

# Adsorption of water and ammonia on TiO<sub>2</sub>-anatase cluster models

Isik Onal<sup>a,\*</sup>, Sezen Soyer<sup>a</sup>, Selim Senkan<sup>b</sup>

<sup>a</sup> Department of Chemical Engineering, Middle East Technical University, Ankara 06531, Turkey

<sup>b</sup> Department of Chemical Engineering, University of California, Los Angeles, CA 90095, USA

Received 11 October 2005; accepted for publication 3 April 2006

Available online 27 April 2006

## Abstract

Density functional theory (DFT) calculations performed at B3LYP/6-31G\*\* level are employed to study water and ammonia adsorption and dissociation on (101) and (001) TiO<sub>2</sub> anatase surfaces both represented by totally fixed and partially relaxed Ti<sub>2</sub>O<sub>9</sub>H<sub>10</sub> cluster models. PM3 semiempirical calculations were also conducted both on Ti<sub>2</sub>O<sub>9</sub>H<sub>10</sub> and Ti<sub>9</sub>O<sub>33</sub>H<sub>30</sub> clusters in order to assess the effect of cluster size. Following dissociation, the adsorption of H<sub>2</sub>O and NH<sub>3</sub> by H-bonding on previously H<sub>2</sub>O and NH<sub>3</sub> dissociated systems, respectively are also considered. It is found that the adsorption energies and geometries of water and ammonia molecules on (101) and (001) anatase cluster models depend on surface relaxation. The vibration frequency values are also calculated for the optimized geometries. The adsorption energies and vibration frequency values computed are compared with the available theoretical and experimental literature.

© 2006 Elsevier B.V. All rights reserved.

**Keywords:** TiO<sub>2</sub>; Anatase; Adsorption; Water; Ammonia; DFT

## 1. Introduction

Titanium oxides are used in a wide variety of technological applications where surface properties play a role. Titanium oxide is used in heterogeneous catalysis and in various other applications as in solar cells for the production of hydrogen and electrical energy, as a gas sensor, as a white pigment (e.g. in paints and cosmetic products), as a corrosion protective coating, as an optical coating, and in electric devices such as varistors. It is important in earth sciences; plays a role in the biocompatibility of bone implants; is being discussed as a gate insulator for the new generation of MOSFETs and as a spacer material in magnetic systems, and it finds application in nanostructured form in Li-based batteries and electrochromic devices. It is hoped that insight into surface properties on the fundamental level will help to improve understanding these tech-

nological materials [1]. In the experimental study of Hengerer et al. [2] on (101) and (001) surfaces carried out by secondary-electron imaging and low energy electron diffraction (LEED) the stability of anatase surfaces is demonstrated and the feasibility of preparing and investigating clean surfaces of this important form of TiO<sub>2</sub> is illustrated.

There are some experimental studies with regard to the surface properties and the adsorption reactions of titanium dioxide-anatase surface. Lin and Bai [3] reported by using in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) that anatase surface is Lewis acidic since V<sub>2</sub>O<sub>5</sub> based catalysts and pure TiO<sub>2</sub> powder yield almost the same intensity of Lewis acidity. In addition they indicated that the formation of Brønsted acidity may be related to the existence of water vapor. Bredziona et al. [4] carried out IR analysis of H-bonded water on pure TiO<sub>2</sub> surface. In the same publication, it is indicated that water adsorption on TiO<sub>2</sub> occurs by several mechanisms as the surface is filled. As a first step, there occurs the dissociative adsorption of water which includes the destruction and formation of identical Ti–O and O–H bonds. Preferable sites for molecular water adsorption are Ti<sup>4+</sup> ions. Adsorbed

\* Corresponding author. Tel.: +90 312 210 2639; fax: +90 312 210 1264.  
E-mail address: [ional@metu.edu.tr](mailto:ional@metu.edu.tr) (I. Onal).

water molecules form additional H bonds with surface OH groups. Primet et al. [5] indicate that molecular water adsorption takes place on anatase but Morterra et al. [6] suggest a mixed type of adsorption. In the study of Srnak et al. [7], desorption activation energies for water and ammonia adsorption reactions are estimated from vacuum TPD studies as 11 and 18 kcal/mol and 14 and 27 kcal/mol, respectively. A heat of desorption value of 50 kJ/mol for water adsorption was reported by Munuera et al. [8]. Sprinceana et al. [9] carried out a calorimetric study of the acidity and interface effects of tin dioxide layers deposited on another metal oxide and reported a differential heat of 130–150 kJ/mol for ammonia adsorption on anatase. Topsøe et al. [10,11] indicated that ammonia adsorbs on the titania surface mainly as coordinated ammonia reflecting that predominantly Lewis acid sites are present on pure titania. On the other hand, Ramis et al. and Busca et al. [12–14] reported that ammonia is activated by coordination over Lewis acidic sites on TiO<sub>2</sub> and this activated ammonia is easily transformed to amide NH<sub>2</sub> species by the hydrogen abstraction.

There are few theoretical studies about the adsorption reactions and surface properties of anatase (101) and (001) surfaces. Vittadini et al. [15] studied the structure and the energetics of water adsorption on the (101) and (001) surfaces at various coverages by use of density functional theory calculations. They have found that on the (101) surface of TiO<sub>2</sub> nondissociative molecular water adsorption is favored; however, on the (001) surface at low coverages, H<sub>2</sub>O is adsorbed dissociatively while at high coverages, molecular water adsorption takes place, but with a state with half of the H<sub>2</sub>O is adsorbed dissociatively and the other half H bonded in a second layer. Previously, Bredow and Jug [16] investigated water adsorption on rutile (110) and anatase (001) surfaces theoretically by means of the semiempirical MO method SINDO1. Kachurovskaya et al. [17] reported a molecular adsorption energy value on (001) anatase surface and did not study a dissociation case. Fahmi and Minot [18] studied water adsorption on various crystallographic faces of TiO<sub>2</sub> anatase by using a periodic Hartree–Fock method. It is reported that titanium oxide is an amphoteric compound. Water adsorbs on the acidic site (the titanium atom), and afterwards it dissociates to give hydroxyl groups. In both of these studies it is reported that dissociative water adsorption is favored on (001) anatase. On the other hand, Selloni et al. [19] pointed out through molecular dynamics calculations that molecular adsorption of water is more favorable on (101) surface of anatase. Redfern et al. [20] also agreed with this finding by using ab initio molecular orbital theory and density functional theory.

The objective of this study is to investigate theoretically the adsorption of small molecules H<sub>2</sub>O and NH<sub>3</sub> on TiO<sub>2</sub> cluster models representing (101) and (001) anatase surfaces by use of density functional theory (DFT).

## 2. Surface model and calculation method

Quantum chemical calculations employing DFT [21] are conducted to investigate the energetics of water and ammonia adsorption on (101) and (001) anatase surfaces. (101) face represents the most probable anatase surface [15] and (001) surface is considered to be the most stable surface of TiO<sub>2</sub> anatase [22]. In addition Kryukova et al. [23] showed by use of high resolution electron microscopy that there is a good geometric complementarity between (010) V<sub>2</sub>O<sub>5</sub> and (001) TiO<sub>2</sub>-anatase for SCR reaction.

In this research (101) and (001) surfaces of TiO<sub>2</sub> are represented by finite neutral cluster models of Ti<sub>2</sub>O<sub>9</sub>H<sub>10</sub> and studied for the adsorption of small molecules such as water and ammonia. This cluster approach is a well known and successful approach applied in quantum chemical calculations [24,25]. However, since there may be limitations to the use of small cluster models to represent oxide surfaces where the peripheral oxygen atoms are saturated with hydrogens, the effect of cluster size is also tested by use of semiempirical PM3 calculations for ammonia adsorption on both Ti<sub>2</sub>O<sub>9</sub>H<sub>10</sub> and Ti<sub>9</sub>O<sub>33</sub>H<sub>30</sub> clusters. DFT calculations were conducted using Becke's [26,27] three-parameter hybrid method involving the Lee et al. [28] correlation functional (B3LYP) formalism. The basis set employed in the DFT calculations was 6-31G\*\* provided in SPARTAN'04 (Wavefunction Inc.). SPARTAN'04 was used for all the semiempirical and DFT calculations reported.

Wyckoff parameters [29] are employed to obtain the unit cell of bulk TiO<sub>2</sub> (Ti<sub>2</sub>O<sub>4</sub>). Neutral cluster models of Ti<sub>2</sub>O<sub>9</sub>H<sub>10</sub> representing (101) and (001) titanium dioxide anatase surfaces are obtained from this unit cell by saturating the peripheral oxygen atoms with hydrogen atoms. These cluster model geometries are then energetically optimized. Computations are carried out for two types of cluster representations: **1.** All of the atoms are fixed and **2.** Partial relaxation is practiced where some of the atoms are relaxed.

