O₂ Interaction and Reactivity on a Model Hydroxylated Rutile(110) Surface

Antonio Tilocca,*,† Cristiana Di Valentin,†,‡ and Annabella Selloni†

Department of Chemistry, Princeton University, Princeton New Jersey 08544, and
Dipartimento di Scienza dei Materiali, Universita' di Milano, 20125 Milano, Italy

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Recently several theoretical studies have examined oxygen adsorption on the *clean*, reduced TiO₂(110) surface. However the photocatalytic behavior of TiO₂ and the scavenging ability of oxygen are known to be influenced by the presence of surface hydroxyls. In this paper the chemistry of O₂ on the hydroxylated TiO₂ surface is investigated by means of first-principles total energy calculations and molecular dynamics (MD) simulations. The MD trajectories show a direct, spontaneous reaction between O₂ and the surface hydroxyls, thus supporting the experimental hypothesis that the reaction does not necessarily pass through a chemisorbed O₂ state. Following this reaction, the most stable chemisorbed intermediates are found to be peroxide species HO₂ and H₂O₂. Although these intermediates are very stable on the short time scale of MD simulations, the energetics suggests that their further transformation is connected to a new 300 K feature observed in the experimental water temperature programmed desorption (TPD) spectrum. The participation of two less stable intermediate states, involving terminal hydroxyls and/or chemisorbed water plus oxygen adatoms, to the desorption process, is not supported by the total energy calculations. Analysis of the projected density of states, however, suggests the possibility that these intermediates have a role in completing the surface oxidation immediately before desorption.

Introduction

The photocatalytic applications of titanium oxide (TiO₂) surfaces often involve the adsorption and interaction of molecular oxygen and water in different forms.[1,2] Although it is established that the main role of oxygen is to scavenge photoexcited electrons, thus preventing undesired electron−hole recombinations, O₂ is also known to have a more direct role in the photooxidation of organics, which would not proceed if another electron scavenger was used, in the absence of O₂.[3]

A convenient way to study the electron scavenging processes that occur during photocatalysis is to examine the interaction of O₂ with the bridging hydroxyls (OH_br) that result from water dissociation at bridging oxygen (O_2c) vacancies on the TiO₂ surface. Each OH_br group is indeed believed to trap one of the two excess electrons in Ti³⁺ states that are associated to the oxygen vacancy,[5] and these states have essentially the same character of the electron trap states that are observed on photoexcited TiO₂ catalysts.

The possibility of a direct interaction between O₂ and surface OH_br groups was proposed a few years ago by Henderson and co-workers,[4] in order to interpret the water TPD spectrum on TiO₂(110) after O₂ exposure. These authors found that when the vacuum-annealed surface (containing ∼10% oxygen vacancy sites) was exposed to submonolayer coverages of water and then to O₂, a new feature appeared at $T \sim 300$ K in the water TPD spectrum (denoted as T₃₀₀ in the following); instead, this feature did not show up if the surface was exposed to water coverages above one monolayer prior to dosing O₂. They proposed that an adsorbed intermediate such as a peroxo group, formed

through the *direct* reaction of O₂ with surface hydroxyls, is involved in the T₃₀₀ desorption feature. Thus, when the surface is exposed to above-ML water coverages, which block surface OH groups through H-bonding, the O₂ + OH reaction is inhibited and the T₃₀₀ peak is not present.[4]

These findings have been recently corroborated by new electron energy loss spectroscopy (EELS) and TPD data.[5] On the basis of these data, it was more specifically proposed that the T₃₀₀ peak may arise from the recombinative desorption of two *terminal* hydroxyl (OH_t) groups at coordinatively unsaturated 5-fold Ti sites (Ti_5c), leaving an oxygen adatom on the surface. The two OH_t groups are possibly formed through an HO₂ or H₂O₂ intermediate, which is in turn the result of the direct O₂−OH_br interaction mentioned above. While the involvement of chemisorbed O₂ species was explicitly excluded, the detailed atomic scale processes leading to the various intermediate species, as well as the actual character of these species, are still highly speculative.

