



Computational study of the adsorption of dimethyl methylphosphonate (DMMP) on the (0 1 0) surface of anatase TiO₂ with and without faceting

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ABSTRACT

The adsorption of dimethyl methylphosphonate (DMMP) on the (0 1 0) surface of anatase TiO₂, which is isostructural with the (1 0 0), has been studied using density functional theory and two-dimensionally-periodic slab models. The experimentally-observed faceting of this surface has, for the first time, been included in the modeling. The relaxations of bare surfaces both with and without faceting are similar, leading to an atomic-scale roughening due to inward (outward) displacement of fivefold-coordinated Ti_{5c} (sixfold-coordinated T_{6c}) atoms together with outward displacement of threefold-coordinated O_{3c} atoms. Molecular adsorption occurs by formation of a Ti_{5c}···O=P dative bond with one or more C—H···O_{2c} bonds between CH₃ groups and unsaturated, twofold-coordinated (O_{2c}) sites. The energies for molecular adsorption, obtained using the B3LYP functional, are virtually identical (about −21.0 kcal/mol) for the two surfaces and are also close to those found elsewhere for the rutile (1 1 0) and anatase (1 0 1) surfaces. A possible first step in the dissociative adsorption of DMMP has also been modeled and is found to be thermodynamically favored over molecular adsorption to a degree which depends on faceting.

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1. Introduction

The surface structure and properties of TiO₂, in both the rutile and anatase forms, have been intensively studied both experimentally and computationally [1]. For either form, the adsorption of a wide variety of molecules has been investigated on several different crystallographic planes. An especially important aspect is adsorption on the isostructural (1 0 0) and (0 1 0) surfaces of anatase.¹ Many of the technological applications for TiO₂, in which the material is used as a catalyst, a photocatalyst [2] or a catalyst support, involve high-surface-area (HSA) powders prepared by high-temperature oxidation of TiCl₄. The Degussa P25 powder, which has been widely used in surface-chemistry experiments on TiO₂, is an example of such material. Typically these powders are ~80% anatase, and experiment [3–5] shows that in this case the (0 1 0) is the dominant surface. The (1 0 0) is also known to make a major contribution to the surface area of anatase nanocrystals [6] and to be especially active in photocatalysis [7]. Recent work by Dzwigaj et al. [8] has clearly shown that the

morphology of anatase powder (i.e., the distribution of exposed crystal planes) depends on the method of fabrication and treatment. However, in general the (1 0 0) surface appears to have a significant, if not always dominant, presence in many forms of anatase powder.

Experimental data for this surface are scarce, due to the difficulty in obtaining anatase samples suitable for single-crystal studies. However, several computational studies of adsorption have been reported, focusing on atomic H [9–11], NH₃ and NO [12], CO₂ [13], H₂O [12,14], O₂ [14], chlorobenzene [15], chlorophenol [16], N heterocycles [17], acetic acid [18] and oxalic acid [19]. In most cases unsaturated, fivefold-coordinated (Ti_{5c}) sites are active as Lewis-acid adsorption sites. In particular the adsorption behavior of the bidentate reagent oxalic acid on anatase (1 0 0) differs from that on rutile (1 1 0) due the differing local arrangement of Ti_{5c} surface sites [19]. Unsaturated, twofold-coordinated (O_{2c}) sites can also be involved in hydrogen bond (H-bond) formation. The effects, on the structure of the (1 0 0) and other anatase surfaces, of hydroxylation and of steady-state ambient pressures of H₂, H₂O and H₂S have been thoroughly investigated in a series of density functional theory (DFT) studies by Arrouvel et al. [20,21]. These studies have provided important insight into the properties of real TiO₂ catalysts.

Fig. 1 shows schematic models for the (0 1 0) surface which, except for the (1 0 1), has the lowest surface energy (σ) for anatase [20,22]. Fig. 1a shows the ideally-terminated (unrelaxed) surface,

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¹ The designations (1 0 0) and (0 1 0) will be used interchangeably since the two anatase surfaces are isostructural, as are the (1 0 1) and (0 1 1). Some of the literature on anatase powder refers to the (0 1 0), and that labeling is used here except, in Section 1, when citing works which refer explicitly to (1 0 0).