The following general computational procedure was followed in the calculations of this research: Initially, both the cluster and the adsorbing molecules are optimized geometrically by means of the equilibrium geometry calculations. The energies of the fixed clusters are obtained by single point geometry calculations. Then, the adsorbing molecule is located over the active site of the cluster at a selected distance and a coordinate driving calculation is performed by selecting a reaction coordinate in order to obtain the variation of the relative energy with a decreasing reaction coordinate to get an energy profile as a function of the selected reaction coordinate distance. Single point equilibrium geometry calculations were also performed where necessary by locating the adsorbing molecule in the vicinity of the catalytic cluster. All of the adsorption calculations are carried out by considering the system as neutral with singlet spin multiplicity.

The relative energy is defined as:

$$\Delta E = E_{\text{System}} - (E_{\text{Cluster}} + E_{\text{Adsorbate}})$$

where  $E_{\text{System}}$  is the calculated energy of the given geometry containing the cluster and the adsorbing molecule at any interatomic distance,  $E_{\text{Cluster}}$  is the energy of the cluster itself and  $E_{\text{Adsorbate}}$  is that of the adsorbing molecule.

After having obtained the energy profile for the desired reaction, the geometry with the minimum energy on the energy profile is re-optimized by means of the equilibrium geometry calculations to obtain the final geometry for the reaction. For the calculated final geometry, vibration frequencies are computed by single point energy calculations. Furthermore, from the energy profile, the geometry with the highest energy is taken as the input geometry for the transition state geometry calculations. Starting from these geometries, the transition state structures with only one negative eigenvalue in Hessian matrix are obtained. If a successful transition state geometry can not be achieved, the geometry with the maximum energy in the energy profile is reported as the approximate transition state geometry.

### 3. Results and discussion

#### 3.1. An example test of cluster size effect

In order to assess the effect of cluster size, semi-empirical PM3 calculations are conducted for ammonia adsorption on both small  $\text{Ti}_2\text{O}_9\text{H}_{10}$  and large  $\text{Ti}_9\text{O}_{33}\text{H}_{30}$  fixed clusters which represent (001)  $\text{TiO}_2$  anatase surface. For these calculations, ammonia molecule is located at a chosen distance from the cluster and a reaction coordinate is selected as the distance between the nitrogen atom of the ammonia molecule (N1) and the titanium atom (Ti1) of the cluster surface. The corresponding adsorption equilibrium geometries are illustrated in Figs. 1 and 2. Ammonia molecule is adsorbed in a similar formation on both of the clusters, the small cluster having a N1–Ti1 distance of 2.149 Å while on the large cluster this distance comes

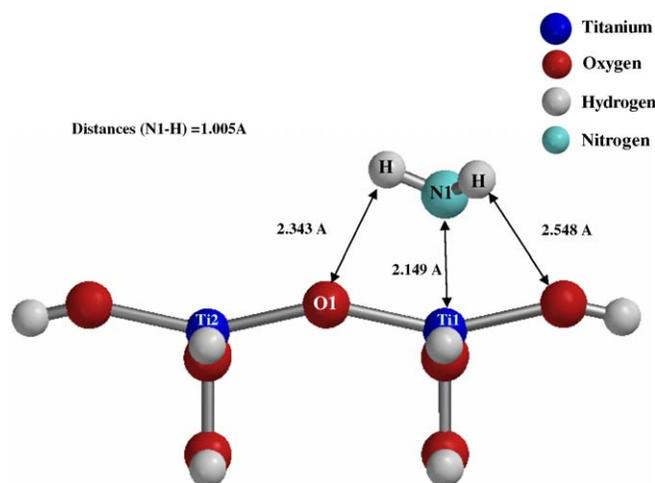


Fig. 1. Equilibrium geometry for  $\text{NH}_3$  adsorption by use of semiempirical (PM3) calculation method on fixed (001)  $\text{Ti}_2\text{O}_9\text{H}_{10}$  (small) cluster.

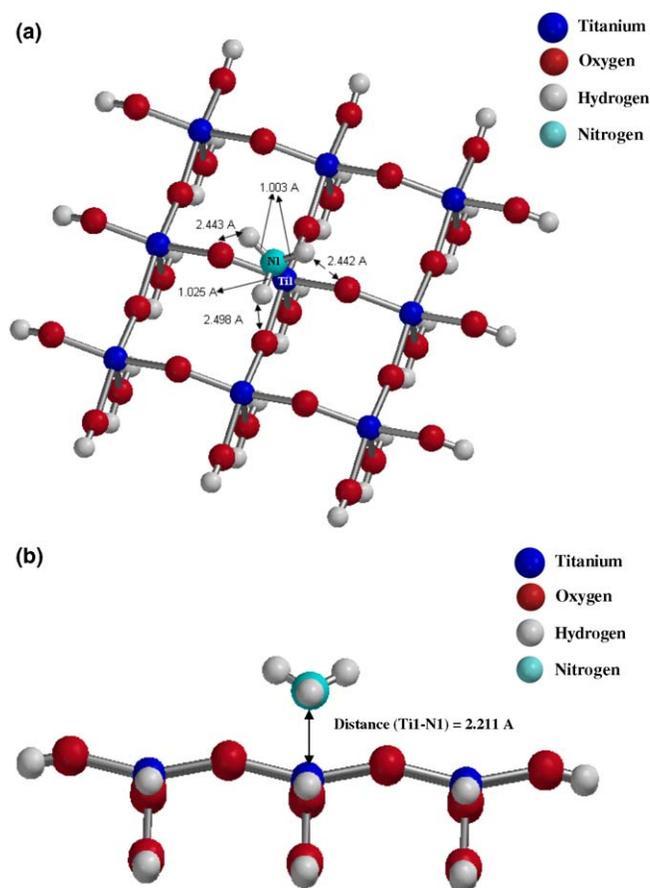


Fig. 2. Equilibrium geometry for  $\text{NH}_3$  adsorption by use of semiempirical (PM3) calculation method on fixed (001)  $\text{Ti}_9\text{O}_{33}\text{H}_{30}$  (large) cluster, (a) top view (b) side view.

out to be 2.211 Å. N–H bond lengths are 1.005 Å and 1.003 Å for the small and large clusters respectively. The resultant energy profile calculations given in Fig. 3 show that on both small and large clusters  $\text{NH}_3$  molecule is adsorbed exhibiting a non-activated mode with adsorption energies of  $-92.64$  and  $-84.35$  kcal/mol respectively. Although the adsorption energies for both clusters are exaggerated values indicating the typical weakness of semi-empirical methods in general, the energy profiles follow very closely for both clusters. These results indicate that the adsorption of small molecules such as  $\text{NH}_3$  is a relatively local phenomenon and a small metal oxide cluster such as  $\text{Ti}_2\text{O}_9\text{H}_{10}$  can sufficiently represent larger cluster surfaces in this case.

#### 3.2. $\text{H}_2\text{O}$ adsorption

##### 3.2.1. $\text{H}_2\text{O}$ adsorption on (101) $\text{TiO}_2$ surface

For molecular water adsorption, a reaction coordinate is selected as the distance between the oxygen atom of the water molecule and the titanium atom of the cluster for both fixed and relaxed clusters which are represented by  $\text{Ti}_2\text{O}_9\text{H}_{10}$ . Five-coordinated Ti1 atom and the bridge oxygen atom (O1) are relaxed in the relaxed cluster as given

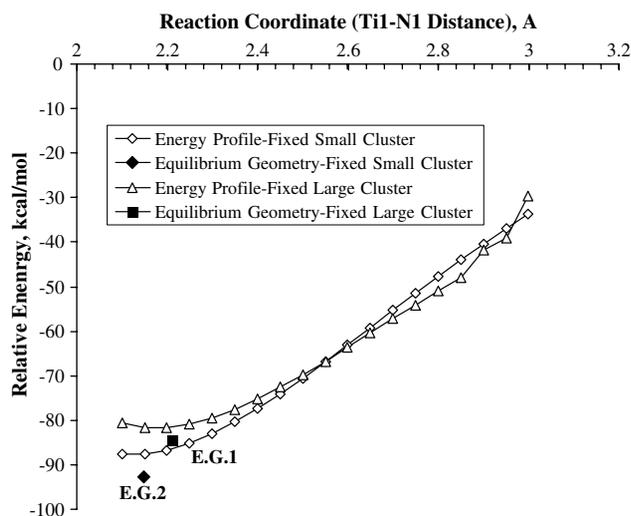


Fig. 3. Comparison of energy profiles for ammonia adsorption by use of semiempirical (PM3) calculation method on fixed (001)  $\text{Ti}_2\text{O}_9\text{H}_{10}$  (small) cluster and on fixed (001)  $\text{Ti}_9\text{O}_{33}\text{H}_{30}$  (large) cluster (E.G.1 and E.G.2 represent equilibrium geometries for fixed (001) large and small clusters, respectively).

in Fig. 4. The rest of the atoms are kept fixed in both clusters. Molecular water adsorption occurs on partially relaxed cluster with an exothermic relative energy difference of  $-25.08$  kcal/mol through a non-activated process. On totally fixed (101) cluster the adsorption energy of molecular water adsorption comes out to be  $-28.97$  kcal/mol. The energy profiles obtained are shown in Fig. 5. The energy values of the points of the energy profile obtained for molecular water adsorption on fixed cluster are lower