To get some insights into the origin of the T₃₀₀ peak in the water TPD spectrum, as well as into the mechanisms by which surface OH groups mediate the electron transfer to O₂ on TiO₂-(110), in this paper we study the adsorption of O₂ on hydroxylated rutile TiO₂(110) using density functional theory (DFT) total energy calculations and first principles molecular dynamics (MD) simulations. We determine the structure and relative energy of the stable intermediates resulting from the OH_br−O₂ interaction, perform molecular dynamics simulations to directly infer the mechanism of their formation from physisorbed O₂, and analyze the electronic structure through density of states (DOS) and projected DOS (PDOS) calculations.

Computational Setup

The Car−Parrinello[6] approach was used both for the geometry optimizations and for the MD simulations. PBE exchange-

* Corresponding author. Present address: Department of Chemistry, University College London, London WC1H 0AJ, UK.
† Princeton University.
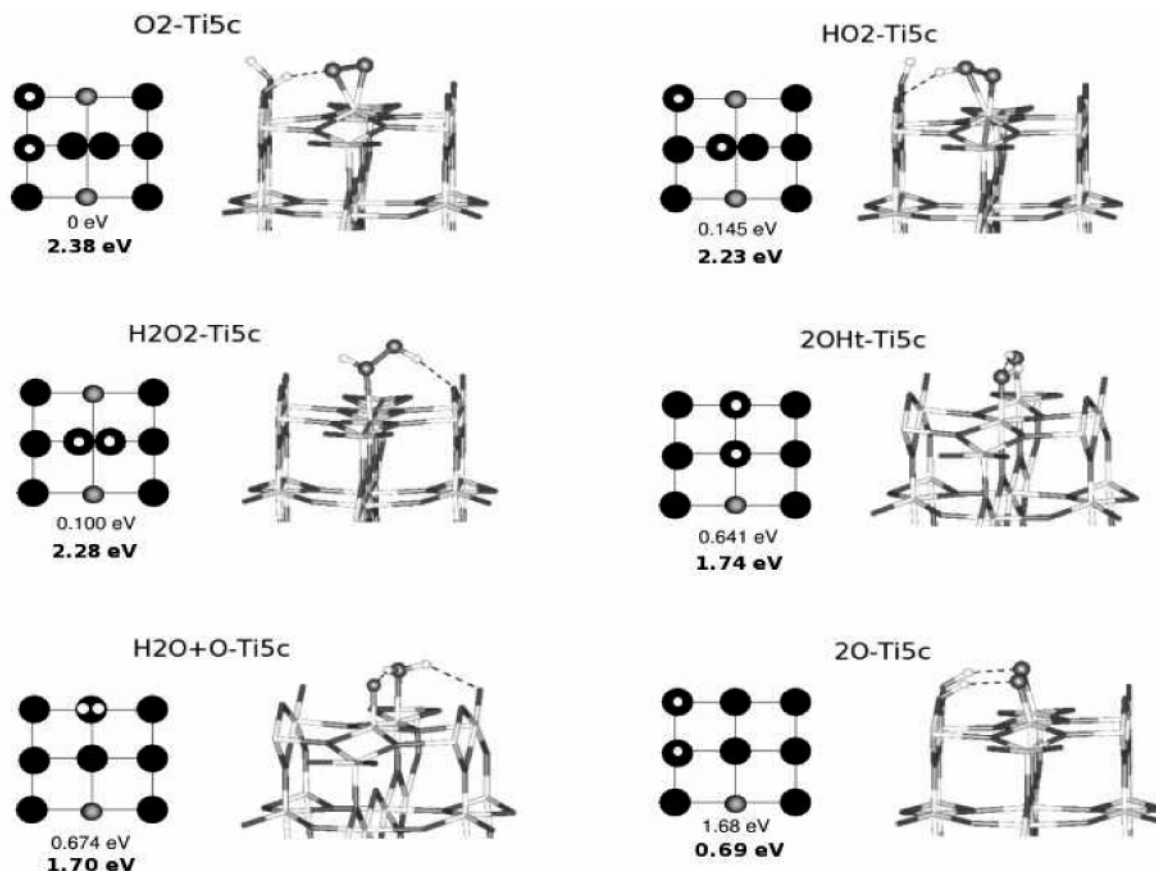‡ Universita' di Milano-Bicocca.

