Imaging Consecutive Steps of $O_2$ Reaction with Hydroxylated TiO$_2$(110): Identification of HO$_2$ and Terminal OH Intermediates

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We report the results of a combined experimental and theoretical investigation of the reaction of molecular oxygen with a partially hydroxylated TiO$_2$(110) surface. The consecutive steps of both primary and secondary site-specific reactions have been tracked with high-resolution scanning tunneling microscopy (STM). We have directly imaged stable, adsorbed hydroperoxyl (HO$_2$) species, which is believed to be a key intermediate in many heterogeneous photochemical processes but generally metastable and “elusive” until now. We also found terminal hydroxyl groups, which are another critical but never previously directly observed intermediates. Conclusive evidence that $O_2$ reacts spontaneously with a single bridging OH group as an initial reaction step is provided. The experimental results are supported by density functional theory (DFT) calculations that have determined the energies and configurations of these species. Reported observations provide a base for a consistent description of the elementary reaction steps and offer molecular-level insight into the underlying reaction mechanisms. The results are also expected to have important implications for various catalytic systems involving the interconversion of O$_2$ and H$_2$O.

Introduction

Oxygen and water are two of the most prevalent and important chemicals on our planet. As such, their chemical interactions have attracted great interest from both fundamental and technological points of view. Although the production of H$_2$ and O$_2$ via photocatalytic water splitting holds promise in providing renewable, clean energy, in a broader perspective, the reduction of O$_2$ to H$_2$O plays a vital role in many important chemical and biological processes, ranging from combustion and atmospheric reactions, to oxygen radical biology and degradation of organic pollutants. Reactions leading from O$_2$ to H$_2$O or vice versa (in particular, on catalytically active surfaces) often involve intricate mechanisms with a number of possible surface-bound reactive intermediates, such as OH, HO$_2$, or H$_2$O$_2$. In general, such reactions on surfaces are challenging to explore with ensemble-averaging spectroscopic techniques because of the relatively small number of participating molecules and the difficulty in resolving intermediates spectroscopically.

In numerous studies of heterogeneous photocatalytic water splitting, titania (TiO$_2$) has emerged as an important model system because of its superior photocatalytic properties and as a prototypical metal oxide. It is recognized that both TiO$_2$ photocatalytic activity and O$_2$ effectiveness as a scavenger of photoexcited electrons are affected by the presence of surface hydroxyl groups. Molecular oxygen is generally recognized as an effective scavenger of photoexcited electrons that prevents photocatalyst deactivation by negative charge accumulation. Recently, a number of studies have focused on fundamental aspects of the interaction of oxygen and water on the reduced rutile TiO$_2$(110) surface that can be easily hydroxylated via water dissociation at oxygen vacancies. Several studies have speculated or invoked the existence of Ti-bonded metastable HO$_2$/H$_2$O$_2$ and terminal OH species as intermediates in these processes. However, direct evidence for these species and reactions leading to their formation has not been available to date.

As a key step in this direction, we followed the consecutive reactive steps of $O_2$ with a partially hydroxylated TiO$_2$(110) surface via high-resolution scanning tunneling microscopy (STM). We report here the first direct imaging of two key O-containing species adsorbed at terminal Ti sites and identify them as hydroperoxyls, HO$_2$, and terminal hydroxyls, OH. By tracking species that result from a sequence of primary and secondary reactions and comparing results with density functional theory (DFT) calculations, we extract molecular-level details about the underlying reaction mechanism.

