In both cases, 16 TiO_2 units per supercell are present. Calculations have been carried out using the Car-Parrinello approach, as described in Refs. [13,14]. The generalized gradient approximation (GGA) is used for the functional of exchange correlation [15]. This approximation has been found to yield satisfactory results in recent studies of molecules on other metal oxide surfaces [16,17]. For Ti and O, electron-core interactions are described by GGA-consistent "ultrasoft" pseudopotentials [18]. Valence states include the Ti $3s$, $3p$, $3d$, and $4s$ states, the O $2s$ and $2p$ states, and the H $1s$ shell. The smooth part of the wave functions is expanded in plane waves with a kinetic energy cutoff of 25 Ry. Only states at Γ are considered. Atomic relaxations were carried out until residual forces were less than 0.05 eV/Å. In all calculations, the four lowest TiO_2 were kept fixed in their bulklike positions. Experimental values of the bulk lattice parameters a, c, and u were used [19].

We start by considering the structure of the clean surfaces. The (101) ideal surface is strongly corrugated ($\sim$1.6 Å) and shows O-Ti-O double chains along the [010] direction. These chains are connected by twofold coordinated ($2c$) bridging oxygens, which also form rows along [010] (see Fig. 1a). Half fivefold ($5c$) and half sixfold ($6c$) coordinated Ti atoms are present, as well as $2c$ and $3c$ oxygens. Upon relaxation, the $2c$ and $3c$ oxygens move into and out of the surface by $\sim$0.06 and $\sim$0.21 Å, respectively. Similarly, coordinatively unsaturated Ti-$5c$ atoms relax inwards by $\sim$0.17 Å, while $6c$ titaniums relax outwards by $\sim$0.11 Å. This relaxation pattern is qualitatively similar to that found in classical simulations based on empirical interatomic potentials [21]; it is also similar to the relaxation of rutile (110) given by first-principles calculations [22]. On the (001) surface only Ti-$5c$ atoms are present. Each of these is bonded to two raised $2c$ and two lowered $3c$ oxygens in the [100] and [010] directions, respectively (see Fig. 1b). We find that upon relaxation the surface corrugation increases slightly, from 0.82 to 0.95 Å. Calculated surface energies are 0.52 and 0.81 J/m^2 for the (101) and (001), respectively, to be compared to a GGA-calculated value of 0.82 J/m^2 for rutile (110) [20,23]. Lower surface energies for anatase with respect to rutile surfaces have been found also in classical simulations [21].

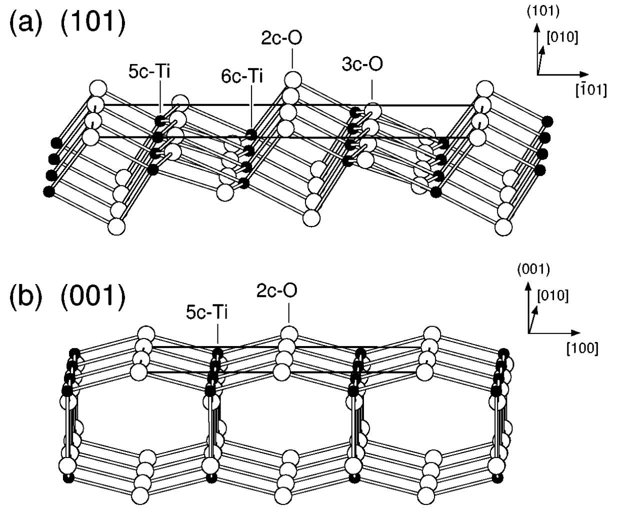

FIG. 1. Clean (101) (a) and (001) (b) surfaces. Large empty and small filled circles represent O and Ti atoms, respectively. Black lines depict the surface cells used in the calculations. Their dimensions are (10.24 × 7.57) Å^2 and (7.57 × 7.57) Å^2 for anatase (101) and (001), respectively. For both surfaces, half of the slab thickness used in the calculations is shown.

