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Methanol Adsorption and Dissociation on TiO$_2$(110) from First Principles Calculations

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In this work we report on theoretical calculations of methanol adsorption and dissociation on the stoichiometric and defective TiO$_2$(110) surface. The periodic implementation of density functional theory (DFT) with plane waves and pseudopotentials was employed. A supercell made of 4 × 1 unit cells was used to represent the surface, which corresponds to methanol coverage of 0.25 ML. The defective surface was modeled by removing one bridging oxygen from the outermost layer. Several adsorption sites were explored through both static and molecular dynamics calculations. The most stable adsorption site on the defective surface is with the molecule directly adsorbed onto the vacancy, whereas adsorption on titania resembles the stoichiometric case. Our estimated adsorption energies are found to be in agreement with the features observed in previous experimental desorption data. One of the main aims of this study was to determine whether methanol could dissociate on the stoichiometric surface. From static calculations we find that both the molecular and the dissociated state are almost degenerate. In addition, molecular dynamics calculations show that the transition barrier between the two species is small. On the other hand, dissociation on defects is thermodynamically favorable by 0.5 eV. However, dynamic calculations show that in this case the conversion from the molecular to the dissociated state is not straightforward. Implications to these findings are discussed within the text.

Introduction

The TiO$_2$(110) surface has received considerable attention in the literature due to its wide application in studying catalytic and photocatalytic reactions, and it has become a prototype of a metal oxide surface.[1] The most prominent feature on this surface is the presence of undercoordinated oxygen in the outermost layer (Figure 1a). These oxygen atoms are called bridging oxygen and can be easily removed to introduce defects on the surface.[2]

The oxidation of alcohols has been extensively studied on TiO$_2$ surfaces as a model for the catalytic oxidation of organic contaminants.[3–13] Despite the abundance of experimental studies, the role of the anion vacancy defects is still unclear. In particular, it is not established whether methanol dissociates on the stoichiometric surface.[7,14] In addition, it has been suggested that methanol adsorption on different sites could induce different reaction channels.[5,10] We recall that a similar situation is found for water, where there is a long-running theoretical controversy about water dissociation on the perfect surface.[15,16] A previous theoretical study of methanol adsorption on the stoichiometric surface suggested that dissociation is spontaneous and proceeds via O–H bond breaking;[14] nevertheless it was limited by small surface models and did not extent its results to defective surfaces.

Theoretical studies are used as a complementary tool to understand molecular reactions at an atomistic level.[17] However, the comparability between experimental and theoretical results is not straightforward. On the experimental side, it is difficult to reproduce surface conditions; on the theoretical side, results are quite dependent on technical parameters and can provide misleading conclusions.
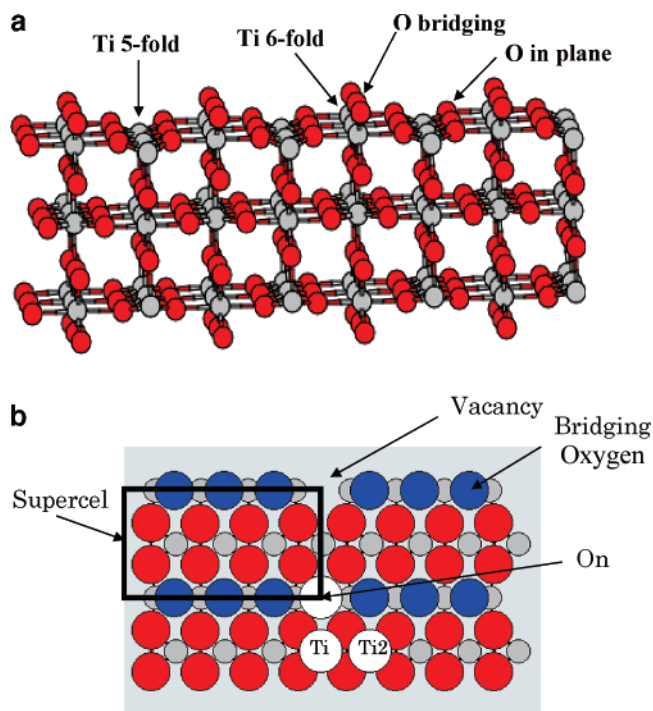

Figure 1. (a) Lateral view of the TiO$_2$(110) surface. A three-layer slab with the most representative kinds of atoms on the surface is shown. Light and dark spheres represent titanium and oxygen atoms, respectively. (b) Top view of the TiO$_2$(110) surface. The supercell, some representative species, and the adsorption sites studied in this work are shown. Light spheres represent titanium, and dark and black spheres represent in-plane and bridging oxygen, respectively. Adsorption sites are marked with big white spheres.