Experimental Section

Experiments in this study were performed in two separate ultrahigh vacuum (UHV) STM systems which have similar setups; thus, only one is described in a detail here. System I (base pressure $3 \times 10^{-11}$ Torr) is equipped with a variable-temperature STM (Omicron), a semispherical electron energy analyzer (Omicron), a mass spectrometer (Ametek), and electron and ion guns (VG and SPECS, respectively). The single-crystal rutile TiO$_2$(110)-(1 $\times$ 1) surface (Princeton Scientific) was prepared by multiple cycles of Ar ion sputtering (2 keV) and UHV annealing (800–900 K), with cleanliness monitored by X-ray photoelectron and Auger electron spectroscopies. At the beginning of each experiment, the sample was flash-annealed to 600 K. Partially hydroxylated TiO$_2$(110) surfaces were obtained by either H$_2$O dosing through a dedicated doser or waiting for water dissociation from UHV background (in both cases, the obtained results have correlated with each other).
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...dosed water was degassed by freeze–pump–thaw cycles prior to use. The interaction of O2(g) with the hydroxylated TiO2(110) surface was studied at 300 K. Oxygen was introduced using a movable directionals doser connected to a 1-mm-i.d. tube that terminated 3 mm from the STM tunneling junction. Because of a tip shadow effect, we have not used an absolute (calibrated) oxygen flux, but rather, a dosing time as a measure of O2 exposure. The vacancy concentration and species coverage were obtained by a direct counting from STM images and expressed in monolayer (ML) units (1 ML corresponds to $5.2 \times 10^{14}$ cm$^{-2}$ Ti atoms). STM tips were homemade from electrochemically etched W wire and cleaned in situ by annealing and ion sputtering. Presented STM (empty state) images were collected in a constant-current (0.1–0.3 nA) mode at positive sample bias voltages of 1.5–1.8 V. The resulting images were processed using WSXM software.

Computational Details

We performed density functional theory calculations using the Vienna ab initio software package (VASP) in conjunction with the PBE functional. Core electrons were represented by projector augmented-wave potentials, whereas valence electrons were described by a plane-wave basis set with a cutoff energy of 400 eV. We used a slab model with four O–Ti–O layers and a (2 × 3) surface supercell to describe the surface. The dimensions of this cell were 13.16 Å × 8.91 Å × 30 Å, giving a vacuum gap of ~18 Å for the clean surface. The top two layers of the slab were allowed to relax. The Brillouin zone was sampled by a single k-point. Tests with a 2 × 2 × 1 k-point mesh gave results equivalent to those using a 1 × 1 × 1 k-point mesh.

The STM line profiles were generated using the Tersoff–Hamann approximation. The method assumes that the tunneling current is proportional to the density of states within the range of the energy scan. A problem inherent in periodic DFT calculations, due to numerical artifacts, is that the zero of energy for the Kohn–Sham eigenvalues is not the same for different systems, so the band structures need to be shifted to the same scale. Because the adsorbate concentration is not in the dilute limit, the Fermi level can also unreasonably shift due to the presence of the adsorbate. To overcome these difficulties, we aligned the band structures relative to a clean surface and used the clean surface Fermi level as the Fermi level for the adsorbate/surface systems. We generated densities from the Fermi level up to a positive bias of 1.8 eV above the Fermi level. The STM line profiles were plotted for a density of $6 \times 10^{-6}$ e/Å$^2$. Importantly, different energy ranges and density contours showed the same trends in the peak heights of the line profiles.

Results and Discussion

A typical STM image of the partially hydroxylated TiO2(110) surface (OH coverage, ~0.04 ML) before O2 exposure is shown in the inset of Figure 1a. The image of TiO2(110) is dominated by electronic contrast where the low lying rows of terminal, 5-fold coordinated Ti atoms appear bright, counter to intuition, and high lying bridging oxygen (O$_b$) rows appear dark. Beyond the periodic surface structure, brighter bridging hydroxyls (OH$_t$) and less bright bridging oxygen vacancies (O$_{vac}$) can be recognized on the dark O$_b$ rows (marked with squares), in accord with previous reports in the literature. The O$_{vac}$’s (here, ~0.09 ML) are a result of the partial reduction of TiO$_2$ during sample preparation with ion sputtering and vacuum annealing. In turn, the OH$_b$’s result from H$_2$O dissociation at O$_{vac}$’s.