We began our study of H_2O adsorption on anatase (101) by placing one molecule parallel to the surface with its nucleophilic end $\sim$2.7 Å above one of the four Ti-$5c$ sites of our surface cell ($\theta = 0.25$). One of the hydrogens of the molecule was in the direction of a $2c$ bridging oxygen. After relaxation, we carried out a long ($\sim$2.3 ps) molecular dynamics (MD) run in which the temperature was gradually raised to about 450 K. During this run the molecule continuously changed its orientation, but never dissociated and always remained in proximity of the same Ti-$5c$ site. A few configurations generated along the run were used as starting points for local optimization procedures, which lead all to the same molecular adsorbed state. In this state both hydrogens of the adsorbed molecule form H bonds with the bridging oxygens of neighboring acidic-basic pairs (see Fig. 2a), and the Ti adsorption site becomes sixfold coordinated. The calculated adsorption energy $\Delta H_{H_2O} = 0.74$ eV is in fair agreement with the experimental estimate of 0.5–0.7 eV [24].

As no dissociation was observed during the MD simulation, we performed additional calculations starting from separate OH^- and H^+ fragments at neighboring Ti-$5c$ and O-$2c$ sites, respectively. For each Ti-$5c$, two nonequivalent sites for H^+ are available: the O-$2c$ directly coordinated to the titanium (intrapair configuration), and any one of the two O-$2c$ involved in the H bonds of the undissociated H_2O molecule (interpair configuration). Both these structures were optimized, and their stability was tested via short ($\sim$0.5 ps) MD runs. The corresponding adsorption energies are $\Delta H_{\mathrm{H,OH}} = 0.23$ and 0.30 eV for the interpair (Fig. 2b) and intrapair (Fig. 2c) configurations, respectively. Thus, molecular adsorption is largely favored on anatase (101) at low coverages.

Calculations analogous to those just described for the (101) surface at low θ have been repeated for the (101) at monolayer coverage and for the (001) surface, at both $\theta \leq 0.5$ and $\theta = 1$. The results are summarized in Table I,

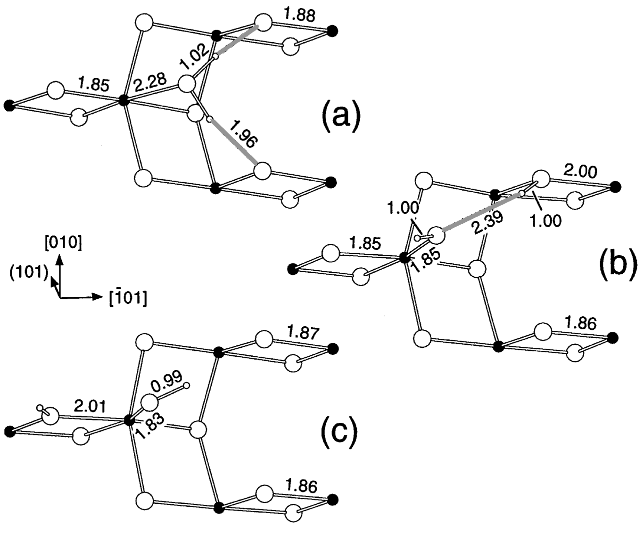

FIG. 2. Atomic structure (top view) for an adsorbed water molecule on anatase (101). Large empty and small filled circles represent O and Ti atoms, respectively, and small circles represent hydrogens. (a) Molecular state. (b) Dissociated, interpair configuration. (c) Dissociated, intrapair configuration. Gray lines in (a) and (b) indicate hydrogen bonds. Bond lengths are in Å.

where the adsorption energies relative to various possible states (all molecular, all dissociated, or "mixed") of the adsorbed water are reported. We can see that for the (101) surface at $\theta = 1$ the molecularly adsorbed state, in which all H_2O molecules are nondissociated, is again energetically favored with respect to the state where all molecules are dissociated. The corresponding adsorption energies are $\Delta H_{H_2O} = 0.72$ eV/molecule and $\Delta H_{H,OH} = 0.44$ eV/molecule. The fact that ΔH_{H_2O} does not vary significantly with coverage indicates that the interactions between the adsorbed molecules are weak. We remark that $\Delta H_{H,OH}$ increases with coverage; i.e., it is easier to dissociate an H_2O when other water molecules are present. This might be due to an increase of the basicity of the $2c$ bridging oxygens.

