Reactivity of Anatase TiO₂ Nanoparticles: The Role of the Minority (001) Surface

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Methanol adsorption on clean and hydrated anatase TiO₂(001)-1 × 1 is studied using density functional theory calculations and first principles molecular dynamics simulations. It is found that (i) dissociative adsorption is favored on clean TiO₂(001) at both low and high methanol coverages; (ii) on the partially hydrated surface, methanol dissociation is not affected by the coadsorbed water and can still occur very easily; (iii) the dissociative adsorption energy of methanol is always larger than that of water under similar conditions. This implies that water replacement by methanol is energetically favored, in agreement with recent experimental observations on colloidal anatase nanoparticles.

Titanium dioxide (TiO₂) is a material of great interest in many fields, e.g., photocatalysis, solar cell devices, gas sensors, and biomaterials.[1−3] Among its polymorphs, anatase is of paramount importance since it exhibits higher activity in many cases.[1,2] Moreover, for sizes up to ∼14 nm, TiO₂ nanocrystals appear to prefer the metastable anatase form rather than the rutile phase, which is the most stable for bulk TiO₂.[4a,b] This is explained by the lower average surface energy of the anatase polymorph, whose equilibrium crystal shape is largely dominated by the very stable (101) surface.[4−6] However, there are indications that the majority anatase (101) surface is not very reactive. For instance water adsorption on anatase (101) is purely molecular,[7,8] and experiments have also provided evidence that this surface has few defects and is harder to reduce in comparison with the widely investigated rutile (110) termination.[1]

The high stability/low reactivity of the majority anatase (101) surface makes it often difficult to understand the observed reactivity of anatase nanoparticles. In particular, recent sum frequency generation (SFG) studies of the coadsorption of water and methanol on anatase colloidal nanoparticles show the presence of hydroxyls and methoxy groups, with the latter being more strongly bound to the surface and capable of replacing surface hydroxyls when the relative concentration of CH₃OH and H₂O is similar.[9] Density functional theory (DFT) calculations for anatase (101) have not been able to reproduce these observations.[10] In fact, the calculations predict that both H₂O and CH₃OH adsorb molecularly on this surface, and the adsorption energies are practically identical for the two molecules.[10]

In the attempt to rationalize the SFG results, in this letter, we examine the anatase (001) surface, which is the minority surface in the equilibrium shape of anatase nanocrystals[4−6] and was found to be especially reactive in previous studies.[5b,c,8,11] We present a systematic DFT study of methanol adsorption on the clean and hydrated anatase (001)-1 × 1 surfaces, and provide

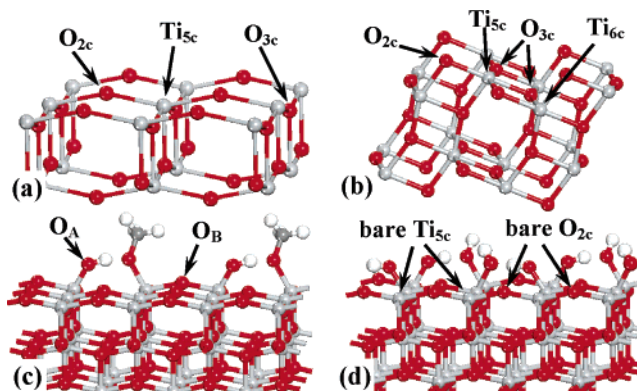* To whom correspondence should be addressed. Fax:+1-(609)258−6746. E-mail:aselloni@princeton.edu.

Figure 1. Top: Structures of (a) TiO₂(001)-1 × 1 and (b) TiO₂(101). Bottom: structures of (c) dissociated methanol on TiO₂(001) and (d) partially hydrated TiO₂(001) (1/3 ML). The O atoms are in red, Ti in light gray, C in deep gray, and H in white.

evidence that these surfaces are very active and may contribute to the unique properties of TiO₂ nanoparticles in the anatase form.

Calculations have been performed using a slab geometry and a periodic DFT approach within the generalized gradient approximation.[12] Geometry optimizations and molecular dynamics (MD) calculations are performed using the Car−Parrinello method.[13] Other computational details are given in the Supporting Information. In Figure 1a, we show the structure of clean TiO₂(001)-1 × 1. For comparison, the TiO₂(101) surface is also shown (Figure 1b). As one can see, TiO₂(001) exposes coordinatively unsaturated atoms, i.e., 5-fold Ti (Ti₅c) and 2-fold O (O₂c) atoms, as well as fully coordinated 3-fold O (O₃c), while TiO₂(101) exposes 6-fold coordinated Ti (Ti₆c), Ti₅c, O₂c, and O₃c.