Figure 1. Oxygen adsorption structures (schematic top view on the left and ball-and-stick side view on the right) and energies obtained using the $c(2 \times 4)$ cell. The two energies reported for each structure are the energy relative to the most stable structure and the adsorption energy calculated with respect to noninteracting hydroxylated slab and O_2 molecule. In the top view, O, H, and Ti atoms are represented as black, white and gray circles, respectively. In the side view, slab Ti and O atoms are represented as white and dark sticks, while adsorbed O and H atoms are represented as large dark and small white spheres, respectively, and dashed lines denote hydrogen bonds.

correlation functional[7] and ultrasoft pseudopotentials[8] for all atomic species, including O 2s, 2p and Ti 3s, 3p, 3d, 4s shells, were used; spin polarization was included. Plane-wave basis set cutoffs for the smooth part of of the wave functions and the augmented density were 25 and 200 Ry, respectively. k-Sampling was restricted to the Γ point. The surface was modeled as a four-layer (i.e., four $O-Ti_2O_2-O$ trilayers) periodic slab, with two hydrogens added to adjacent bridging oxygens so as to represent the final state of water adsorption and dissociation at a vacancy site.[9-11] A $c(2 \times 4)$ surface cell geometry was used; this cell has the same area of a $p(2 \times 2)$ cell, but the periodic images of the surface hydroxyls are staggered so that their nearest neighbor distance is larger and their interaction weaker.[12,13] The atoms in the bottom layer were fixed to their bulk positions, and molecules were adsorbed on the top layer only. 3D periodic boundary conditions were applied throughout, with a ~10 Å vacuum between adjacent slabs. All the approximations involved in our model have been extensively tested and found adequate in previous works[12,14] As a further validation of our model, we calculated the energetics of water adsorption at the perfect and defective surfaces; dissociation turned out to be favored only on the defective surface, in agreement with experiment.[9,10] The calculated adsorption energies for dissociative vs molecular adsorption were 0.97 vs 0.54 eV on the defective surface, and 0.66 vs 0.76 eV on the ideal surface, in good agreement with recent theoretical studies.[9,15] Geometry optimizations were carried out through damped MD until the largest component in the ionic forces was less than 0.025 eV/Å. Molecular dynamics simulations were performed

with a time step of 0.17 fs, using the deuterium mass for hydrogen atoms and a fictitious mass of 700 atomic units. No temperature control was imposed, except for the high-temperature runs where the Nosé thermostat was used.