Here we report calculations on methanol adsorption and dissociation for both the stoichiometric and the defective TiO$_2$(110) surface. This work has several aims. First, several

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adsorption sites are explored and adsorption energies are compared with the experimental temperature-programmed desorption (TPD) spectra.[7] Second, the relative stability of the molecular and dissociated states on both the perfect and defective surfaces is analyzed. Third, most of the previous theoretical work has been done in static conditions (i.e., geometry optimizations that involve no temperature effect). However, it is evident that temperature plays a critical role in adsorption—decomposition processes. We have employed an approach that combines static and dynamic calculations. Finally, some technical parameters have been shown to be crucial on this kind of calculation, and their influence on results is considered.

Technical Methods

In the present work the implementation of density functional theory (DFT) with plane waves and the PAW (plane augmented waves) potentials has been used.[18-20] We use the generalized gradient approximation (GGA) for the exchange-correlation energy, which seems to describe better the formation and creation of bonds on surfaces.[21] In particular, we use the GGA due to Perdew and co-workers.[22,23]

The calculations were performed with the VASP (Vienna ab initio simulation package) code,[24-26] using the projector augmented wave method (PAW).[20,27] Valence electrons are described using a plane wave basis set with a cutoff of 400 eV. In the case of Ti, the semicore 3s3p states were also included.

Most of the calculations from this work used a surface model represented by means of a slab made of 4×1 unit cells. The optimized lattice parameters for the bulk are $a = 4.616$ Å, $c = 2.974$ Å, and $u = 0.304$, where u is a parameter that defines the position of the atoms in the unit cell. The calculated a and c values have been used for the (110) surface throughout the present work and maintained fixed during the atomic positions relaxation.[28]

In order to check whether our results were dependent on technical conditions, some calculations were repeated using a smaller 2×1 supercell. We also checked that using a vacuum width of 10 Å was enough to obtain energy convergence. The influence of slab thickness on the results is more critical. It has been noted previously[29] that there is an odd—even oscillating behavior with the number of layers. This can be rationalized by surface-induced hybridization of Ti 3d and O 2p orbitals among the layers.[30] In the present work we use slabs with 3—6 layers. When necessary, this is mentioned explicitly within the text.

With the purpose of modeling defective surfaces, one bridging oxygen atom has been removed from the supercell, and thus the system represents a surface with a 25% oxygen vacancy concentration and contains vacancies separated by ~6 Å. We recall here that in typical TiO_2 experiments[2] the vacancy concentration is about 10%. Results taken from these calculations constitute our best approximation to the behavior of an isolated vacancy. However, we showed previously that this is enough to make vacancy—vacancy interaction almost negligible. Calculations were performed in the singlet state since the vacancy energy formation was found to be independent of the spin. Full convergence tests and technical details can be found in a previous work.[28]

In this work two complementary sets of calculations were performed. First, we carried out static calculations, i.e., geometry optimizations, in order to have adsorption energies. This set of calculations was carried out at a relatively high level of precision that involved a 400 eV energy cutoff and the $2 \times 4 \times 1$

TABLE 1: Adsorption Energies[a]

surface	adsorption energy (eV)		
	molecular	dissoc bridge	dissoc in plane
stoich	0.88	0.86	0.23
def On	0.92	1.43	0.84
def Ti1	0.62	0.66	0.19
def Ti2	0.84	0.79	0.19

[a] Adsorption energies for the molecular and dissociated methanol on the stoichiometric and the defective surface. In the latter case both dissociation on the bridging and on the in-plane oxygen are included. Data corresponds to calculations using six-layer slabs. Positive numbers mean stable adsorption.

Monkhorst—Pack k-points set.[31] In addition, in order to analyze dynamical effects, molecular dynamics (MD) calculations were performed in the canonical ensemble at several temperatures. The precision for these long simulations was lowered to a 300 eV energy cutoff, and they were performed at the Γ point of the Brillouin zone. Most of the MD calculations were performed using four-layer slabs. A typical simulation at a certain temperature spanned about 3 ps and consisted of 1 ps of equilibration run followed by 2 ps of production run. For hydrogen, a fictional mass of 3 uma was used, which allowed us to use a time step of 1 fs. This has no effect on properties that do not depend on time explicitly[14] and we checked out on some specific cases that our main results do not depend on this particular choice.