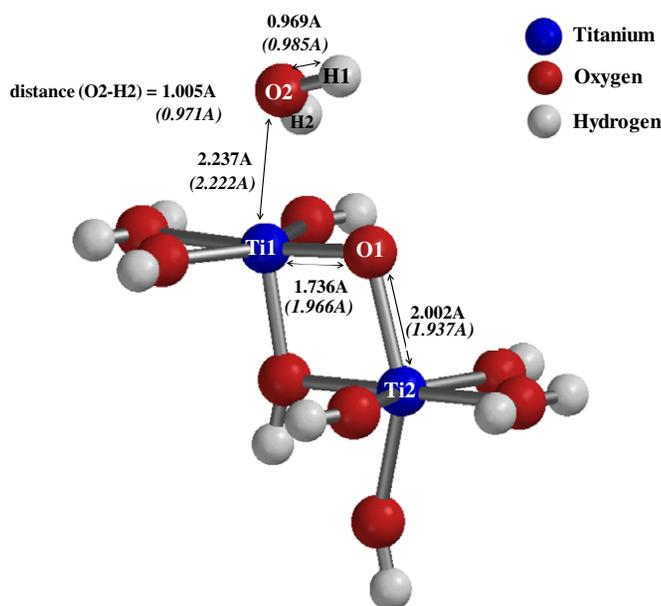


Fig. 4. Equilibrium geometry of molecular  $\text{H}_2\text{O}$  adsorption on partially relaxed and fixed (101)  $\text{Ti}_2\text{O}_9\text{H}_{10}$  clusters (bond lengths without parentheses belong to the partially relaxed (101) cluster, while the values given in parentheses are for the fixed cluster).

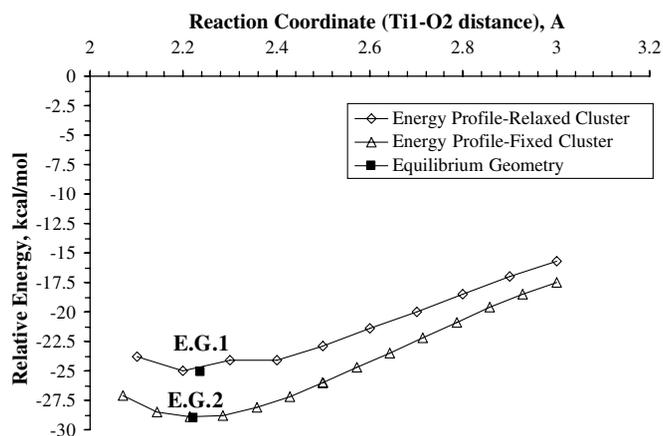


Fig. 5. Energy profile for molecular  $\text{H}_2\text{O}$  adsorption on partially relaxed and fixed (101)  $\text{Ti}_2\text{O}_9\text{H}_{10}$  clusters (E.G.1 and E.G.2 represents equilibrium geometries for relaxed and fixed clusters, respectively).

than those on relaxed cluster. The equilibrium geometries of this interaction are also given in Fig. 4. In this figure the bond lengths are for optimized geometries of the relaxed clusters while the values given in parentheses belong to the totally fixed cluster models. As seen in the figure water is molecularly adsorbed on the clusters with Ti1–O2 distance of  $2.237$  Å in the case of relaxed cluster and with Ti1–O2 distance of  $2.222$  Å on fixed cluster.

Dissociative water adsorption is also considered on (101) anatase clusters starting from the optimized geometries of molecular water adsorption. For this purpose, for both clusters, a reaction coordinate is selected as the distance between the oxygen atom of the water molecule (H1) and the bridge oxygen (O1) of the cluster. As it is evident from the energy profiles obtained (see Fig. 6), water dissociatively adsorbs on relaxed (101) cluster by an activation barrier of  $18.76$  kcal/mol with an endothermic relative energy difference of  $5.87$  kcal/mol, while on the fixed (101) cluster water dissociates with an activation barrier

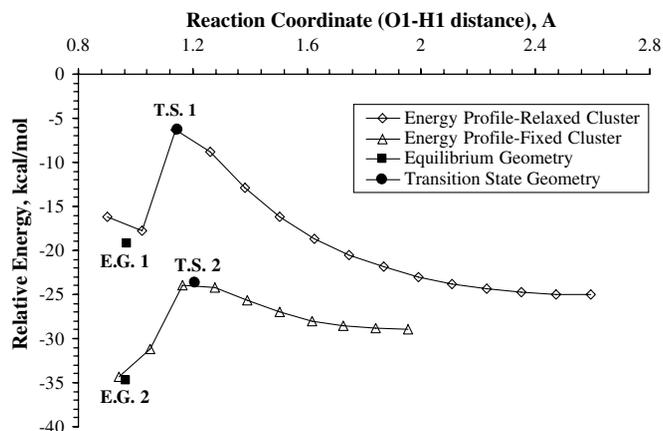


Fig. 6. Energy profiles for dissociative  $\text{H}_2\text{O}$  adsorption for partially relaxed and fixed (101)  $\text{Ti}_2\text{O}_9\text{H}_{10}$  clusters. (E.G.1 and E.G.2 represent equilibrium geometries; T.S.1 and T.S.2 stands for the transition state geometries calculated on relaxed and fixed (101) clusters, respectively).

of 5.22 kcal/mol with an exothermic relative energy of 5.81 kcal/mol. It is seen that the activation barrier and adsorption energy for water dissociation on fixed cluster are both much lower than the values obtained on relaxed cluster. The transition state and equilibrium geometries of this interaction are illustrated in Fig. 7. It is found by DFT calculations that molecular water adsorption is more favorable than dissociative adsorption ( $-25.08$  kcal/mol vs  $-19.26$  kcal/mol) for relaxed (101)  $\text{Ti}_2\text{O}_9\text{H}_{10}$  cluster while dissociative water adsorption is more favorable ( $-34.78$  kcal/mol vs  $-28.97$  kcal/mol) on fixed (101)  $\text{Ti}_2\text{O}_9\text{H}_{10}$  cluster. The water adsorption energies calculated on relaxed and fixed (101) surfaces are compared with the available theoretical information in Table 1. All of the theoretical literature agrees that molecular water adsorption is more favorable on (101) anatase. However, by the calculations carried out on fixed (101) cluster the situation is the

Table 1

Comparison of the calculated  $\text{H}_2\text{O}$  adsorption energies on (101) surface with the theoretical values in the literature

Theoretical values	Method	Surface	Adsorption energy (kcal/mol)	
			Molecular	Dissociative
This work	DFT B3LYP/ 6-31G**	101 Anatase relaxed $\text{Ti}_2\text{O}_9\text{H}_{10}$ cluster	$-25.08$	$-19.26$
		101 Anatase fixed $\text{Ti}_2\text{O}_9\text{H}_{10}$ cluster	$-28.97$	$-34.78$
Vittadini et al. [15]	DFT	101 Anatase slab	$-16.60$ ( $\theta = 1$ ) <sup>a</sup>	$-10.15$ ( $\theta = 1$ ) <sup>a</sup>
Redrefn et al. [20]	B3LYP/6-31G**// B3LYP/6-31G*	101 Anatase $\text{TiO}_5\text{H}_6$ cluster	$-29.5$ ( $-31.1$ ) <sup>b</sup>	$-11.7$ ( $-11.5$ ) <sup>b</sup>
Selloni et al. [19]	Molecular dynamics	101 Anatase surface	$-17.30$	$-6.92$ , $-8.76$

<sup>a</sup>  $\theta$  is the coverage of the  $\text{H}_2\text{O}$  molecules on (101) anatase surface.

<sup>b</sup> Values in parentheses are calculated by MP2/6-31G\*\*//MP2/6-31G\* method.