Results and Discussion

Energetics. A number of molecular/dissociated O_2 adsorption structures on the hydroxylated rutile(110) surface are sketched in Figure 1, where the optimized structures and the corresponding relative and adsorption energies are also shown. The most stable structure is O_2-Ti_{5c}, with molecular oxygen chemisorbed on the 5-fold-coordinated Ti atom next to the bridging hydroxyl groups. Here, O_2 sits with its bond axis slightly inclined toward the surface plane, making one O−Ti distance much shorter than the other (2.30 vs 3.27 Å) and allowing the O atom closest to the surface to accept a strong (R(O−H) = 1.75 Å) hydrogen bond from one of the two hydroxyls. Two slightly less stable structures are obtained if one or both protons are transferred from the hydroxyl group(s) to O_2-Ti_{5c}, forming HO_2 or H_2O_2 chemisorbed on Ti_{5c}, respectively. The HO_2 plane is roughly parallel to the surface plane, resulting in two shorter Ti−O bonds (2.13 and 1.88 Å) and a longer (1.86 Å) H-bond, with respect to O_2-Ti_{5c}. On the other hand, the $H_2O_2-Ti_{5c}$ molecule is coordinated to the Ti atom through a single O atom at 2.30 Å, and the O−O axis is significantly tilted with respect to the surface plane. In this coordination mode, a hydrogen points roughly toward an O_{2c} (the H-bond distance is 1.81 Å), while the other hydrogen points slightly upward. Another, more symmetrical, $H_2O_2-Ti_{5c}$ structure with both hydrogens donated
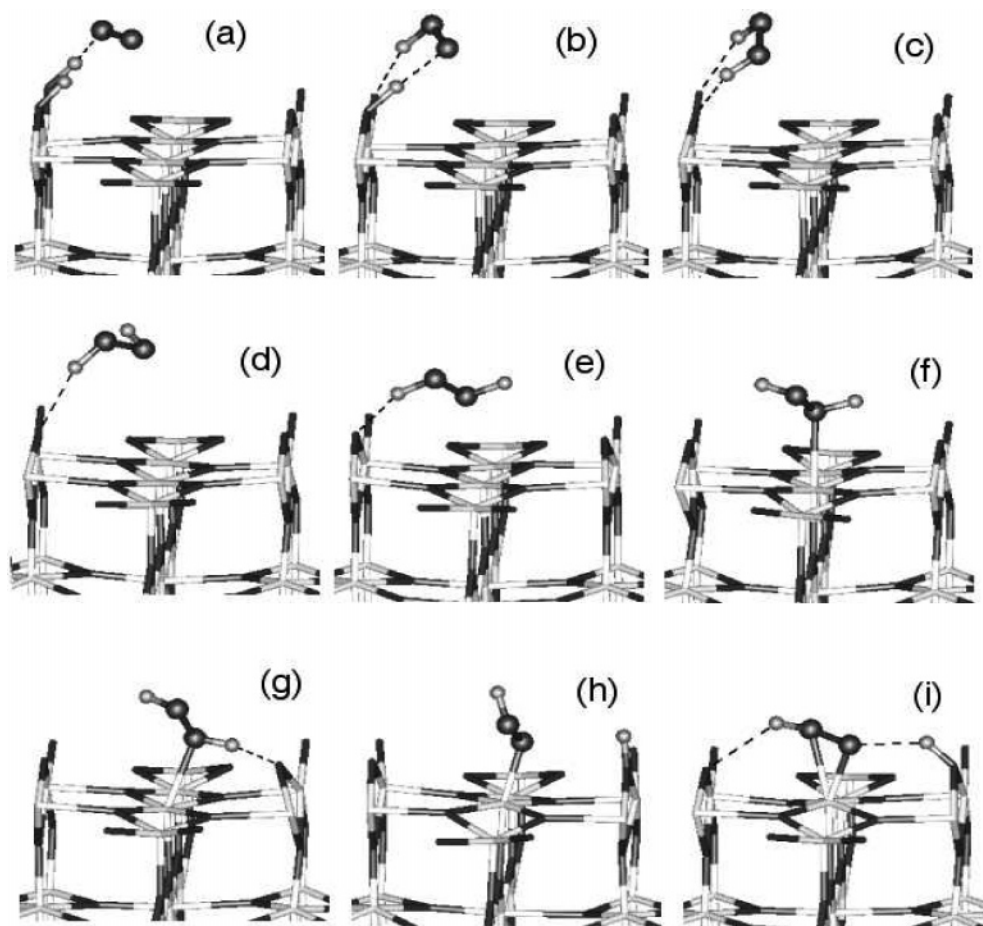
Figure 2. Selected snapshots from the MD trajectory started with an O$_2$ molecule above the surface, illustrating the formation of H$_2$O$_2$, its adsorption, and further transformation. Slab Ti and O atoms are represented as white and dark sticks, while adsorbed O and H atoms are represented as large dark and small white spheres, respectively; dashed lines denote hydrogen bonds.

to O$_{2c}$ on opposite sides was found to be only 0.03 eV less stable, indicating that both conformations should be relevant.