$$\text{H}_2\text{O} + \text{O}_{\text{vac}} + \text{O}_b \rightarrow 2\text{OH}_t$$

and as the reaction scheme suggests, OH$_b$’s appear in pairs upon their creation, as shown in Figure 1a (as one large spot labeled 2OH$_b$). There are two known mechanisms leading to the separation of the OH$_b$ pairs into OH$_b$ groups: cross-row hydrogen diffusion assisted by molecularly bound H$_2$O and intrinsic along-row hydrogen diffusion. To investigate the surface reactions between OH$_b$’s and O$_2$(g), we exposed the partially hydroxylated surface (0.04 ML of OH$_b$’s) to O$_2$ at 300 K, and the resulting STM image is displayed in Figure 1a. Three new features (marked with circles) can be seen on the Ti rows. The small bright spots (dotted circles) are assigned to O adatoms (O$_a$), which are known to be a direct result of O$_2$ dissociation on O$_{vac}$ sites. One oxygen atom of O$_2$ fills the vacancy, and the other atom resides as an O$_a$ on Ti row. In this report, we will provide evidence that O adatoms on Ti rows can form also as a result of reactions of molecular oxygen with bridging hydroxyl groups.

The other two features result from reactions of partially hydroxylated TiO$_2$(110) with O$_2$(g). They are HO$_2$ (dashed circles, Figure 1a) and OH$_t$ (solid circles). The detailed explanation of our assignment is provided below along with the discussion of Figures 2–6. Here, we focus on the relative appearance and position of all of the features (O$_{vac}$, OH$_b$, O$_a$, HO$_2$, and OH$_t$) observed in the STM images. The cross-row line profiles are provided in Figure 1b to quantitatively illustrate the observed differences. The empty-state, bias-dependent appearances of OH$_b$’s and O$_{vac}$’s, which are both centered on

Figure 1. (a) STM empty-state image of partially hydroxylated (0.04 ML) TiO$_2$(110) surface after 14 min of exposure to O$_2$. Inset shows a partially hydroxylated surface before O$_2$ exposure. (b) Averaged line profiles along the [1-10] direction of the different surface features. (Profiles are vertically displaced for ease of viewing, and the measurement of feature height is illustrated).
Ob rows, have been extensively studied. Generally, at a typical tunneling bias (1–2 V), the OHb feature is higher than Ovac, as shown in the line scans plotted in the left part of Figure 1b. The line profiles for the Ti-centered features are shown in the right part of Figure 1b; the feature height, measured relative to the top of the neighboring Ti row, is the largest for OHt (0.09 ± 0.2 nm), followed by the HO2 (0.05 ± 0.1 nm) and the Oa (0.03 ± 0.1 nm). Spatially, both O2 and OH appear round, but HO2 is slightly elongated along the Ti row.

In what follows, we focus on the assignments of the Oa, HO2, and OH features on the basis of the changes observed on the same area of the surface before and after step-by-step O2 doses. Knowledge of the original positions of the Ovac’s and OHb’s is proving critical in resolving the assignments and in tracking site-specific reactions. Figure 2a and b displays two images of the identical surface area after 9 and 14 min O2 doses, respectively. Magnified views of three specific areas (labeled I, II, and III), marked to point out the features that have changed, are shown in the middle of Figure 2. Additionally, ball models are displayed alongside to illustrate the surface reactions assigned to these changes.

Changes in area I, Figure 2, illustrate the Oa formation via O2 dissociation on Ovac sites:

\[
\text{Ovac} + \text{O}_2(g) \rightarrow \text{Ob} + \text{Oa}
\]  

Here, the original Ovac is healed by one oxygen atom of an O2 molecule, with the other atom deposited on the neighboring Ti row as an adatom, Oa. Note that the Oa is shifted by one lattice constant from the original Ovac configuration along the [001] direction (see the corresponding ball models). We have shown previously that this is the most probable Oa configuration (relative to Ovac), resulting from a transient mobility of the hyperthermal Oa upon O2 dissociation at Ovac sites.