On the stoichiometric surface there is only one site for methanol adsorption; this is the 5-fold-coordinated titanium. On the other hand, on the defective surface, some other sites are also available. In this work we explore adsorption directly onto the vacancy (On site) and onto titanium atoms in front of the vacancy (Ti1 site) and next to the Ti1 site (Ti2 site) as shown in Figure 1b. A single molecule is placed on one side of the slab, which represents a methanol coverage of $\theta = 0.25$. Dissociated molecules by the breaking of the O—H bond are also included in this study, with the hydrogen atom bound to nearby bridging or in-plane oxygen atoms. The breaking of the C—O bond has not been considered here since it has been found to be less favorable from previous theoretical calculations,[14] and recent STM measurements have also confirmed this fact.[13] Here we express a note of caution since the results can be influenced decisively by the starting geometries both for geometry optimizations and MD calculations. It is a useful strategy to perform preliminary MD simulations at low temperature that show which are the most stable configurations prior to starting optimizations. Sometimes it is necessary to start from several geometries in order to ensure that we have found the most stable one.

Results and Discussion

Stoichiometric Surface. For the stoichiometric surface the most stable geometry for methanol adsorption on the 5-fold-coordinated titania was found (Tables 1 and 2). In the optimized geometry the methanol hydrogen is pointing to one nearby bridging oxygen (Figure 2a). The adsorption energy for the molecule at this site is 0.88 eV. This value has to be compared with higher adsorption energies on the defective surface and will be discussed below in relation to the experimental measured TPD spectra.[7] With respect to whether methanol dissociation is feasible on the stoichiometric surface, our static calculations show that the energy difference between dissociated and nondissociated states is very small ($\Delta E = 0.02$ eV) and the optimized geometries resembled each other (Figure 2). Dissociation on in-plane oxygen atoms is considerably less stable ($\Delta E = 0.65$ eV).

TABLE 2: Optimized Distances for Adsorbed Methanol[a]

surface		d O$-$H	d O$-$Ti	d C$-$O	d H$-$O$_{sup}$
stoich	mol	1.00	2.21	1.44	
	dis bridge	2.10	1.83	1.42	0.98
	dis in plane	2.35	1.78	1.40	0.98
def On	mol	0.98	2.34	1.46	
	dis bridge	3.08	2.03	1.42	0.97
	dis in plane	2.46	2.04	1.43	0.98
def Ti1	mol	0.97	2.27	1.45	
	dis bridge	3.82	1.80	1.41	0.97
	dis in plane	2.61	1.80	1.41	0.98
def Ti2	mol	1.00	2.21	1.45	
	dis bridge	1.96	1.85	1.42	0.99
	dis in plane	1.69	1.88	1.42	1.00

[a] Some selected optimized distances (Å) for the molecular and dissociated methanol on the stoichiometric and the defective surface. Data corresponds to calculations using six-layer slabs. O and O$_{sup}$ refer to methanol oxygen and surface oxygen, respectively.
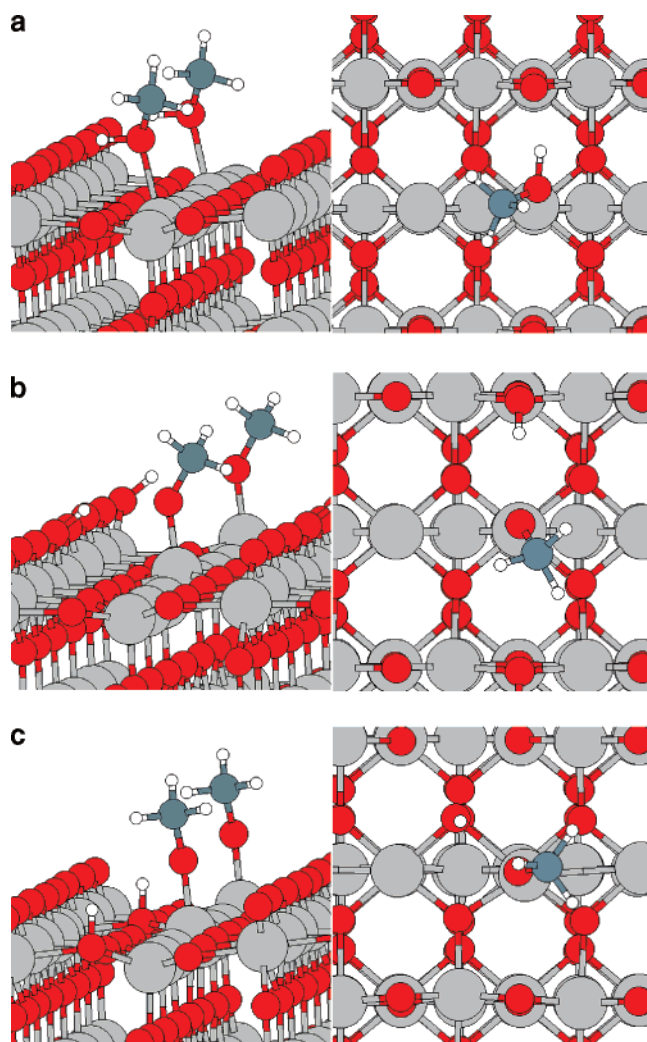