In agreement with previous studies,[10,11,16] structures with terminal hydroxyls such as 2OH$_t$−Ti$_{5c}$, obtained by breaking the O−O bond in the above intermediates, are found to be significantly less stable.[17] This may be considered as an indication that OH$_t$ groups do not play an important role in the desorption process giving rise to the T$_{300}$ peak in the water TPD spectrum. Vice versa, the much higher stability of peroxide intermediates seems to suggest a desorption path where such intermediates decompose directly to (desorbed) water and a surface adatom. A possible immediate precursor of the final desorption step could be the H$_2$O + O−Ti$_{5c}$ state involving an O adatom and a H$_2$O−Ti$_{5c}$ molecule on two adjacent sites. However, the stability of this state is practically the same as that of the 2OH$_t$−Ti$_{5c}$ configuration discussed above.

The relative stabilities discussed so far support the formation of HO$_2$ or H$_2$O$_2$ intermediates at Ti$_{5c}$ sites.[18] This agrees with experimental observations, in particular: (i) isotopic labeling studies[5] show that O$_2$ does not displace bridging hydroxyls groups from the vacancies to the Ti$_{5c}$, but extracts protons from them to form the intermediate; (ii) high-resolution EELS (HREELS) data[5] show that the O−H bonds of the unknown intermediate formed by the O$_2$ + OH$_{br}$ reaction are inclined almost parallel to the surface (this feature is much more evident in HO$_2$−Ti$_{5c}$ than in H$_2$O$_2$−Ti$_{5c}$ (Figure 1)); (iii) some indications that the O−O bond is preserved in the intermediate have also been obtained.[19]

The desorption temperatures of the various possible intermediates can be roughly estimated from their energies relative to the desorption products, which consist of a gas-phase water molecule and the surface with an oxygen adatom left on a Ti$_{5c}$.[5] The 2OH$_t$−Ti$_{5c}$ and H$_2$O + O−Ti$_{5c}$ states are only 0.22 and 0.19 eV more stable than the desorption products, respectively. Using Redhead's analysis[20] with 1 K/s temperature ramp and 10^{13} s^{-1} attempt frequency, the corresponding desorption temperatures, T_{des}, in the water TPD spectrum would be in the range 70−80 K. This seems to exclude the possibility that the T$_{300}$ feature arises from the direct decomposition of either 2OH$_t$−Ti$_{5c}$ or H$_2$O + O−Ti$_{5c}$. On the other hand, the relative energy of H$_2$O$_2$−Ti$_{5c}$ with respect to the desorption products is 0.76 eV, which corresponds to $T_{des} \sim 275$ K. This opens up a possible interpretation of the T$_{300}$ peak as due to the decomposition of H$_2$O$_2$−Ti$_{5c}$. However, the mechanism for this process is not straightforward, as the H$_2$O$_2$−Ti$_{5c}$ species are found to be quite stable, at least on the short time scales of our ab initio MD simulations (see below).

Molecular Dynamics Simulations. The experimental results in ref 5 point to the possibility of a direct OH$_{br}$−O$_2$ interaction not involving the very stable chemisorbed O$_2$−Ti$_{5c}$ species. To locate a reaction path compatible with these observations, we have carried out molecular dynamics simulations starting from two different configurations, in which the O$_2$ molecule was initially above the bridging hydroxyl groups, and then left free (without any temperature control) to find an energetically favorable conformation. In both cases a very fast reaction

occurred (snapshots a–c in Figure 2), in which O_2 captured both hydroxyl protons in rapid sequence, forming a short-lived H-bonded complex $H_2O_2\cdots O_{2c}$ (with a calculated energy of +0.63 eV, relative to O_2–Ti_{5c}). The H_2O_2 molecule was immediately attracted toward the surface and coordinated to a surface Ti_{5c} (snapshots d–f), with the whole process taking less than 1 ps. In the first trajectory the H_2O_2–Ti_{5c} molecule was further transformed to HO_2–Ti_{5c} after transferring a proton back to a bridging oxygen (snapshots g–i), and then remained stable for 2 more ps. In the other trajectory, no further transformation of H_2O_2–Ti_{5c} occurred.