We first consider the adsorption of methanol on TiO₂(001)-1 × 1 at low coverage (1/6 ML). From our MD simulations, we find that dissociative adsorption occurs spontaneously at temperatures as low as 160 K. The resulting structure is illustrated in Figure 1c, and the computed adsorption energy, 1.36 eV, is listed in Table 1. From Figure 1c, we can see that CH₃O binds

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TABLE 1: Adsorption Energies (in eV) of Methanol and Water on Different Surfaces[a]

Clean TiO$_2$(001) (1/6 ML)		
	CH$_3$OH	H$_2$O
E_d (eV)	1.36	1.25
Clean TiO$_2$(001) (1/2 ML) Average E_d (eV)	1.23	1.17
Partially hydrated TiO$_2$(001) (water coverage = 1/3 ML)		
	CH$_3$OH	H$_2$O
E_m (eV)	0.84	0.82
E_d (eV)	1.42	1.29
Full hydrated TiO$_2$(001) (water coverage = 1/2 ML)		
	CH$_3$OH	H$_2$O
E_m (eV)	0.83	0.85

[a] E_d (E_m) denotes the energy of dissociative (molecular) adsorption.

to Ti$_{5c}$ and H binds to a nearby O$_{2c}$, and at the same time this Ti$_{5c}$–O$_{2c}$ bond is broken. With increasing coverage, dissociative adsorption remains favored up to the saturation coverage of 1/2 ML,[8] with average adsorption energy of 1.23 eV per methanol (Table 1). This is at variance with TiO$_2$(101), on which methanol dissociation is unfavored.[10a]

We next consider the adsorption of water on the same TiO$_2$-(001)-1 × 1 surface. In agreement with previous theoretical studies,[5b,c,8] we find that dissociative adsorption is favored, with average adsorption energies of 1.25, 1.11, and 1.17 eV per H$_2$O at 1/6, 1/3 (see Figure 1d), and 1/2 ML coverage, respectively, thus slightly smaller than the corresponding values for methanol (Table 1). By combining the values of the water adsorption energy with the calculated surface energy of 0.98 J·m^{-2} for the clean (001)-1 × 1 surface, we can estimate the surface energies of the hydrated surfaces,[5b,c,14] for which we find substantially lower values, 0.57 and 0.33 J·m^{-2} at 1/3 and 1/2 ML coverage, respectively (see the Supporting Information for details). This indicates that hydration provides an efficient way to stabilize the (001)-1 × 1 surface. On the other hand, recent experiments have found that carefully annealed anatase (001) surfaces under UHV conditions exhibit a 1 × 4 reconstruction.[15] By calculating the surface energy of reconstructed (001)-1 × 4 on the basis of the model proposed in ref 16, which agrees well with all the available information, we find a value of 0.48 J·m^{-2}, i.e., about half the surface energy of the clean unreconstructed surface. This value is close to the energy of the (partially) hydrated "1 × 1" surface, indicating that the latter will have very little tendency, if any, to reconstruct. Furthermore, if we consider that formation of the 1 × 4 reconstruction implies a considerable mass transport, which can occur only at sufficiently high temperature, we may conclude that the (001) surfaces of anatase nanoparticles grown in a wet environment are well described by a hydrated 1 × 1 TiO$_2$(001) model.