Figure 2. Optimized geometries for methanol adsorbed and dissociated on the stoichiometric surface: (a) methanol molecule, (b) methanol dissociated on a bridging oxygen, and (c) methanol dissociated on an in-plane oxygen.

Extensive MD calculations with four-layer slabs were performed starting from the molecular state with temperatures ranging from 100 to 400 K. During these simulations, the methyl group is quite free to move and rotate and only the Ti$-$O (methanol) distance is maintained relatively constant.[32] In spite of this, methanol is stable toward dissociation, and there is no
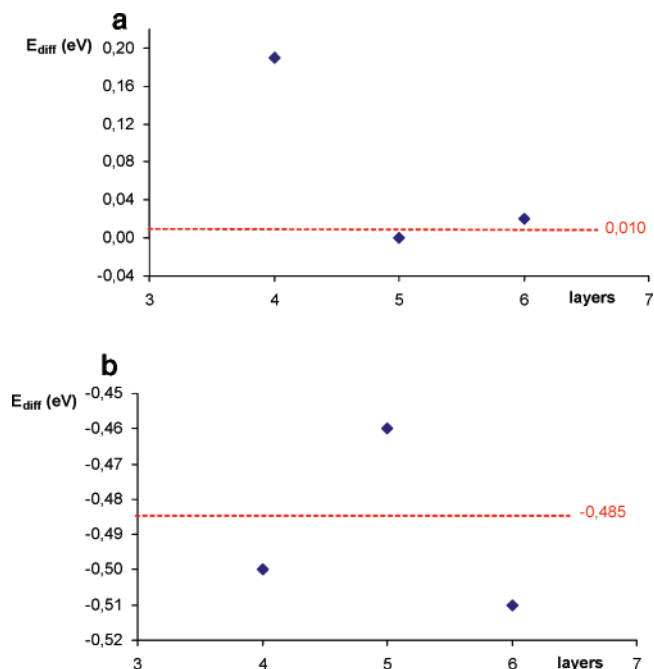

Figure 3. Dependence on slab thickness of the energy difference between the molecular and the dissociated states. Positive numbers mean that the molecular form is more stable. The average between the values from five- and six-layer calculations is shown in a broken line: (a) stoichiometric surface, (b) defective surface, On site.

proton transfer in simulations spanning a long time (5 ps). In addition, MD simulations starting from the dissociated species returned to the molecular form. We should conclude, therefore, that dissociation is not spontaneous onto the stoichiometric surface. This result is at odds with previously published work.[14] In order to get a deeper insight into this discrepancy we performed additional calculations. First, we confirmed that dissociation of a molecule was spontaneous in an MD simulation when the technical conditions of the previous work were reproduced, i.e., a 2 × 1 supercell and a three-layer slab model; the same holds for a larger 4 × 1 supercell. However, we note that this was not further true for the four-layer slab, neither for the 2 × 1 nor the 4 × 1 supercells.

In a previous work[28] it was shown that an average value between energies calculated for slabs with even and odd numbers of layers (i.e., five and six) was a good estimate of the converged value. Therefore, the calculations were repeated with 4−6-layer slabs. In addition, MD simulations showed to favor either the dissociated form (three and five layers) or the molecular form (four and six layers). Thus, it seems that slab thickness is a crucial technical parameter for the relative stability of the two states. The energy difference seems to converge toward a small value (Figure 3a), so the molecular and the dissociated forms are almost degenerate.