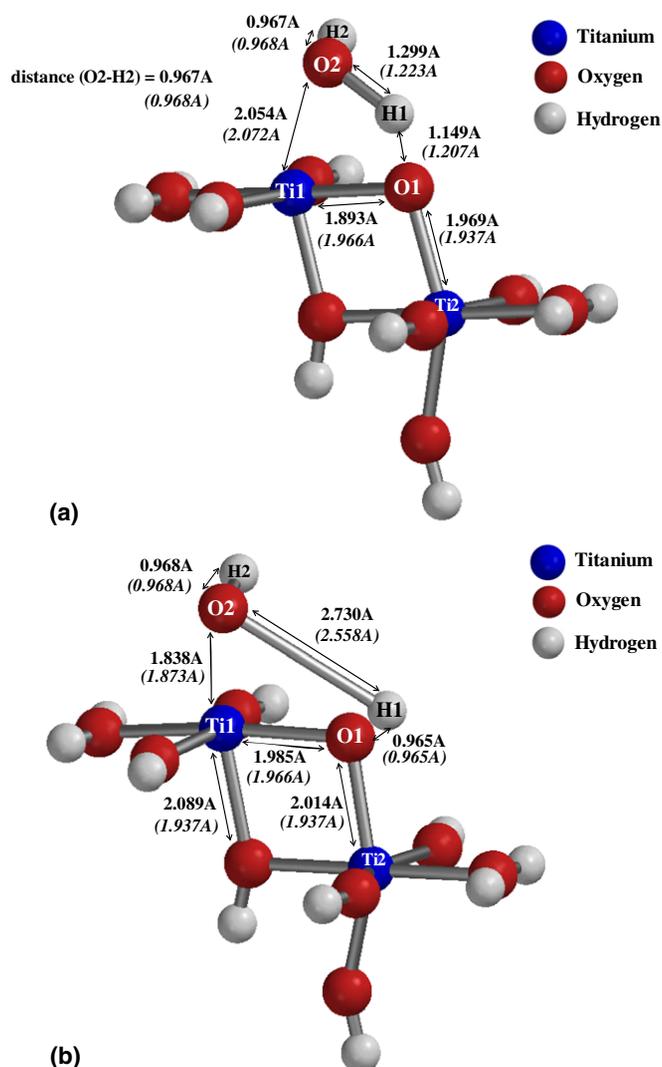


Fig. 7. (a) Transition state and (b) Equilibrium geometries of dissociative  $\text{H}_2\text{O}$  adsorption on partially relaxed and fixed (101)  $\text{Ti}_2\text{O}_9\text{H}_{10}$  clusters (bond lengths without parentheses belong to the partially relaxed (101) cluster, while the values given in parentheses are for the fixed cluster).

opposite case. The trend in the theoretical literature is met by the results obtained on the relaxed cluster.

In the experimental literature it is indicated that after water dissociates on titanium dioxide surface water molecules could form hydrogen bonds with the surface hydroxyl groups [4]. This case is also simulated on relaxed and fixed (101) clusters by single point equilibrium geometry calculations. Water molecule forms hydrogen bonding with pre-water dissociated system on fixed and relaxed (101)  $\text{Ti}_2\text{O}_9\text{H}_8$  clusters (see Fig. 8) with exothermic relative

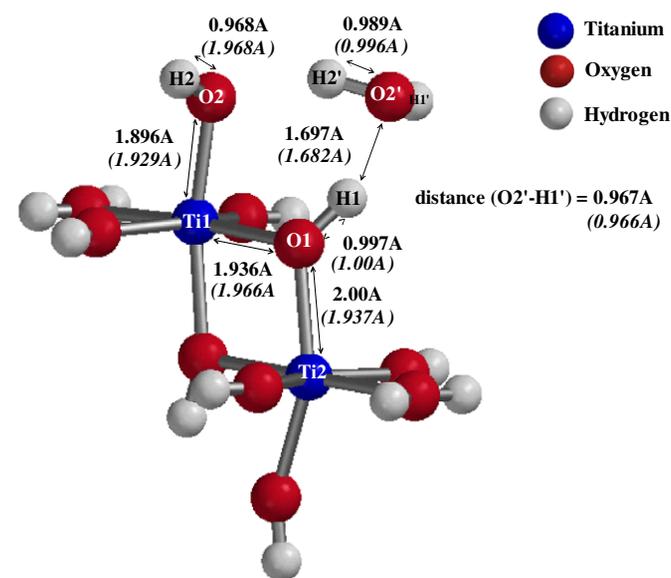


Fig. 8. Optimized geometries of H-bonded  $\text{H}_2\text{O}$  adsorption on partially relaxed and fixed (101)  $\text{Ti}_2\text{O}_9\text{H}_{10}$  clusters (bond lengths without parentheses belong to the partially relaxed (101) cluster, while the values given in parentheses are for the fixed cluster).

Table 2  
Comparison of the calculated adsorption energy of H<sub>2</sub>O by H-bonding on (101) and (001) surfaces with the experimental values in the literature

Theoretical values	Method	Surface	Adsorption energy (kcal/mol)
This work	DFT B3LYP/6-31G**	101 Anatase relaxed Ti <sub>2</sub> O <sub>9</sub> H <sub>10</sub> cluster	−18.12
		101 Anatase fixed Ti <sub>2</sub> O <sub>9</sub> H <sub>10</sub> cluster	−18.72
		001 Anatase relaxed Ti <sub>2</sub> O <sub>9</sub> H <sub>10</sub> cluster	−11.47
Experimental values			
Srnak et al. [7]	TPD	TiO <sub>2</sub> Anatase	−11, −18
Munuera et al. [8]	TPD	TiO <sub>2</sub> Anatase	−12

energy differences of 18.12 and 18.72 kcal/mol, respectively. As seen in Table 2, these adsorption energies of H-bonded water molecule on relaxed and fixed cluster models (18.12 and 18.72 kcal/mol) agree well with the experimental estimate of −18 kcal/mol [7]. Therefore, our results indicate that the experimentally obtained value of 18 kcal/mol may belong to the H-bonded water molecule on (101) surface. The fact that (101) face is exposed in anatase samples in majority might have played a role in this result.

### 3.2.2. H<sub>2</sub>O adsorption on (001) TiO<sub>2</sub> surface

Firstly, molecular water adsorption is aimed to be studied on a partially relaxed Ti<sub>2</sub>O<sub>9</sub>H<sub>10</sub> cluster (Ti1, Ti2, and O1 are relaxed) representing (001) surface (see Fig. 9). As previously described, a coordinate driving calculation is performed by selecting the reaction coordinate as the distance between the oxygen of the water molecule and one of the Ti atoms of the cluster. As a result of energy profile calculations it is found that water molecule is dissociated on

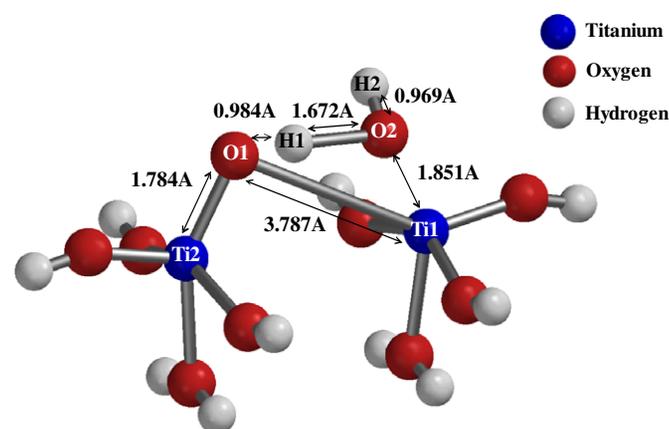


Fig. 9. Equilibrium geometry for dissociative H<sub>2</sub>O adsorption on relaxed (001) Ti<sub>2</sub>O<sub>9</sub>H<sub>10</sub> cluster.

the cluster surface by a non-activated process with an exothermic relative energy difference of 54.12 kcal/mol. The equilibrium geometry of this interaction including the bond lengths is shown in Fig. 9. The water molecule is dissociated on this surface by destroying the oxygen bridge structure of the cluster geometry. The sudden energy decrease is thought to arise from this change. By this interaction, two inequivalent hydroxyls terminally bound to adjacent Ti sites along (100) direction are formed. The equilibrium geometry obtained (Fig. 9) is similar to what Vittadini et al. [15] previously reported by DFT method on (001) anatase slab.

An additional water molecule adsorption by hydrogen bonding on the system obtained in Fig. 9 is also studied by a single point equilibrium geometry calculation. Water adsorption by hydrogen bonding occurs with an exothermic relative energy difference of 11.47 kcal/mol. The optimized geometry of this event is illustrated in Fig. 10. The adsorption energy calculated for H-bonded water on (001) anatase cluster is compared with the experimental values in Table 2. As it is evident from this table the computed value provides agreement with the experimental data. It can be conjectured by this finding that the experimentally reported second TPD site (−11 and −12 kcal/mol) can be represented by (001) surface.

By dissociative adsorption of water on (001) relaxed cluster surface two OH groups, Ti1–O2H2 and Ti2–O1H1, are formed (Fig. 9). Therefore, according to DFT computations it is shown that if only one water molecule is present on the cluster it dissociates. Then, the situation when two H<sub>2</sub>O molecules are approaching to the cluster simultaneously is also investigated. For this purpose, two separate reaction coordinates are selected: the distances between the titanium atoms and the oxygen atoms of the two H<sub>2</sub>O molecules. The resultant energy profile shows that both water molecules are adsorbed molecularly (similar to the result of Vittadini et al. [15]) on the cluster with an exothermic relative energy of 49.85 kcal per two moles of H<sub>2</sub>O or −24.93 kcal/mol. The equilibrium geometry of this interaction is illustrated in Fig. 11.

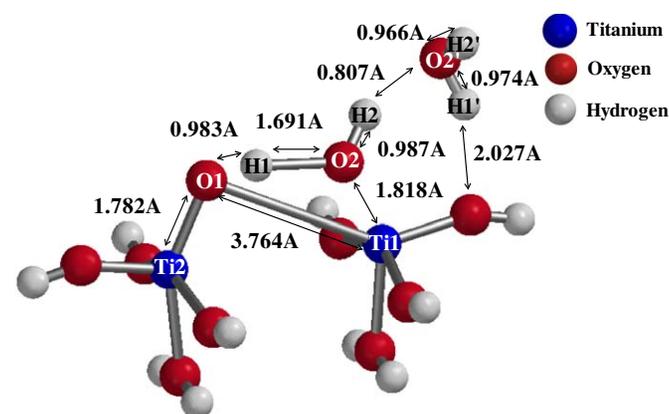


Fig. 10. Equilibrium geometry for H-bonded water adsorption on relaxed (001) Ti<sub>2</sub>O<sub>9</sub>H<sub>10</sub> cluster.