Changes in area II, Figure 2, show two events involving reactions of isolated OHb with O2(g), whereby the OHb group is converted to Oa and a new feature appears on the adjacent Ti row. A similar reaction takes place in area III. There, a pair of OHb species is initially present, and then a H atom from one OHb group disappears. The same new feature as observed in area II is detected on a nearby Ti site, while a single OHb is still seen to be located on the Oa row. These changes indicate that a H atom of the OHb group has reacted with the O2(g) in both areas II and III. A reaction that is consistent with the overall stoichiometry can be written as

\[
\text{OHb} + \text{O}_2(g) \rightarrow \text{Ob} + \text{HO}_2
\]

suggesting that the new species might be HO2, hydroperoxyl. (Further observations discussed below will confirm this assignment.) A key finding from our results is that HO2 is formed by reaction of O2(g) with both an isolated OHb (see area II of Figure 2) and paired OHb’s (area III of Figure 2). Earlier DFT work had suggested that only reactions of O2 with a pair of OHb’s should lead to a stable HO2 (and H2O2) species. Our observations provide evidence that in an initial reaction step, O2 reacts directly and spontaneously with a single bridging OH group to form HO2.

The formation of the second new feature, terminal Ti-bound hydroxyl OHt, is revealed in Figure 3, which displays a sequence of three STM images taken after stopping the O2 dosing. The first image, Figure 3a, shows a pair of OHb’s and a single O2 formed by the preceding O2 exposure. In the second image, Figure 3b, the H atom from the top OHb has moved one lattice
constant up along the Oa row, which brings it in close proximity to the Oa species. (Intrinsic H diffusion along OHb rows has been investigated in our recent study.\textsuperscript{17}) When OHb location is in the vicinity of the Oa, both species participate in further reactions: the H atom from the OHb group disappears, and a new bright feature appears at the position of Oa, which we assign to OHt in Figure 3c. Since the latter process occurs without O2 flowing, the observed change has to be due to an H transfer from OHb to Oa, creating OHt as a result.

\[
O_a + OH_b \rightarrow OH_t + O_b \quad (3)
\]

Although the existence of OHt has been proposed in a number of previous studies,\textsuperscript{11,30,31} this is the first direct observation of this species by STM. In a side comment to reaction 3, illustrated in Figure 3b and c, note that we cannot exclude the possibility that H diffuses one more lattice constant up and then H transfer happens spontaneously, since we have never observed OHb and Oa at nearest adjacent sites. (A similar observation is valid for a secondary reaction 5, described later.) Note also that observing OHt formation during O2 dosing revealed a small increase in the number of detected events in comparison with the case without O2 flowing. We attribute this to a possible minor reaction channel involving an intermediate HO2 formation adjacent to Oa site (via reaction 2), reacting to form OHt according to modified reaction 3.

\[
O_a + OH_b + O_2(g) \rightarrow O_a + HO_2 + O_b \rightarrow OH_t + O_2(g) + O_b
\]

Both new Ti-bonded HO2 and OHt species are observed to be quite stable and immobile at 300 K and can be imaged over extended periods of time (>60 min). However, in a few instances, we observed HO2 dissociation into Oa and OHt, according to

\[
HO_2 \rightarrow O_a + OH_t \quad (4)
\]

The STM image sequence illustrating this reaction is shown in Figure 4, where panels a and b display the initial event of HO2 formation at this site (via reaction 2). HO2 spontaneous dissociation can be seen in panels b and c. Reaction 4 provides strong additional evidence for the chemical makeup of the HO2 species. We believe that the first direct observation of HO2 species also validates the interpretation of the pioneering TPD studies by Henderson, in which HO2 had been postulated to be an intermediate in the reactions of O2 with OHb groups on TiO2(110).\textsuperscript{10,11}

Reaction 2 is the primary process that leads to the formation of HO2 species when hydroxylated TiO2(110) is exposed to O2(g). However, when another OHb is present in the vicinity of HO2, our observations indicate that a secondary reaction may occur, with the formation of Oa and H2O.

\[
OH_b + HO_2 \rightarrow O_b + O_a + H_2O \quad (5)
\]