There is a long-running controversy about water dissociation on the same surface. It has been concluded that technical conditions are paramount to determine which species are more favorable.[15,16] In addition, it has been suggested that the intrinsic errors could be as large as the energy difference, and thus, a definite conclusion is elusive. It is beyond the scope of this work to fully answer such a delicate question for methanol since obtaining higher accuracy would demand using prohibitively large unit cells. However, from our averaged numbers it is concluded that both states are almost degenerate. In addition, since MD allows conversion between the molecular and the dissociated states, the transition barrier might be quite small.
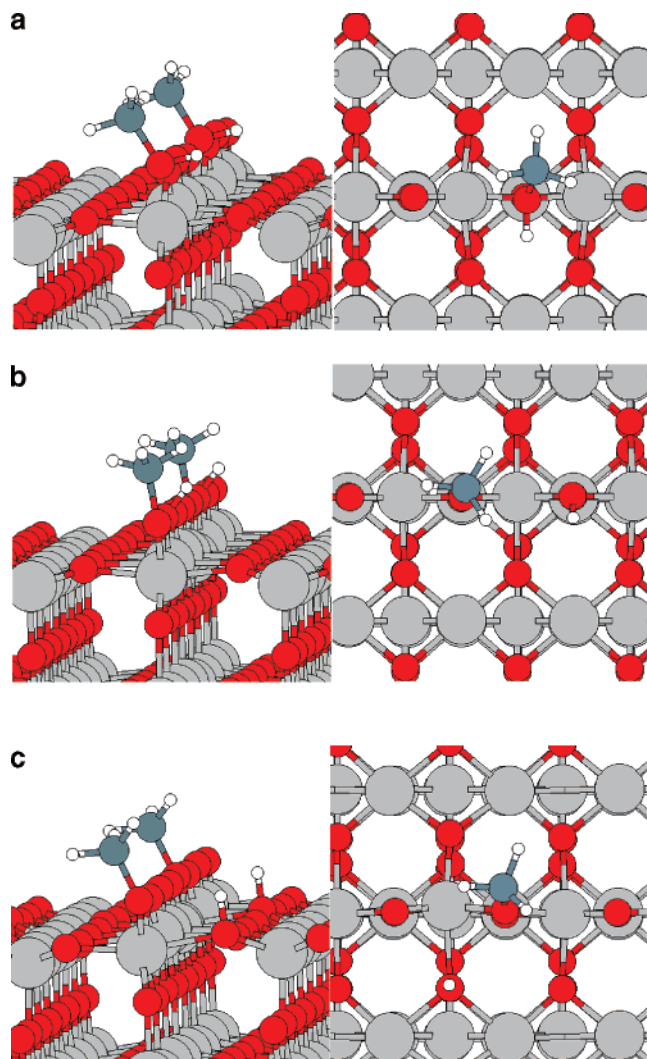
Figure 4. Optimized geometries for methanol adsorbed and dissociated on the defective surface (On site): (a) methanol molecule, (b) methanol dissociated on a bridging oxygen, and (c) methanol dissociated on an in-plane oxygen.

Figure 5. Optimized geometries for methanol adsorbed and dissociated on the defective surface (Ti1 site): (a) methanol molecule, (b) methanol dissociated on a bridging oxygen, and (c) methanol dissociated on an in-plane oxygen.

It would be highly desirable to have quantitative information of transition barriers. However, explicit calculations are technically demanding. Since the number of atoms involved in the transformation is high, including some of them within the surface, the reaction path is not clear. Furthermore, calculations are computationally demanding, and the precision has to be lowered, which can provide misleading results. Having this in mind, a rough estimation of the barrier transition is around 1 eV for the stoichiometric case. From our results it is not possible to determine whether a small barrier would imply that dissociation could be thermally activated. Clearly, more experimental and theoretical work is needed to settle this important topic.