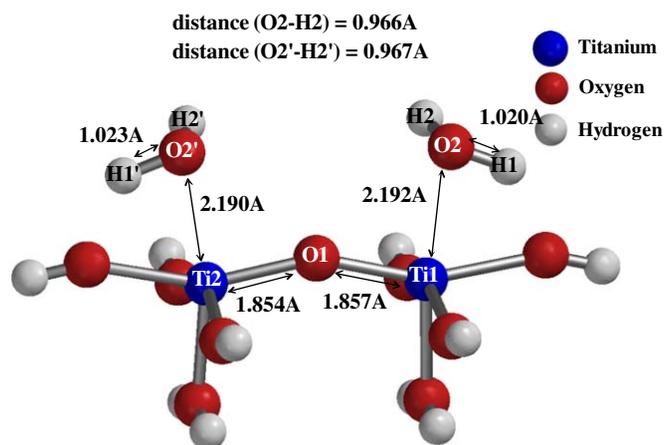


Fig. 11. Equilibrium geometry for molecular adsorption of two H<sub>2</sub>O molecules on relaxed (001) Ti<sub>2</sub>O<sub>9</sub>H<sub>10</sub> cluster.

If molecular water adsorption is simulated on a fixed Ti<sub>2</sub>O<sub>9</sub>H<sub>10</sub> cluster by choosing a reaction coordinate as the distance between the oxygen of the water molecule (O2) and one of the Ti atoms of the cluster (Ti1), it can be concluded from the energy profile obtained that water molecule is adsorbed on the cluster surface by a non-activated process with an exothermic relative energy difference of 23.46 kcal/mol with Ti1–O2 distance of 2.230 Å. Starting from the molecularly adsorbed water, water dissociation is further studied by a coordinate driving calculation selecting the distance between O1–H1 atoms as the reaction coordinate. The resulting energy profile shows that water dissociates on the fixed Ti<sub>2</sub>O<sub>9</sub>H<sub>10</sub> cluster with an endothermic relative energy difference of 12.25 kcal/mol and an activation barrier of 12.92 kcal/mol. Transition state and equilibrium geometries of water dissociation on (001) fixed cluster are given in Fig. 12.

A comparison of the water adsorption energetics on (001) surface with the available theoretical literature is given in Table 3. It is found that when partial relaxation is applied on the cluster, dissociative water adsorption is more favorable than molecular adsorption (–54.12 kcal/mol vs –24.93 kcal/mol). However, the calculations carried out on the fixed cluster showed the reverse situation. An agreement with the theoretical literature in terms of the favorable adsorption mode of water is satisfied by the relaxed (001) cluster model.

The vibration frequencies for water adsorption on (101) and (001) cluster surfaces are calculated by single point energy calculations. The results are compared with the relevant experimental information in Table 4. As seen in the table O–H stretching vibration data of 3666, 3713 cm<sup>–1</sup> and 3657, 3711 cm<sup>–1</sup> computed for dissociative water adsorption on relaxed and fixed (101) surfaces respectively agree very well with the experimental values of 3665, 3715 cm<sup>–1</sup>. However, the same frequencies calculated on (001) anatase clusters for dissociative water adsorption shows some discrepancies with the experimental data.

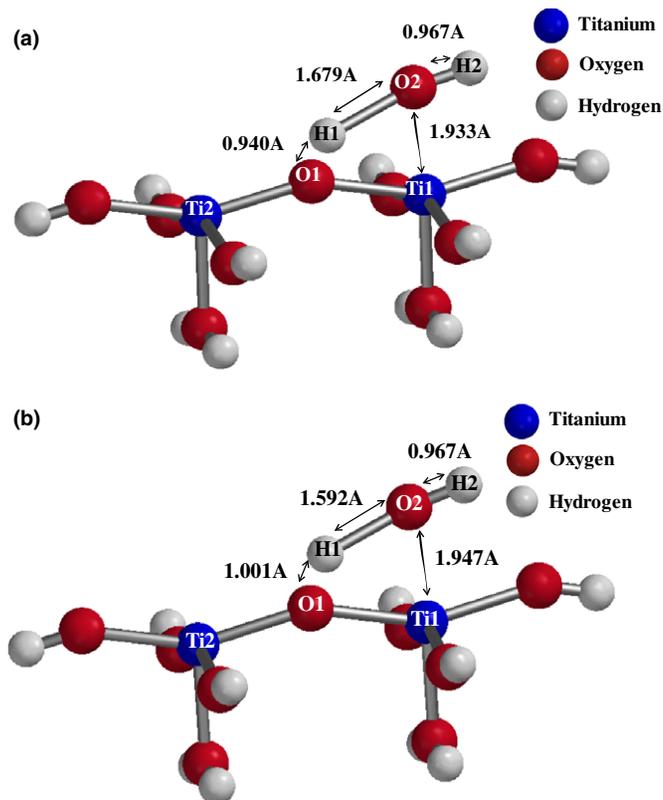


Fig. 12. (a) Transition state and (b) Equilibrium geometry for dissociative H<sub>2</sub>O adsorption on fixed (001) Ti<sub>2</sub>O<sub>9</sub>H<sub>10</sub> cluster.

Stretching frequencies of 3331 and 3035 cm<sup>–1</sup> for relaxed and fixed (001) surfaces are out of the experimentally predicted range (3600–3800 cm<sup>–1</sup>). To sum up the findings given in Table 4, it can be concluded that calculated vibration frequency data for dissociative water adsorption on (101) surface agree better with the experimental data than those on (001) anatase surface. This could be an expected result since (101) surface is statistically more exposed on TiO<sub>2</sub> than (001) surface as previously mentioned.

The vibrational frequencies (cm<sup>–1</sup>) of H-bonded H<sub>2</sub>O molecule adsorbed on (101) and (001) Ti<sub>2</sub>O<sub>9</sub>H<sub>10</sub> clusters are compared with the experimental values in Table 5. As seen in the table, the symmetric stretching frequency of H<sub>2</sub>O calculated on (101) relaxed cluster (3299 cm<sup>–1</sup>) is within the experimental 3200–3550 cm<sup>–1</sup> range. On the other hand, the asymmetric stretching frequency of 3679 cm<sup>–1</sup> is out of the experimentally estimated range of 3200–3500 cm<sup>–1</sup>. Deformation frequency of water molecule (1666 cm<sup>–1</sup>) adsorbed on Ti<sup>4+</sup> cation of relaxed (101) cluster compares with the experimental value of 1600 cm<sup>–1</sup>. The symmetric and asymmetric stretching frequencies computed for fixed (101) surface come out to be slightly out of the experimentally reported range of 3200–3500 cm<sup>–1</sup>. Similar to relaxed (101) surface the deformation frequency value on this surface (1672 cm<sup>–1</sup>) compares with the experimental value. For the relaxed (001) cluster, the H-bonded water molecule has symmetric

Table 3

The comparison of the calculated H<sub>2</sub>O adsorption energy on (001) surface with the theoretical information in the literature

Theoretical values	Method	Surface	Adsorption energy (kcal/mol)	
			Molecular	Dissociative
This work	DFT B3LYP/6-31G**	001 Anatase relaxed Ti <sub>2</sub> O <sub>9</sub> H <sub>10</sub> cluster	–24.93	–54
		001 Anatase fixed Ti <sub>2</sub> O <sub>9</sub> H <sub>10</sub> cluster	–23.46	–11.21
Bredow and Jug [16]	MO/SINDO	001 Anatase 2X2X3 cluster	–35.61	–52.82
		001 Anatase 3X3X3 cluster	–32.50	–38.72
		001 Anatase 4X4X3 cluster	–25.33	–31.79
Vittadini et al. [15]	DFT	001 Anatase	–18.68 ( $\theta = 0.5$ ) <sup>a</sup> –18.91 ( $\theta = 1$ ) <sup>a</sup>	–33.21 ( $\theta = 0.5$ ) <sup>a</sup> – ( $\theta = 1$ ) <sup>a</sup>
Kachurovskaya et al. [17]	DFT	001 Anatase Ti <sub>6</sub> O <sub>19</sub> H <sub>12</sub> cluster	–13.6	–
Fahmi and Minot [18]	Periodic	001 Anatase	–14.34	–28.68

<sup>a</sup>  $\theta$  is the coverage of the molecules on (101) anatase surface.