On the (001) surface, by contrast, no molecular state is found at low coverage. We examined a few initial starting configurations for one H_2O molecule above one of the four Ti-$5c$ sites of our surface cell ($\theta = 0.25$), and always found spontaneous dissociation with no activation barrier and $\Delta H_{H,OH} \sim 1.6$ eV. The structure of the dissociated state (see Fig. 3a) is characterized by the breaking of the bond between the bridging $2c$ oxygen and the Ti-$5c$ atoms involved in the adsorption. In this way two (inequivalent) hydroxyls terminally bound to adjacent Ti sites along [100] are formed. In addition, these hydroxyls are bound one to another by a strong H bond.

TABLE I. Adsorption energy ΔH per H_2O molecule (eV) on anatase (101) and (001) at various coverages θ. Subscripts refer to the character of the adsorption state: H_2O = molecular, H, OH = dissociative, mix = mixed. The two values of $\Delta H_{H,OH}$ in the first line refer to two different isomers (interpair and intrapair) of the dissociated molecule.

Surface, θ	ΔH_{H_2O}	$\Delta H_{H,OH}$	ΔH_{mix}
(101), 0.25	0.74	0.23, 0.30	
(101), 1	0.72	0.44	
(001), 0.25	⋯	1.59	
(001), 0.5	0.81	1.44	
(001), 1	0.82	⋯	1.01

For $\theta = 0.5$, corresponding to two H_2O molecules in our surface cell, two different states are found, depending on the relative positions of the two molecules. If the two molecules are initially placed above adjacent Ti-$5c$ sites along [100], they remain undissociated (see Fig. 3b), and the adsorption energy is $\Delta H_{H_2O} \sim 0.8$ eV/molecule. On the surface, alternating $\langle 100 \rangle$ rows are present, one having adsorbed H_2O molecules, and the other empty Ti-$5c$ sites. Vice versa, if the two water molecules are placed above Ti-$5c$ atoms belonging to different $\langle 100 \rangle$ rows, they dissociate, with $\Delta H_{H,OH} = 1.44$ eV/molecule. In this energetically (and entropically) favored configuration, all surface Ti atoms carrying an hydroxyl group are still pentacoordinated, and may act as traps for electrons.

At monolayer coverage, again two different states of the adsorbed molecules are identified. Starting from an H_2O above each Ti-$5c$ site of our cell, all the molecules remain undissociated and the adsorption energy is practically