Defective Surface. After removing a bridging oxygen atom, there are several adsorption sites available (See Figure 1b). Geometry optimizations were carried out with the molecule starting on these sites. The most remarkable geometry is that corresponding to adsorption directly onto the vacancy (On site, Figure 4a). We found that a short MD calculation at low temperature was enough to induce the molecule to adopt such geometry, where the methanol O−H bond is perpendicular to the bridging row. On the other hand, optimized geometries for the Ti1 and Ti2 sites resembled that one on the stoichiometric surface (Figures 5a and 6a, respectively), particularly for the Ti2 case with the hydrogen pointing to a nearby bridging oxygen
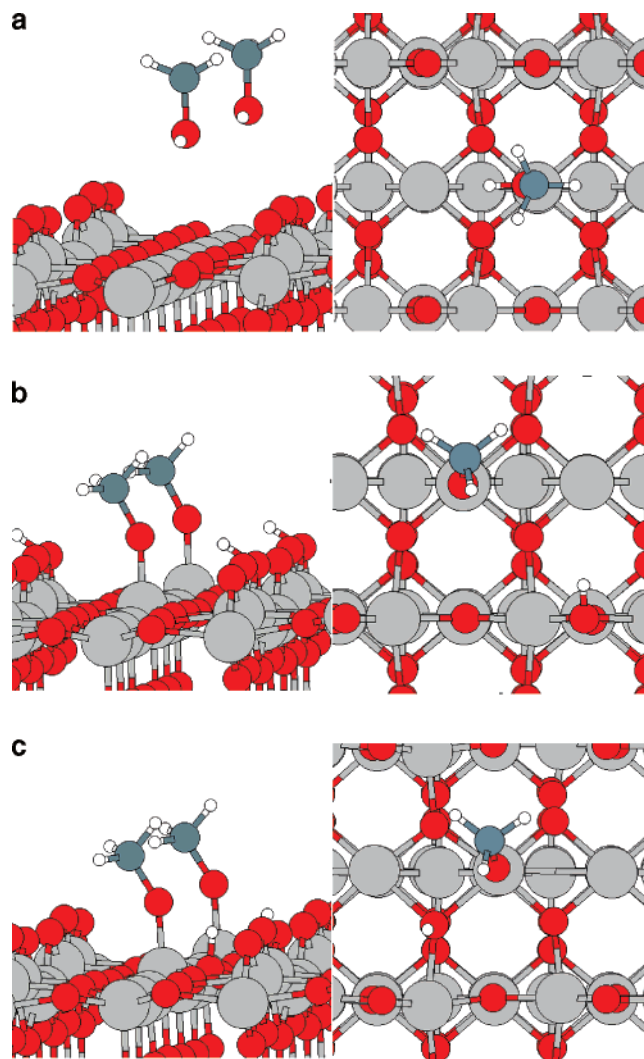
atom. Dissociation was also explored by optimizing proton transfer from the methanol molecule to the bridging or in-plane oxygen (Figures 4−6). Adsorption energies and some selected parameters for the optimized geometries are given in Tables 1 and 2.

The adsorption is stable on every site (i.e., there is no spontaneous desorption). Dissociation transferring the hydrogen to a bridging oxygen is more favorable than to an in-plane oxygen. It is remarkable that the dissociated state is preferred to the molecular state by 0.5 eV for the On site, which, in turn, is the most stable on the defective surface (see discussion below). Overall, adsorption on the vacancy is more stable than on the stoichiometric surface. Since results are dependent on slab thickness we performed calculations for 4−6-layer slabs for the On case. The converged values (Figure 3b) show that the dissociated state is more stable than the molecular state by approximately 0.5 eV, which seems to be quite robust to technical uncertainties.

In a previous experimental work, the TPD spectrum of methanol adsorbed on $TiO_2(110)$ with 10% bridging oxygen vacancies was reported.[7] From those data, the peaks below 200 K were assigned to multilayer desorption. At low coverage, two main peaks at 350 and 480 K were observed. Assuming the Redhead formula[33] with a preexponential factor of 10^{13} s^{-1} and
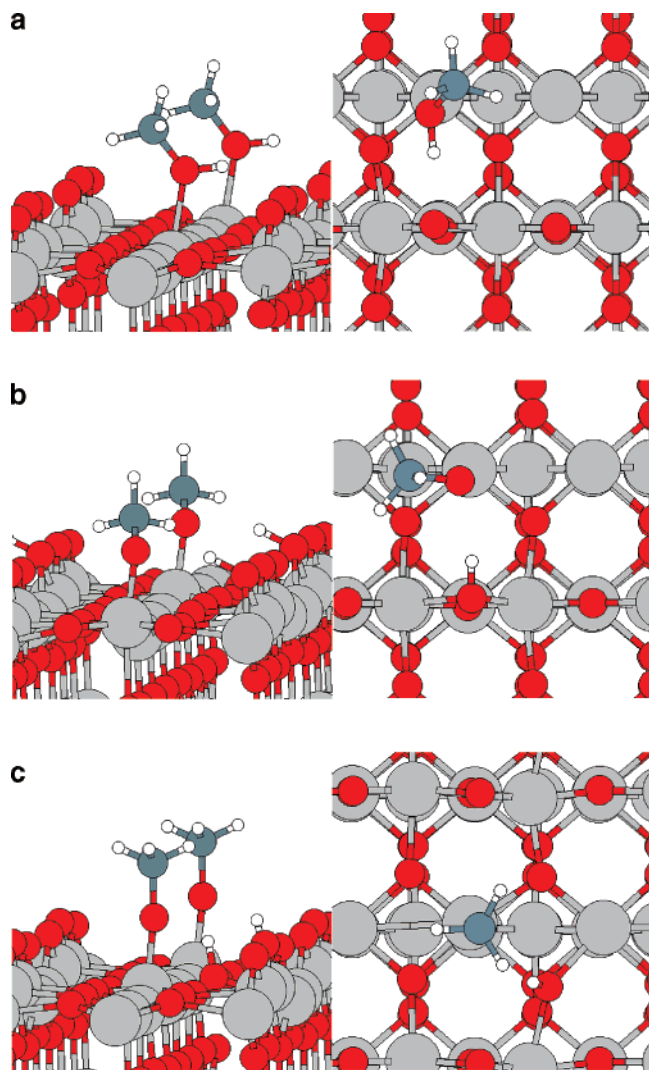
Figure 6. Optimized geometries for methanol adsorbed and dissociated on the defective surface (Ti2 site): (a) methanol molecule, (b) methanol dissociated on a bridging oxygen, and (c) methanol dissociated on an in-plane oxygen.