Table 4

The comparison of the vibrational frequencies (cm<sup>–1</sup>) of H<sub>2</sub>O adsorbed on (101) and (001) Ti<sub>2</sub>O<sub>9</sub>H<sub>10</sub> clusters with the literature values

H <sub>2</sub> O adsorption on 101 anatase Ti <sub>2</sub> O <sub>9</sub> H <sub>10</sub> cluster <sup>a</sup>				H <sub>2</sub> O adsorption on 001 anatase Ti <sub>2</sub> O <sub>9</sub> H <sub>10</sub> cluster <sup>a</sup>				Experimental values
Relaxed cluster		Fixed cluster		Relaxed cluster		Fixed cluster		Dissociative
Molecular	Dissociative	Molecular	Dissociative	Molecular	Dissociative	Molecular	Dissociative	
3005, 3661	3666, 3713	3381, 3634	3657, 3711	2753, 3692	3331, 3656	3256, 3692	3035, 3681	3600–3800 <sup>b</sup> (O–H stret.)
1605		1622		1532		1543		3665, 3715 <sup>c</sup> (O–H stret.)

<sup>a</sup> Calculated values are scaled by 0.9613 [30].<sup>b</sup> Morterra et al. [6].<sup>c</sup> Primet et al. [5].

Table 5

Comparison of the vibrational frequencies (cm<sup>–1</sup>) of H-bonded H<sub>2</sub>O molecule adsorbed on (101) and (001) Ti<sub>2</sub>O<sub>9</sub>H<sub>10</sub> clusters with the experimental values

H <sub>2</sub> O adsorption on 101 anatase Ti <sub>2</sub> O <sub>9</sub> H <sub>10</sub> cluster <sup>a</sup>		H <sub>2</sub> O adsorption on 001 anatase Ti <sub>2</sub> O <sub>9</sub> H <sub>10</sub> cluster <sup>a</sup>		Experimental values
Relaxed cluster		Fixed cluster		Relaxed cluster
3299, 3679 (O–H stret.)		3199, 3688 (O–H stret.)		
				3350–3500 <sup>b</sup> 3200–3550 <sup>c</sup> (O–H stret.)
1666, 1145 (O–H deform.)		1672 (O–H deform.)		1635, 1024 (O–H deform.)
				1640 <sup>b</sup> , 1600–1630 <sup>c</sup> (O–H deform.) 1048, 1137, 1222 <sup>c</sup> (O–H deform.)

<sup>a</sup> Calculated values are scaled by 0.9613 [30].<sup>b</sup> Morterra et al. [6].<sup>c</sup> Bezrodna et al. [4].

and asymmetric OH stretching frequencies of 3295, 3352 cm<sup>–1</sup> which agree well with the experimentally predicted range of 3200–3500 cm<sup>–1</sup>. 1635 cm<sup>–1</sup> of deformation frequency also compares with the experimental values. Moreover, another deformation mode of water at 1024 cm<sup>–1</sup> is in good agreement with what Bredziona et al. [4] reported as 1048 cm<sup>–1</sup> for H-bonded water molecule on TiO<sub>2</sub>. In brief, experimental adsorption energy (TPD) results are met by H-bonded water adsorption on fixed and relaxed (101), and on relaxed (001) Ti<sub>2</sub>O<sub>9</sub>H<sub>10</sub>

clusters (Table 2). The interesting point is that the vibration frequency calculations for these geometries also showed agreement with the experimentally reported values as given in Table 5.

### 3.3. NH<sub>3</sub> adsorption

Ammonia adsorption is also studied on fixed and relaxed Ti<sub>2</sub>O<sub>9</sub>H<sub>10</sub> clusters for both molecular and dissociative adsorption reactions. To the best of our knowledge there is

no theoretical study for ammonia adsorption on (101) and (001) anatase surfaces.

### 3.3.1. $NH_3$ adsorption on (101) surface

For both clusters, a reaction coordinate is selected as the distance between the nitrogen atom of the ammonia molecule (N1) and the titanium atom (Ti1) of the fixed and relaxed cluster surfaces. The resultant energy profiles given in Fig. 13 show that  $NH_3$  molecule is adsorbed on  $Ti^{4+}$  site exhibiting a non-activated mode with adsorption energies of  $-25.66$  kcal/mol and  $-30.78$  kcal/mol on relaxed and fixed  $Ti_2O_9H_{10}$  clusters, respectively. The equilibrium geometry of this interaction is given in Fig. 14. Ammonia

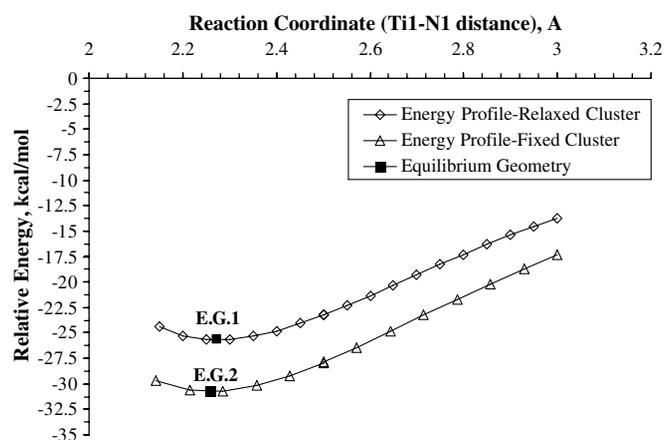


Fig. 13. Energy profile for  $NH_3$  adsorption on relaxed and fixed (101)  $Ti_2O_9H_{10}$  clusters (E.G.1 and E.G.2 represent equilibrium geometries on relaxed and fixed (101) clusters, respectively).

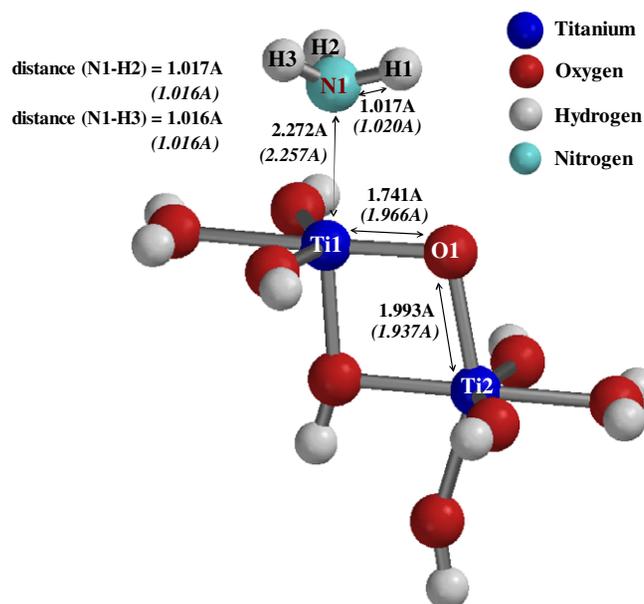


Fig. 14. Equilibrium geometry of ammonia adsorption on relaxed and fixed (101)  $Ti_2O_9H_{10}$  clusters (bond lengths without parentheses belong to the partially relaxed (101) cluster, while the values given in parentheses are for the fixed cluster).

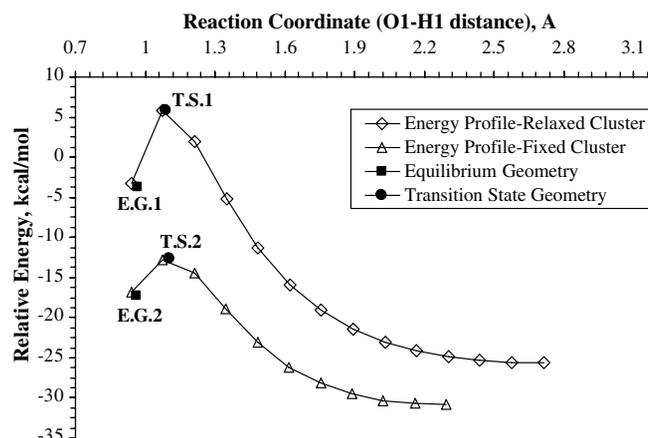


Fig. 15. Energy profile for ammonia dissociation on relaxed and fixed (101)  $Ti_2O_9H_{10}$  clusters (E.G.1 and E.G.2 represent equilibrium geometries; T.S.1 and T.S.2 stands for the transition state geometries calculated on relaxed and fixed (101) clusters, respectively).

is molecularly adsorbed on the relaxed Ti1 and O1 atoms and fixed cluster models representing the surface of (101) anatase.

Ammonia dissociation reaction is also studied following molecular  $NH_3$  adsorption. For this purpose the distance between H1 and O1 (in Fig. 14) is selected as the reaction coordinate for both clusters. According to the resulting energy profile given in Fig. 15, it is seen that ammonia dissociates on relaxed and fixed  $Ti_2O_9H_{10}$  clusters with endothermic relative energy differences of 22.02 and 13.58 kcal/mol and having activation barriers of 31.52 and 18.01 kcal/mol, respectively. Transition state and equilibrium geometries of this reaction are illustrated in Fig. 16 which includes the distances between the atoms.

After obtaining the equilibrium geometries of dissociated ammonia given above, the adsorption of another  $NH_3$  molecule by H-bonding on this system is also studied by single point equilibrium geometry calculations. H-bonded ammonia on relaxed and fixed (101)  $Ti_2O_9H_{10}$  clusters (shown in Fig. 17) has exothermic relative energy differences of 13.22 and 14.38 kcal/mol, respectively.