These MD simulations show that a direct attack of the bridging OH groups by O_2 does not require a prior chemisorption of the molecule on an unsaturated Ti site: the reaction proceeds spontaneously on a very short time scale as soon as the molecule approaches the active OH groups from above. The MD trajectories also confirmed the significant stability of HO_2 or H_2O_2 intermediates when coordinated to Ti_{5c}, as well as the possibility of interconversion between them, based on their similar stability, as discussed in the previous section.

In the attempt to make more direct contact with the TPD experiments, where the decomposition of the reactive intermediate leading to water desorption is observed above 300 K,[5] we extended the MD simulation for five more picoseconds, after increasing the temperature to 350 K. A few interconversions between HO_2–Ti_{5c} and H_2O_2–Ti_{5c} were observed, but neither further transformation or desorption occurred. Most likely, the time scale for desorption is in this case longer than the one accessible to our simulations.

Electronic Density of States. To obtain insight into surface-molecule charge-transfer processes and the electron-scavenger properties of O_2, it is useful to examine the electronic density of states (DOS) of the various metastable adsorption configurations in Figure 1. Before starting our analysis, however, it is important to point out some limitations of the DFT approach in the description of electronic energy levels: (*i*) the computed band gap of $TiO_2(110)$ is about 2 eV, against the experimental value of 3 eV; (*ii*) while experiments indicate that reduced TiO_2 surfaces have localized Ti^{3+} defect states that lie in the band gap, ∼0.8 eV below the conduction band edge,[2] DFT calculations yield very shallow and quite delocalized states at the bottom of the conduction band;[12,13,21] (*iii*) experimentally, the band gap states remain, slightly shifted to lower energies, when water dissociatively adsorbs at the surface oxygen vacancy to form two bridging hydroxyls,[2] whereas the energy of the computed defect states is not significantly modified upon water dissociation and surface hydroxylation. On the positive side, the computed energy of the defect states relative to the top of the TiO_2 valence band (∼2 eV) agrees very well with the experiment. This provides support for expecting that several aspects of the surface ↔ molecule charge transfers should be adequately described by the calculations.

The DOS for the stable structures of Figure 1 are shown in Figure 3, together with the projection onto the atomic orbitals of adsorbed O_2 (PDOS).[22] As a reference, in the bottom panel the DOS of the noninteracting clean *stoichiometric* slab and of an isolated O_2 molecule are shown. For the clean slab, the bottom part of the conduction band involves the d states of Ti atoms, including both Ti_{5c} d states (with only a tiny contribution from the TiO_{br} d states) and d states of fully coordinated Ti atoms in the slab.

The filled "defect" states of the hydroxylated surface (not shown) are found right at the bottom of this band, where also the O_2 LUMO is present. This favors charge transfer to the
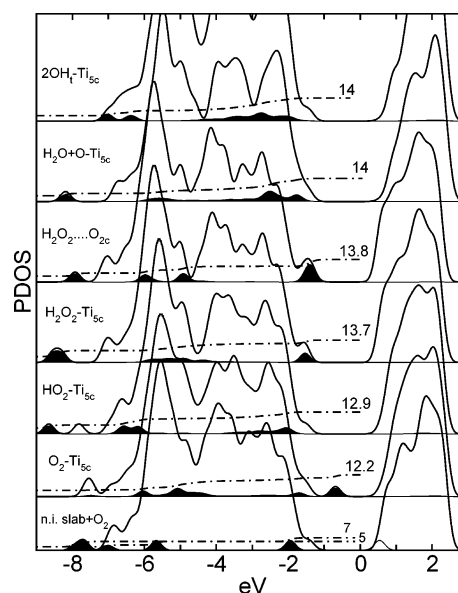