Figure 7. Top view of the charge density on the surface. The bridging oxygen rows are shown in vertical lines, where the three spheres in a row correspond to bridging oxygen atoms present on the surface. The large charge cloud assigned to the methanol molecules has been cut in order to allow a vision of the methanol atoms.

a heating rate of 2 K s^{-1}, these temperatures corresponds to adsorption energies of 0.95 and 1.31 eV, respectively. The first peak drifts to lower temperatures (295 K) as coverage rises, whereas the second one is saturated first.

Accurate adsorption energies were obtained from calculations with five and six layers, and the averaged values were 1.09 and 1.34 eV for adsorption on stoichiometric and defective sites, respectively. Recall that in the latter case the most favorable state corresponds to dissociation on the On site. From our calculations, we tentatively assign the peak at 350 K to desorption from stoichiometric sites, whereas the peak at 480 K is assigned to desorption from vacancies. Our calculated energies are in good agreement with the experimental ones. It is worth mentioning that this correspondence implies that molecules desorbing from vacancies were previously dissociated. As coverage increases, the adsorption energy on the stoichiometric case might decrease because of different factors such as repulsion between adsorbates or heterogeneity of adsorption sites (i.e., a mixture of stoichiometric and Ti2 sites, for example).

In order to get further insight into the dissociation process for the On case, MD calculations were performed at several temperatures. One striking result is that dissociation is not spontaneous for the molecule adsorbed into the vacancy despite that it would be thermodynamically favorable. This was
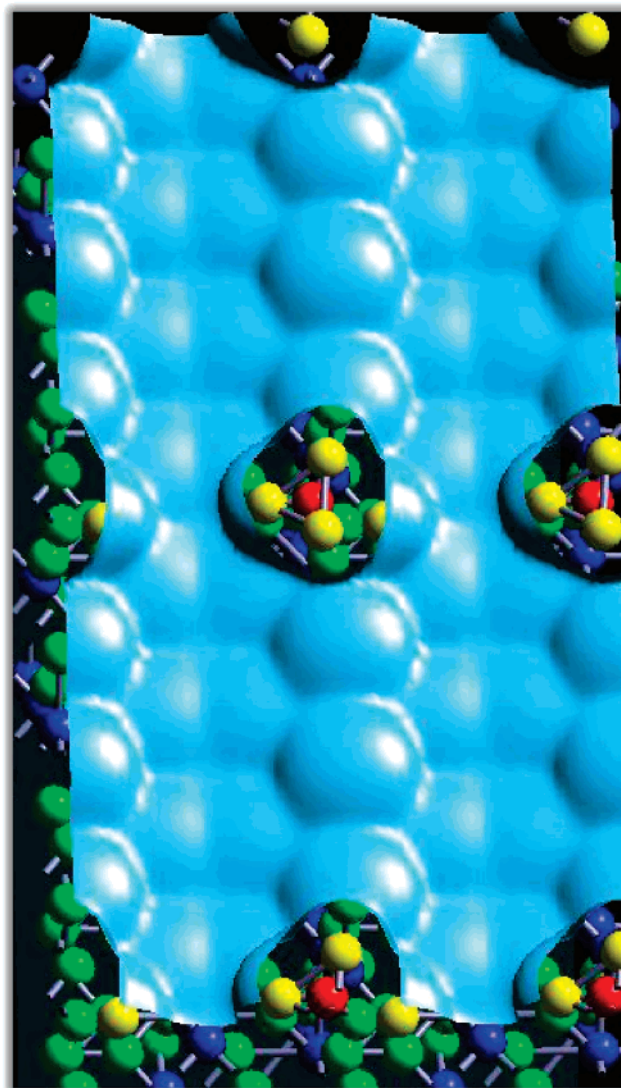
confirmed at temperatures up to 400 K for the 2 × 1 and 4 × 1 supercells. Since the O–H bond is initially oriented perpendicular to the bridging oxygen row (Figure 4a) the proton should first rotate around the C–O bond to start the process. From our simulations, the barrier for such rotation must be large and the O–H bond is pointed to the in-plane oxygen atoms all the time. The molecule adopts a quite fixed orientation, and this is maintained at high temperatures for long simulations. We also checked that the same behavior is observed on a five-layer slab. In addition, as expected, simulations starting from the dissociated molecule failed to obtain recombination into the molecular form because the former is more stable and the barrier for the inverse transformation is high. It is worth mentioning that failure to observe a particular dissociation route or recombination in the dynamics simulations does not necessarily preclude one from existing, because of the short time spanned by the simulations. Preliminary calculations (see above) show that the transition barrier for dissociation in this case is around 2.5 eV.