### 3.3.2. $NH_3$ adsorption on (001) surface

For both relaxed (Ti1, O1 and Ti2 atoms are relaxed) and fixed clusters, ammonia molecule is located at a chosen distance from the cluster and a reaction coordinate is selected as the distance between the nitrogen atom of the ammonia molecule (N1) and the titanium atom (Ti1) of the cluster surface. The resultant energy profile calculations given in Fig. 18 show that  $NH_3$  molecule is adsorbed on the cluster exhibiting a non-activated mode with adsorption energies of  $-26.57$  and  $-23.72$  kcal/mol on relaxed and fixed clusters, respectively. The equilibrium geometry of this reaction is illustrated in Fig. 19. Ammonia molecule is adsorbed on the relaxed cluster having a N1–Ti1 distance of 2.272 Å while on the fixed cluster this distance comes out to be 2.261 Å. The energy profile for the fixed cluster given

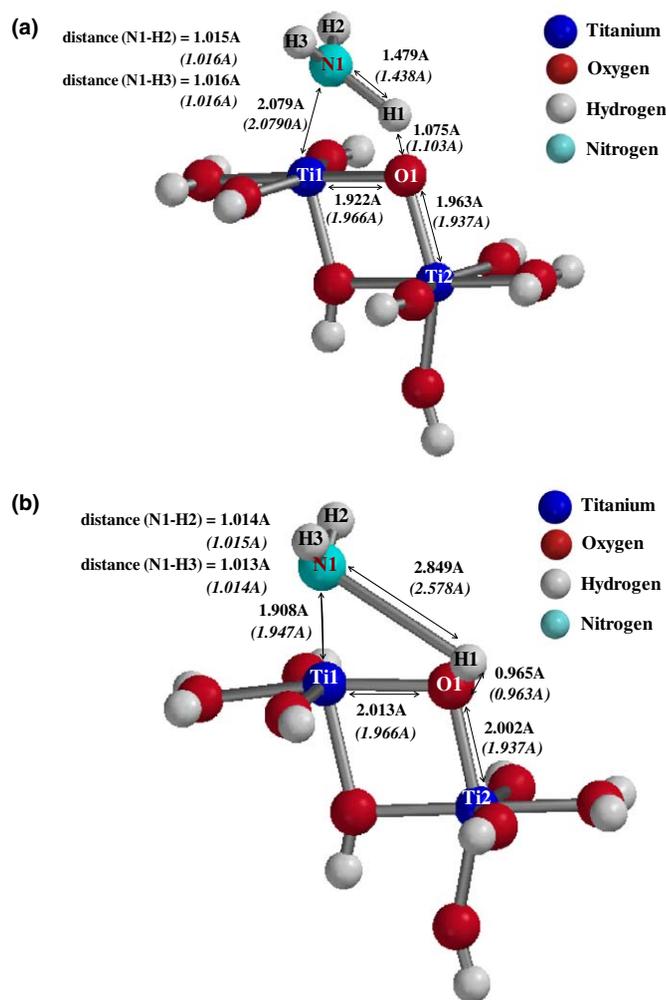


Fig. 16. (a) Transition state and (b) Equilibrium geometries of dissociated ammonia on relaxed and fixed (101)  $\text{Ti}_2\text{O}_9\text{H}_{10}$  clusters (bond lengths without parentheses belong to the partially relaxed (101) cluster, while the values given in parentheses are for the fixed cluster).

in Fig. 18 and the equilibrium geometry in Fig. 19(b) can also be compared with the semiempirical PM3 calculations in Figs. 1 and 3. Although equilibrium geometries do not deviate too much, the energy values are highly exaggerated in the case of PM3 calculations. The overall energy profile trends, however, are somewhat similar.

Ammonia dissociation is also studied starting from molecularly adsorbed ammonia geometries given in Fig. 19. Coordinate driving calculations are performed by choosing the distance between O1 and H1 atoms as reaction coordinates. Since the resulting energy profile obtained for the fixed cluster shows a continuous increase with decreasing reaction coordinate it is concluded that ammonia dissociation on fixed (001)  $\text{Ti}_2\text{O}_9\text{H}_{10}$  cluster turns out to be an unfavorable process.

On contrary to the fixed cluster, ammonia dissociation occurs on relaxed  $\text{Ti}_2\text{O}_9\text{H}_{10}$  cluster with an exothermic relative energy difference of 9.75 kcal/mol and a small activation barrier of 3.63 kcal/mol. The resulting equilibrium geometry of this reaction is given in Fig. 20. At the equilib-

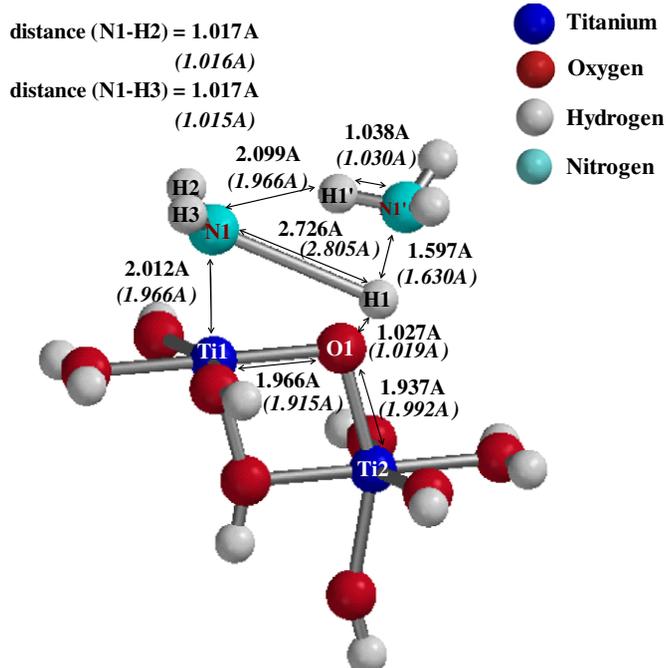


Fig. 17. Equilibrium geometry of H-bonded ammonia on relaxed and fixed (101)  $\text{Ti}_2\text{O}_9\text{H}_{10}$  clusters (bond lengths without parentheses belong to the partially relaxed (101) cluster, while the values given in parentheses are for the fixed cluster).

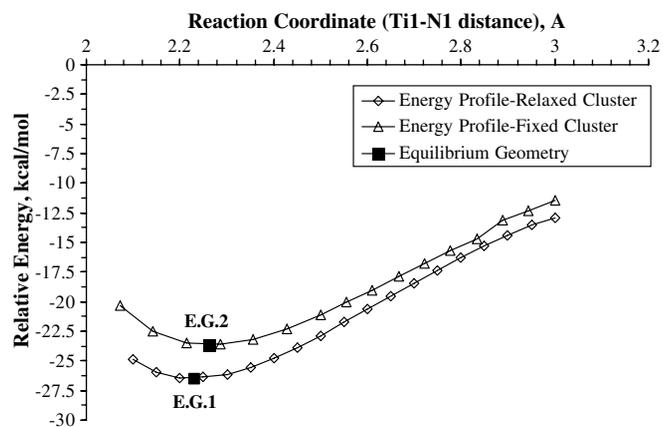


Fig. 18. Energy profiles for ammonia adsorption on relaxed and fixed (001)  $\text{Ti}_2\text{O}_9\text{H}_{10}$  clusters (E.G.1 and E.G.2 represent equilibrium geometries for relaxed and fixed (001) clusters, respectively).

rium geometry ammonia molecule is dissociated into  $\text{NH}_2$  and H atoms destroying the bridge structure of the cluster. This configuration has Ti1–N1 and O1–H1 distances of 1.955 Å and 1.005 Å, respectively.

Ammonia adsorption by H-bonding on the geometric configuration shown in Fig. 20 is also studied by single point equilibrium geometry calculations. It is found that ammonia molecule is adsorbed by H-bonding (Fig. 21) with an exothermic relative energy difference of 6.02 kcal/mol.