Figure 3. Total density of states (continuous lines) and its projection onto the adsorbing/adsorbed O_2 molecule (full curves for filled states and hollow for empty ones). The $H_2O_2\cdots O_{2c}$ is the physisorption structure obtained from the geometry optimization of the configuration in Figure 2d. The zero of energy corresponds to the conduction band minimum; DOS levels are aligned by matching the energy of a 3s-like Ti state in the bottom layer of the slab. The bottom curves are the reference DOS for an isolated O_2 molecule and the clean slab. For each system the dashed line represents the integral of the O_2 PDOS over the energy range of the occupied valence states, with the contribution of the hydrogen(s) added where needed. The two values of the PDOS integral in the lowest panel refer to the spin up and spin down states.

molecule and reoxidation of the surface.[12] The charge transfer leads to the partial filling of the O_2 LUMO, and thus to the appearance of an additional band of occupied states in the O_2 PDOS. This state lies in the band gap for the O_2–Ti_{5c} structure (see Figure 3) and is further stabilized when proton transfer occurs from the bridging hydroxyls to the adsorbed O_2, as, for instance, in the case of the H_2O_2–Ti_{5c} structure. For what concerns the empty states, for the O_2–Ti_{5c}, $2OH_t$–Ti_{5c}, and H_2O–Ti_{5c} configurations the Ti_{5c} d states (including those at the Ti adsorption site) are shifted to higher energies with respect to the bottom of the conduction band, which is then formed only by the d states of fully coordinated (surface and bulk) Ti atoms. On the other hand, for the H_2O_2–Ti_{5c} and HO_2–Ti_{5c} structures, the Ti_{5c} d states (including the d states of the Ti atom on which the hydroperoxo species is adsorbed) still lie at the bottom of the conduction band, suggesting the possibility that TiOOH species may behave as electron traps.

Since, as noted before, the energy of the defect states is not modified upon water dissociation in the vacancy, the initial oxidation state of the hydroxylated surface and of the defective clean surface are essentially the same: both surfaces are reduced, with an excess of two electrons with respect to the perfect surface. These two electrons are gradually transferred to the oxygen molecule as the surface is reoxidized. To assess the progress of surface reoxidation, the flow of charge out of the surface can be monitored by integrating the PDOS over the filled states of the adsorbed species, including the hydrogens transferred along the process.[23] Figure 3 shows that the PDOS integral gradually increases from the initial value of 12 for the isolated neutral O_2 molecule to 12.2 for O_2–Ti_{5c}, 12.9 for HO_2–Ti_{5c}, and 13.7 for H_2O_2–Ti_{5c}. According to these calculations, the electronic charge transfer from the surface to the adsorbed

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molecule is thus coupled to proton transfer from the bridging hydroxyls; in other words, the transfer involves "H species" consisting of a proton plus a fraction of electronic charge e (approximately 0.6 e) localized around it. We also notice that the higher degree of surface oxidation in the HO$_2$−Ti$_{5c}$ and H$_2$O$_2$−Ti$_{5c}$ structures with respect to O$_2$−Ti$_{5c}$ is reflected in the stabilization of the highest occupied state in the PDOS of the adsorbed molecule.[24] Nonetheless, the O−O distance is very similar in all these species: 1.46 Å for O$_2$−Ti$_{5c}$ (close to a O$_2{}^{2-}$ anion, as already found for O$_2$ on the non-hydroxylated surface[12]) vs 1.47 Å for both H$_2$O$_2$−Ti$_{5c}$ and H$_2$O$_2$−Ti$_{5c}$.