In order to rationalize this fact we display in Figure 7 the charge density on the surface. The bulky electronic charge around the methanol, that could be related to a lone electron

10028 *J. Phys. Chem. C, Vol. 111, No. 27, 2007*

de Armas et al.

pair, acts as a barrier for rotation. Here we must point out that classical MD, as used in our simulations, is not well suited to surmount barriers since the short period of time spanned by the calculations does not guarantee enough attempts along the correct trajectory. With this in mind, we can only conclude that the barrier for dissociation along this path is high. The search for alternative routes for methanol dissociation will be the subject of future work.

A thorough dynamical study was also performed for the molecules adsorbed on the Ti1 and Ti2 sites. In principle, according to Table 1, dissociation on a Ti1 site could be energetically feasible. However, this is an artificial conclusion, since the molecule adsorbed on Ti1 is quite far from bridging oxygen atoms and dissociation is precluded. This is confirmed by simulations which show the molecule vibrating, making no contact with bridging oxygen atoms, even at high temperatures. The same holds for simulations starting from the dissociated species where recombination is not possible.

Finally, simulations for the Ti2 adsorption site showed a behavior quite similar to the stoichiometric case. The energy difference between the molecular and the dissociated state is 0.05 eV. There is a small barrier for dissociation, and it is possible to simulate direct recombination from the dissociated species. An analysis of dependence with slab thickness shows that the energy difference converges toward a small value, so the molecular and the dissociated forms are almost degenerate. Logically, as we move far from the vacancy, the adsorption on titania should converge to the stoichiometric case.

Conclusions

In this work the adsorption and dissociation of methanol on the stoichiometric and defective $TiO_2(110)$ surface were studied. For the stoichiometric case it is found that the molecular and dissociated states are essentially degenerate. Molecular dynamic calculations show that transformation between species is feasible, so the transition barriers between the molecular and dissociated forms must be small. Results are quite dependent on technical parameters, such as slab thickness, and a careful analysis is required.

On the defective surface three different sites were considered. Direct adsorption onto the vacancy is the most favorable case, with the dissociated state being more stable by 0.5 eV, whereas adsorption on Ti sites results in smaller adsorption energies. We tentatively assign previous published TPD data to desorption from stoichiometric and vacancy sites. Remarkably, this assignment implies that the molecules on vacancy sites are dissociated.

Despite the dissociated state being thermodynamically favored, MD calculations failed to produce spontaneous dissociation at high temperatures. We believe there is a high barrier for the O−H bond breaking and this is related to the presence of a

bulky electron density around the methanol oxygen which maintains the molecule anchored to the surface.

Finally, the dynamical behavior for the Ti1 and Ti2 sites resembled that one from the stoichiometric surface. For the Ti2 case, it was possible to observe direct conversion from dissociated to molecular species, which again implies a small transition barrier for a hydrogen transfer. However, for the Ti1 case, the absence of vicinal bridging oxygen excluded the dissociation.

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