Since molecularly bound H2O is very mobile at 300 K,\textsuperscript{24,25} it cannot be imaged with STM. The evidence for H2O formation comes from its immediate dissociation on a nearby Ovac site. The overall sequence of events can thus be written as follows:

\[
OH_b + HO_2 \rightarrow O_b + O_a + H_2O \quad \text{(reaction 5)}
\]

In about 85% of cases, we have, indeed, observed the dissociation of a newly created H2O molecule on a neighboring Ovac. We consider this to be strong confirmation that the identified H2O molecules are direct products of reaction 5 and do not originate from the UHV background. The initial reactants and final products for reaction 5 are shown in the STM images in Figure 5. Although the initial event of HO2 formation via reaction 3 is not imaged here by scanning after O2 exposure (because of the related time delay), we have been able to detect it by scanning during O2 dosing (albeit with lower resolution), as shown in Figure S1 of the Supporting Information, confirming the reaction mechanism. Note also that the above results indicate that, on partially hydroxylated reduced TiO2(110), Oa’s could be formed not only via O2 dissociation at Ovac sites (reaction 1), but also as a result of HO2 dissociation (reaction 4) and HO2 reacting with nearby OHb (reaction 5).

Figure 4. Time-lapse STM images of (4.3 × 2.7) nm² area imaged during O2 dosing with time stamps of (a) 0, (b) 12, and (c) 64 min, illustrating reaction 4. Following HO2 formation (a to b), after awhile, the HO2 spontaneously dissociates (b to c) to form Oa and OHt species.

Figure 5. Time-lapse STM images of (2.9 × 2.8) nm² area after O2 dosing of (a) 9 and (b) 14 min, illustrating reaction 5. Two OHb groups in panel a are replaced in panel b by an Oa and two adjacent OHb groups resulting from H2O dissociation at nearby Ovac. The model in the dashed box schematically shows an assumed but not captured initial event of HO2 formation via reaction 2.

A side note to reaction 5 is that from our experiments, it is unclear whether the short-lived hydrogen peroxide (H2O2) intermediate is present before Oa and H2O formation, as discussed in the literature.\textsuperscript{30,32,33} The fact that we do not observe H2O2 as an intermediate in this reaction suggests that if it exists, its lifetime is short as compared to our STM sampling rate (2 min/frame). The short lifetime is in accord with the results of electron paramagnetic resonance studies that show that H2O2 decomposes when in contact with TiO2.\textsuperscript{34}

Similar to the secondary reaction 5 between HO2 and OHb, the OHt and OHb species can also recombine when the OHb
location is in the vicinity of the OHb, and we have, indeed, observed this reaction with the formation of H2O.

\[ \text{OH}_b + \text{OH}_t \rightarrow \text{O}_b + \text{H}_2\text{O} \]  \hspace{1cm} (6)

(In the same way, mobile molecularly bound H2O may be detected from its dissociation on a nearby Ovac site). Reaction 6 is illustrated in Figure 6, which displays that both initial species of OHb and OHt in panel a undergo further reactions: the H atom from the OHb group and the entire OHt feature disappear in panel b.

Although, as mentioned above, the OHt species is immobile and stable at 300 K, it is possible that two adjacent OHb groups can further recombine (if their concentrations are sufficient or if the temperature is increased),

\[ \text{OH}_b + \text{OH}_b \rightarrow \text{H}_2\text{O} + \text{O}_2 \]

also producing water as a final product.\textsuperscript{11} Indirect experimental evidence in the literature strongly supports such a mechanism.\textsuperscript{11,30} In particular, this reaction, together with water producing reactions 5 and 6, would be consistent with previous TPD studies, in which a new H2O desorption feature at >300 K has been observed.\textsuperscript{10,11} We currently do not have direct evidence for such a OHb recombination process, most likely because of a low initial OHb coverage or slow species diffusion. Further TPD studies on fully hydroxylated surfaces, or at elevated temperatures (or both) are thus warranted. However, described above are five primary and secondary elementary reaction steps (reactions 2–6), which for the first time have been visualized at the atomic level, provide a basis for consistent description of the O2 interaction with hydroxylated TiO2(110) surface.