There are a few additional points which are worth noting. (i) For the H$_2$O$_2$···O$_{2c}$ complex, the HOMO location, PDOS integral, and O−O distance suggest that charge transfer occurs also *before* chemisorption. (ii) For the most stable intermediates, such as H$_2$O$_2$−Ti$_{5c}$, our calculations predict an incomplete surface reoxidation, with a residual delocalized charge remaining in the slab. By contrast, the two less stable structures, 2OH$_t$−Ti$_{5c}$ and H$_2$O−Ti$_{5c}$, yield PDOS integrals of ∼14, corresponding to a complete surface reoxidation/O$_2$ species reduction. This may indicate that, despite their low stability, the latter species are also required to complete the surface oxidation process.

Conclusions

This work represents one of the first attempts to study the chemistry of O$_2$ on the hydroxylated TiO$_2$ surface by means of first-principles static and dynamics calculations. Due to the reduced state of the hydroxylated surface, studying the properties of this system is useful for obtaining insights into the photocatalytic behavior of titanium oxide surfaces and the scavenging ability of oxygen.

The MD results support the experimental hypothesis that physisorbed O$_2$ reacts directly with the surface hydroxyls; that is, the reaction does not pass through a chemisorbed O$_2$ state. The products of this interaction are hydroperoxide species, which are eventually chemisorbed onto the 5-fold coordinated surface Ti atoms. While the computed energetics suggest that these hydroperoxides may be the intermediates involved in the observed T$_{300}$ TPD feature, the detailed desorption mechanism could not be resolved, as these species are found to be stable within the limited duration of our first principles molecular dynamics simulations. On the other hand, the assignment of the T$_{300}$ peak to an intermediate involving terminal hydroxyls, as invoked in previous experimental works, is not supported by our total energy calculations.

While our analysis of surface ↔ molecule charge transfer is hampered by the limitations of current DFT approaches in describing electronic energy levels, our calculations suggest that reoxidation of the surface by the molecule is favored by the overlap of the O$_2$ LUMO and the surface defect state, as observed for O$_2$ adsorption on the defective surface[12] (the position of the O$_2$ LUMO at the bottom of the conduction band is similar on the defective and hydroxylated surfaces). Scavenging by O$_2$ starts as soon as the oxygen molecule captures a

hydrogen from the bridging hydroxyls, and does not require O$_2$ chemisorption to take place. According to our calculations, indeed, the electronic charge transfer from the surface to the molecule is largely coupled to the transfer of the protons from the bridging hydroxyls.

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(17) Also much less stable is the dissociation of the adsorbed O$_2$ molecule on the hydroxylated surface, leading to two O adatoms at adjacent Ti$_{5c}$ sites (structure 2O−Ti$_{5c}$ in Figure 1) or at nonadjacent sites (not shown).
(18) On the other hand, preliminary static and dynamics calculations for O$_2$ interacting with a single surface hydroxyl per supercell indicate that in this case the formation of HO$_2$ is not energetically favored, as the total energy of HO$_2$−Ti$_{5c}$ is 0.03 eV higher than that of the noninteracting gas-phase molecule and hydroxylated slab. Further work is in progress to assess the structural and electronic reasons for this effect.
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(22) Both DOS and PDOS have been computed with a Gaussian broadening of 0.2 eV. For this reason the band gap for the n.i. slab + O$_2$ obtained from the DOS is less than 1.5 eV, instead of 1.92 eV, as obtained from the computed eigenvalues. The contribution to the DOS from the Ti and O atoms which are kept fixed during geometry optimization has been removed.
(23) For all H-containing species, such as HO$_2$−Ti$_{5c}$ and H$_2$O$_2$−Ti$_{5c}$, this integral includes the electronic charge contribution of the relevant H atoms, obtained by integrating the corresponding PDOS. This contribution is found to be of ∼0.6 electrons/H atom for all configurations.
(24) Note, however, that the deeper location of the HOMO would suggest a more effective charge transfer toward HO$_2$−Ti$_{5c}$ than H$_2$O$_2$−Ti$_{5c}$, at variance with the value of the PDOS integral.