We now consider methanol adsorption on hydrated surfaces. On the fully hydrated surface (1/2 ML), only molecular adsorption via H-bond with surface OH groups is feasible and the computed adsorption energy is 0.83 eV (Table 1). On the partially hydrated surface (Figure 1d), adsorption both at surface OH groups (0.84 eV) and at bare Ti$_{5c}$ sites is possible. At Ti$_{5c}$, MD simulations again show that dissociative adsorption occurs very easily. The corresponding adsorption energy is 1.42 eV, a value very close to the one for the clean surface, indicating that
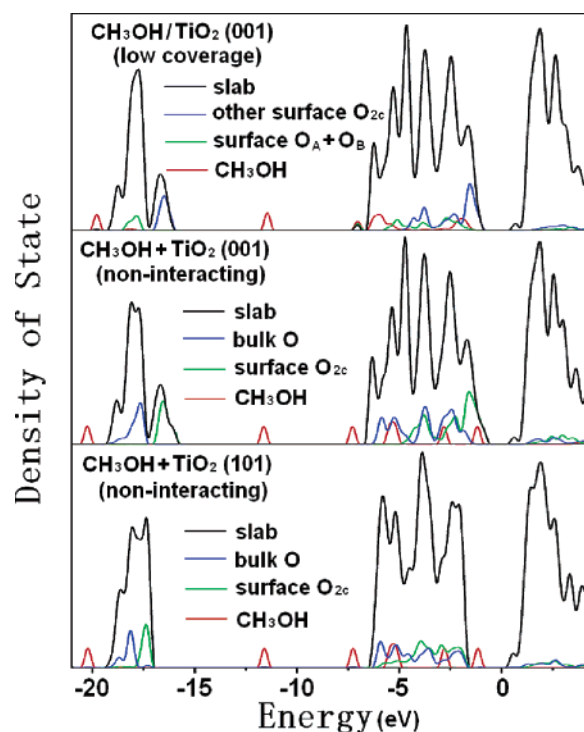

Figure 2. DOS of noninteracting (bottom) CH$_3$OH/TiO$_2$(101) and (middle) CH$_3$OH/TiO$_2$(001) systems, and (top) dissociated CH$_3$OH on TiO$_2$(001) (Figure 1c). The curves in bottom and middle plots are aligned by matching the HOMO of gas-phase CH$_3$OH and those in top and middle are aligned by matching a semicore Ti state in the bottom layer of the slab.

partial hydration has very little effect on methanol dissociation. Water dissociation on the same partially hydrated TiO$_2$(001) yields an adsorption energy (1.29 eV) lower than that of methanol, similar to what was found on the clean surface (Table 1). This implies that the replacement of dissociated water by methanol is always energetically favored on TiO$_2$(001), consistent with the SFG results.[9]

By comparing our present results for the (001) surface with previous calculations for anatase (101),[10a] it appears that these two surfaces exhibit very different activities for methanol dissociation: it is unfavored on the majority TiO$_2$(101), while it easily occurs on TiO$_2$(001). To understand the origin of this difference, in Figure 2 the electronic densities of states (DOS) for the two anatase surfaces are shown. From the DOS projected onto slab and gas-phase CH$_3$OH of the noninteracting systems, it is evident that the valence band of TiO$_2$(001) extends to somewhat higher energies with respect to TiO$_2$(101). This agrees with both experimental[11a] and theoretical[11b] studies of the photoreactivity of anatase particles. From the DOS further projected onto different O species of the slab, we can see that the upper edge of TiO$_2$(001)'s valence band, mainly responsible for its activity, is actually formed by the states from surface O$_{2c}$, while those from middle-layer (bulk) O contribute to the lower part of the band. On the other hand, for TiO$_2$(101), the states from O$_{2c}$ and bulk O are similarly distributed in the various parts of the valence band, indicating that the O$_{2c}$ of TiO$_2$(101) are not particularly reactive. Thus, the high reactivity of anatase (001) can be associated with its surface O$_{2c}$ atoms.

The geometric and electronic structures (Figure 1c, 2(top)) of chemisorbed methanol at low coverage provide further insight into the stabilization of the (001) surface induced by dissociative adsorption. As shown in Figure 1c, surface O$_A$ accepts the H from the dissociated CH$_3$OH and is therefore directly stabilized; O$_B$ is not directly involved in the dissociation; however, the

two nearby Ti_{5c}, which are released from the stiff $O_{2c}-Ti_{5c}-O_{2c}-Ti_{5c}$ framework, can form tighter bonds with O_B, similarly to what is found in the (1×4) reconstruction of the clean surface.[16] Accordingly, Figure 2 (top) shows that the states from O_A and O_B become deeper in energy, while those from other surface O_{2c} are substantially unchanged.

In conclusion, our results show that the minority (001)-1×1 surface exhibits a very high reactivity, and can account for observed properties of anatase TiO_2 nanoparticle under real conditions that cannot be explained by restricting the majority (101) surface only. Our finding that minority surfaces have a crucial role in nanoparticle reactivity may be valid for other oxide nanoparticles as well. Furthermore, within the same logic, also edges and possibly corners may be expected to have an important role in the reactivity of nanoparticles.

Supporting Information Available: Computational details (PDF). These materials are available free of charge via the Internet at http://pubs.acs.org.

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