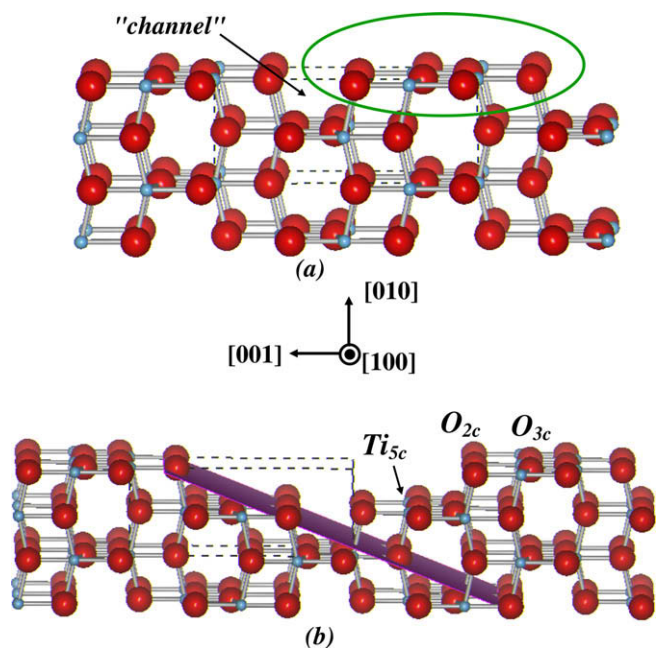


Fig. 1. The anatase (0 1 0) surface with the bulk unit cell shown by the dashed lines. Blue (red) spheres are Ti (O). (a) Shows the ideally-terminated surface and (b) shows a (1 × 2) faceted structure [23]. Both structures are shown before relaxation. The different models are not to scale. The encircled section in (a) shows what is removed in forming the facet. Various surface sites are labeled (see text), and the region referred to as the “channel” in the text is indicated. The plane shown in (b) is the (0 1 1), which is isostructural with the (1 0 1). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

and Fig. 1b shows the (1 × 2) faceted surface (also unrelaxed) observed [23] in scanning tunneling microscopy. Faceting of the (1 0 0) surface exposes the more stable (1 0 1), which is isostructural with the (0 1 1). Computation [20,22] shows $\sigma = 0.44$ and 0.53 J/m^2 for the relaxed (1 0 1) and (1 0 0) surfaces, respectively, vs. 0.31 J/m^2 for rutile (1 1 0). The effect of faceting on the anatase (1 0 0) σ is unknown at present. All (1 0 0) surface Ti sites are Ti_{5c} while half the surface O atoms are O_{2c} and half are saturated, three-fold-coordinated O_{3c} sites. With equal numbers of singly-unsaturated Ti_{5c} and O_{2c} sites the surface is auto-compensated, meaning that the excess electron density on a Ti_{5c} is transferred to an O_{2c} to maintain a closed-shell configuration on both. Hence, there is no indication [10,17] of surface states in the band gap of the relaxed but unrelaxed surface. Adsorption on the faceted surface, which has not to our knowledge been studied previously, should be especially interesting. For an appropriately-chosen molecule the structure of this surface, with rows of Ti_{5c} sites set below and in close proximity to rows of O_{2c} sites, holds out the possibility of both dative bonding to a Ti_{5c} and H-bonding to multiple O_{2c} sites.

The purpose of this work is to examine the adsorption of a fairly complex molecule, $(\text{CH}_3\text{O})_2(\text{CH}_3)\text{P}=\text{O}$ (dimethyl methylphosphonate, DMMP), on the anatase (0 1 0) surface both with and without faceting. Our interest in DMMP stems from the use of this species as a simulant for chemical warfare agents (CWAs) such as Sarin and the demonstrated utility of TiO_2 in the catalytic destructions of CWAs (Refs. [24–28] and works cited). The growing interest in HSA TiO_2 powders for this application, and the wide-spread use of DMMP in experimental work relating to CWAs, makes such a study timely. For two reasons, the present work focuses on adsorption of DMMP on bare surfaces, free of defects or co-adsorbed species. Firstly, the adsorption of DMMP on TiO_2 , even under these

ideal conditions, remains controversial. Secondly, the experimental data for this system [29–32] with which we will compare our results were all obtained in vacuum or in ultra-high vacuum (UHV).