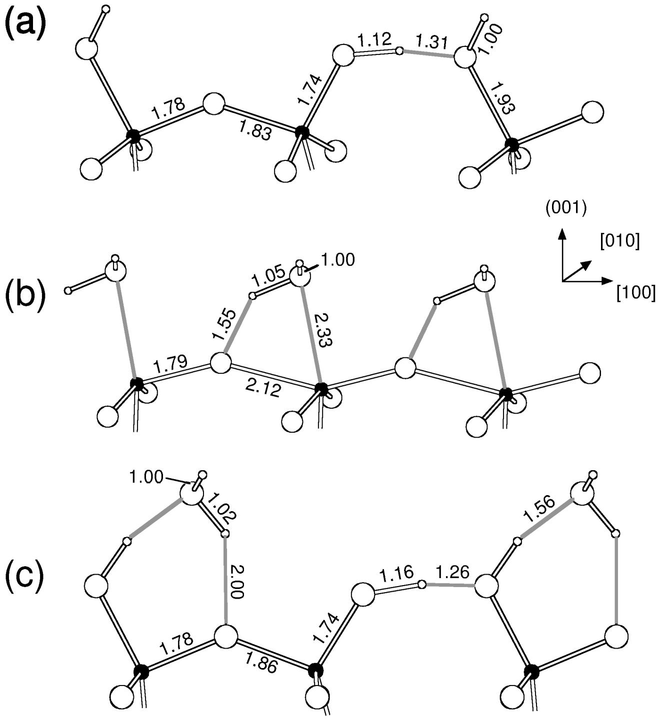

FIG. 3. Atomic structure (side view) for adsorbed water molecule(s) on anatase (001). For better clarity, a single $\langle 100 \rangle$ row is shown. (a) Dissociated state. (b) Molecular state. (c) Mixed state. Gray lines in (b) and (c) indicate hydrogen bonds. Bond lengths are in Å.

identical to that for molecular adsorption at $\theta = 0.5$ (see Table I and Fig. 3b). Instead, if we start from the preferred surface configuration at $\theta = 0.5$ and add further H_2O up to one monolayer, we end up in a mixed state where half of the molecules are dissociated while the other half are molecularly adsorbed by formation of two H bonds, one with a terminal hydroxyl and the other with a bridging oxygen (Fig. 3c). Remarkably, the adsorption energy for this mixed state, $\Delta H_{\text{mix}} = 1.01$ eV/molecule, is substantially higher than that for the molecular state, $\Delta H_{\text{H}_2\text{O}}$. We note that this mixed state is qualitatively different from that for one monolayer of water on rutile (110) discussed in Ref. [17]. On the rutile surface, the water molecules which remain undissociated are directly coordinated to Ti-5c sites, whereas on anatase (001) at (formally) $\theta = 1$ half of the H_2O molecules are undissociated and form a kind of "second layer" above the "first layer" of dissociated molecules. The reason why no fully dissociated state with $\theta = 1$ occurs for anatase (001) is related to the fact that already at $\theta = 0.5$ all surface Ti atoms carry terminal hydroxyls.

The results of this paper together with the scanning electron microscopy (SEM) data of Ref. [12] provide a convenient framework for understanding the available experimental information on water adsorption on the anatase surface. Since the environments of the Ti-5c sites of the (101) and (100)/(010) surfaces are very similar, molecular H_2O adsorption is likely to be preferred for the (100)/(010) surface too [25]. As most of the surface is made up of anatase (101) and (100)/(010), we infer that most of the adsorbed water is in a molecular state. This agrees with the conclusions of Refs. [3,6]. On anatase (001) fragments, dissociated water is present, while molecular water is adsorbed in a second layer through H bonds. Thus residual hydroxyl groups observed experimentally should originate from these fragments (or other surfaces), and should give rise to two (or more) features in IR spectra. The adsorption energy of the H-bonded molecular water on anatase (001) is quite large, viz. ~0.6 eV, which is fairly close to $\Delta H_{\text{H}_2\text{O}}$ for molecular water on the (101) surface. This seems consistent with the character of TPD spectra for anatase [6,24].

In conclusion, we have presented density functional calculations of water adsorbed on the (101) and (001) surfaces of TiO_2 anatase at various coverages, from low θ up to $\theta = 1$. The very different behavior of these two surfaces illustrate well the strong dependence of chemisorption properties on surface structure. Our results support the idea that on the anatase surface, basically two distinct states of the adsorbed water are present, one related to undissociated water on the (101) and (100)/(010) majority surfaces, and the other to dissociated water on the anatase (001) minority surface. The latter can also account for the residual hydroxyl groups observed after heating the surface.

The calculations presented in this Letter have been performed on the NEC-SX4 of the CSCS at Manno (Switzerland). We thank Dr. A. Pasquarello for continuous support with the Car-Parrinello code, and Dr. V. Shklover for discussions concerning his SEM/TEM results. The TiO_2 (anatase) samples referred to in this work have been prepared by P. Comte and Dr. S. D. Burnside.

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