To further support our assignments, we performed DFT calculations of Ti-bonded HO2 and OHt surface species. Our calculations show that both HO2 and OHt can exist as stable species adsorbed on the surface, as shown in Figure 7. Reaction 2 of an O2 molecule with a single OHb species to form a Ti-bonded HO2 moiety is predicted to be exothermic by −0.66 eV. This stable conformation of the HO2 species adsorbed directly on top of a 5-fold coordinated Ti atom has a monodentate Ti−O bond and a strong hydrogen bond to a nearby Ob atom (“transverse” conformation) (Figure 7a). Our structure is markedly different from a previously reported unstable structure of HO2 that was much flatter over the surface.\textsuperscript{12} We also explored such a structure with calculations and found it energetically unfavorable (with formation energy of 0.08 eV). Consistent with the earlier work\textsuperscript{12} as well, the presence of a second OHb species near the adsorbed HO2 was found to lead to an increased stability of ∼1.0 eV for the reaction

\[ 2\text{OH}_b + \text{O}_2(g) \rightarrow \text{OH}_b + \text{O}_b + \text{HO}_2 \]

(Experimental evidence for this process was discussed earlier; see area III in Figure 2.) Note that the transverse structure does not agree completely with STM appearance of the HO2 feature (elongated along Ti row). Although we have also found an HO2 stable structure aligned along the Ti row, it is less thermodynamically favorable (ΔE of −0.09 eV) (Figure S2 of the Supporting Information). Nevertheless, our calculations indicate that an isolated HO2 species can exist on the surface. The optimized structure for the second new species, a terminal hydroxyl group, is shown in Figure 7b. Reaction 4 for formation of OHt by H transfer from OHb to Oa is calculated to be exothermic by −0.38 eV.

To compare the experimentally observed appearance of HO2, OHb, and Oa species with the theory, we employed the Tersoff−Hamann approach\textsuperscript{22} and calculated isodensity contours.
resulting from the empty states in an energy range between the Fermi level and +1.8 eV, as shown in Figure 8. The projected densities of states for these species (used to create the STM line profiles) are displayed in Figure S3 of the Supporting Information. Simulated STM line profiles show that the OH feature is the highest, followed by HO₂ and then O₂, in qualitative agreement with the experimental profiles in Figure 1b (further details for the HO₂ STM profile calculations are given in the Supporting Information).

Summary

We have performed a combined experimental and theoretical investigation of the reaction of molecular oxygen with a partially hydroxylated TiO₂(110) surface. Using high-resolution STM imaging, we have directly monitored the initial surface defects (oxygen vacancies and bridging hydroxyls) and tracked (atom-by-atom) changes caused by the interaction of single O₂ molecules. Both primary and secondary reactions (five overall) have been visualized at an atomic level, and the identification of two key reactive intermediates of HO₂ and OH₄ species reported here opens an important research direction. The experimental results are complemented by density functional theory calculations that have determined the energies and configurations of these species and support our assignments. We believe that the direct observation of adsorbed HO₂ and OH₄ species reported here opens an important research avenue for characterization of molecular-level details of catalytic interconversions of O₂ and H₂O. In a broader perspective, we envision that our observations and findings have implications for stimulating discussions. This work was supported by the U.S. Department of Energy (DOE), Office of Basic Energy Sciences, Division of Chemical Sciences, and performed at the W. R. Wiley Environmental Molecular Sciences Laboratory (EMSL), a DOE User Facility sponsored by the Office of Biological and Environmental Research. Computational resources were provided by the Molecular Science Computing Facility located at the EMSL and the National Energy Research Scientific Computing Center in Berkeley, CA.

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Supporting Information Available: Complementary STM image illustrating reaction 5, further computational details, calculated geometries, and bond distances for various HO₂ structures and projected densities of states. This information is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(4) Fridovich, I. Science 1978, 201, 875.