2. Computational and modeling details

2.1. Geometry optimization and energy calculations

All calculations were done using two-dimensionally-periodic slab (2-DPS) models and the *CRYSTAL 06* code [33–35] which employs Bloch functions constructed from localized Gaussian basis sets. To reduce the computational cost, geometry optimization was done at the restricted Hartree Fock (RHF) level. This has previously been shown [36,37] to give results for the bulk and surface structures of TiO_2 which are very close to those obtained using DFT. Optimization at the RHF level has also been shown to give reliable results for molecular geometries [38]. For Ti, the Hay–Wadt small-core effective-core pseudopotential (ECP) was used with the 411(311d)G basis set previously optimized for perovskite titanates [33,39]. For O, a 6-31G(d) all-electron basis set [40] was used with the exponents of the outermost shells re-optimized² for bulk rutile. The optimized parameters were 0.27281 and $0.31201 \text{ Bohr}^{-2}$, respectively, for the *sp* and *d* shells. The bulk lattice constants and atom positions optimized using this procedure show good agreement with experiment (Table 1). In subsequent geometry optimizations, the lattice constants were fixed at these values while the positions of all Ti and O atoms (as well as those of the DMMP atoms) were allowed to vary. For DMMP, 6-31G(d,p) basis sets from a standard database [40] were used without modification.

After geometry optimization, a single-point calculation of the total energy was done using DFT with all-electron basis sets and the B3LYP functional, which has been shown [37,41] to give reliable results for the bare surfaces of both rutile and anatase. A discussion of the use of B3LYP in describing the adsorption of DMMP is given elsewhere [42]. For TiO_2 the basis sets are designated 86-411(d31)G for Ti and 8-411d1G for O, while the 6-31G(d,p) basis sets were again used for DMMP. For Ti and O the outermost *sp* and *d* shells have been optimized [41] for TiO_2 , and the complete basis sets are obtained by combining these with the inner shells given elsewhere [33]. Preliminary calculations using somewhat larger 6-311G(d,p) basis sets [40] for DMMP led to difficulties in converging the self-consistent field (SCF). This may result from the small exponent in the outermost *sp*-shell of the P atom ($0.0684930 \text{ Bohr}^{-2}$) which can cause linear-dependency problems in calculations for periodic structures [33].

The bulk calculations used an $(8 \times 8 \times 4)$ sampling grid, giving a *k*-point spacing of ~ 0.1 atomic units (au). Calculations for the (4×1) and (4×2) supercells used in adsorption (see Section 2.2) were done with (1×2) and (1×1) grids respectively, giving a *k*-point spacing of ~ 0.2 au. Reducing the *k*-point spacing to 0.1 au for the (4×1) supercell had a negligible effect on the energy. Following Labat et al. [37], an “extra-large” (75,974) integration grid was used for all DFT calculations. In *CRYSTAL*, truncation of the sums of Coulomb and exchange terms in the Fock matrix is determined by five overlap criteria [33,35] (T1–T5). These were set at 10^{-8} for T1–T4 and 10^{-18} for T5. A high numerical accuracy in integration is generally required for TiO_2 [37,41] and is further necessitated by the small exponent ($0.09983 \text{ Bohr}^{-2}$) in the outermost *sp*-shell of the P 6-31G(d) basis set. In the multipolar expansion zone [33–35] a maximum order of $L = 6$ was used. The geometry convergence criteria were 1×10^{-5} Hartree for energy, 1.8×10^{-3}

² Basis-set optimization was done using *CRYSTAL 03* with the *LoptCG* script (C. Zicovich-Wilson; Universidad Autonoma del Estado de Morelos; Cuernavaca, Mexico).

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