A comparison of the calculated  $\text{NH}_3$  adsorption energies on (101) and (001) cluster surfaces with the literature

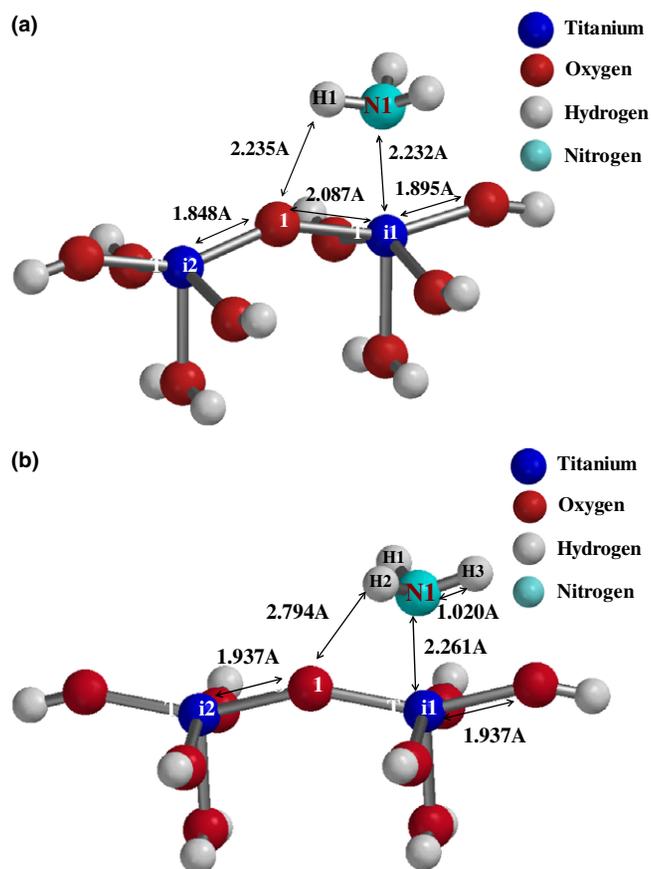


Fig. 19. Equilibrium geometry for  $\text{NH}_3$  adsorption on (a) relaxed (001)  $\text{Ti}_2\text{O}_9\text{H}_{10}$  cluster, (b) fixed (001)  $\text{Ti}_2\text{O}_9\text{H}_{10}$  cluster.

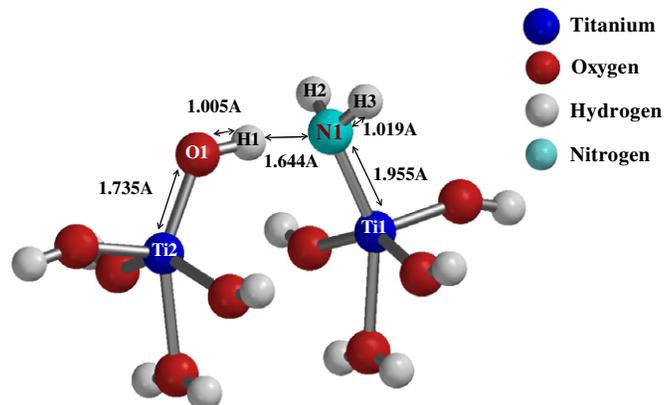


Fig. 20. Equilibrium geometry of dissociated ammonia on relaxed (001)  $\text{Ti}_2\text{O}_9\text{H}_{10}$  cluster.

values are given in Table 6. The calculated results are compared only with what is available in the experimental literature since there is no theoretical study on this topic. Molecular ammonia adsorption energies of  $-13.22$  and  $-25.66$  kcal/mol obtained on relaxed (101)  $\text{Ti}_2\text{O}_9\text{H}_{10}$  cluster are comparable with  $-14$  and  $-27$  kcal/mol of ammonia desorption enthalpies reported by Srnak et al. [7]. This is again reasonable in view of the fact that (101) sur-

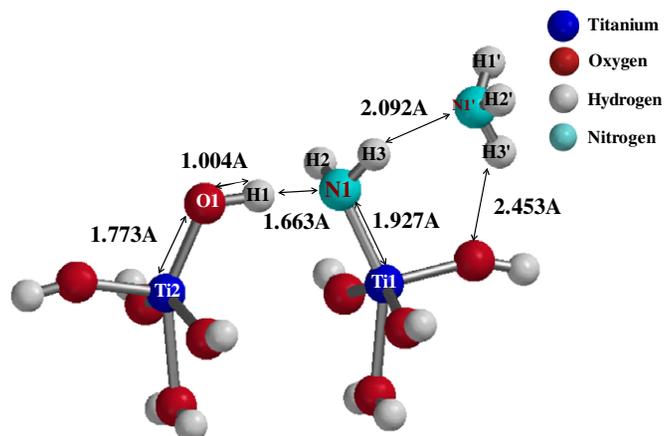


Fig. 21. Equilibrium geometry of H-bonded ammonia on relaxed (001)  $\text{Ti}_2\text{O}_9\text{H}_{10}$  cluster.

Table 6  
The comparison of the calculated  $\text{NH}_3$  adsorption energy with the literature

Theoretical values	Method	Surface	Adsorption energy (kcal/mol)	
			Molecular	Dissociative
This work	DFT B3LYP 6-31G**	101 Anatase relaxed $\text{Ti}_2\text{O}_9\text{H}_{10}$ cluster	$-13.22^a$ , $-25.66$	$-3.64$
		101 Anatase fixed $\text{Ti}_2\text{O}_9\text{H}_{10}$ cluster	$-14.38^a$ , $-30.78$	$-17.20$
		001 Anatase relaxed $\text{Ti}_2\text{O}_9\text{H}_{10}$ cluster	$-6.02^a$ , $-26.57$	$-36.32$
		001 Anatase fixed $\text{Ti}_2\text{O}_9\text{H}_{10}$ cluster	$-23.72$	–
Experimental values				
Srnak et al. [7]	TPD	$\text{TiO}_2$ Anatase	$-14$ , $-27$	
Sprinceana et al. [9]	XRD, BET	$\text{TiO}_2$ Anatase	$-31$ , $-36$	

<sup>a</sup> Values for molecularly adsorbed  $\text{NH}_3$  molecule by H bonding on hydroxyl groups.

face is a majority surface in anatase. The enthalpy values obtained on fixed (101) cluster ( $-14.38$  and  $-30.78$  kcal/mol) deviate slightly from the experimental values. On the other hand, only one enthalpy value for ammonia adsorption agrees with the experiment ( $-26.57$  vs  $-27$  kcal/mol) on relaxed (001) surface. This could also be expected since (001) surface is minority in anatase. Dissociation of ammonia is more favorable on relaxed (001) surface than (101) relaxed surface ( $-37$  vs  $-3.64$  kcal/mol); however, there seems to be no experimental data concerning this aspect.

Table 7

The comparison of the vibrational frequencies ( $\text{cm}^{-1}$ ) of  $\text{NH}_3$  adsorbed on (101) and (001)  $\text{Ti}_2\text{O}_9\text{H}_{10}$  clusters with the literature values

NH <sub>3</sub> Adsorption on 101 anatase Ti <sub>2</sub> O <sub>9</sub> H <sub>10</sub> cluster <sup>a</sup>				NH <sub>3</sub> Adsorption on 001 anatase Ti <sub>2</sub> O <sub>9</sub> H <sub>10</sub> cluster <sup>a</sup>				Experimental values	
Relaxed cluster		Fixed cluster		Relaxed cluster		Fixed cluster			
Molecular	Dissociative	Molecular	Dissociative	Molecular	Dissociative	Molecular	Dissociative	Molecular	Dissociative
1115	1486	1132	1485	1103	1485	1070	–	1190 <sup>d</sup> , 1225 <sup>d</sup> , 1215 <sup>e</sup>	1480 <sup>f</sup> , 1540 <sup>g</sup>
1618		1642		1605		1609		(sym. bend.)	
3350		3338		3339		3358		1599 <sup>d</sup> , 1600 <sup>f</sup>	
3478		3462		3477		3498		(asym. bend.)	
1221 <sup>b</sup>	1486 <sup>c</sup>	1258 <sup>b</sup>	1490 <sup>c</sup>	1071 <sup>b</sup>	1528 <sup>c</sup>	–	–	3350 <sup>f</sup>	
1624 <sup>b</sup>		1618 <sup>b</sup>		1644 <sup>b</sup>				(sym. stret.)	
3380 <sup>b</sup>		3359 <sup>b</sup>		3327 <sup>b</sup>				3400 <sup>f</sup>	
3486 <sup>b</sup>		3411 <sup>b</sup>		3454 <sup>b</sup>				(asym. stret.)	

<sup>a</sup> Calculated values are scaled by 0.9613 [30].<sup>b</sup> Values for molecularly adsorbed  $\text{NH}_3$  molecule by H bonding on hydroxyl groups.<sup>c</sup> Values for vibration frequency of  $\text{NH}_2$  species in H-bonded  $\text{NH}_3$  configuration.<sup>d</sup> Amores et al. [31].<sup>e</sup> Terammura et al. [32].<sup>f</sup> Schneider et al. [33].<sup>g</sup> Lietti et al. [34].

Vibration frequencies for ammonia adsorption on these clusters are also calculated by single point energy calculations. A comparison of these findings with experimental data is given in Table 7. As it is evident from the table, vibration frequency data for molecular ammonia adsorption on  $\text{Ti}^{4+}$  sites resemble each other for all of the cluster models. The theoretical data also agree with the experimental stretching and bending frequencies with the exception of symmetric bending frequency. However, when vibration frequency calculations with regard to H-bonded  $\text{NH}_3$  molecules are considered for (101) relaxed and fixed clusters, all of the values agree better with the experimental data including symmetric bending frequency values. The symmetric bending frequency of  $1070 \text{ cm}^{-1}$  for H-bonded ammonia adsorption on (001) relaxed surface deviates substantially from the experimental values of 1190, 1215 and  $1225 \text{ cm}^{-1}$ . This is also consistent with enthalpy information again reflecting the fact that (001) surface is minority in anatase. The calculated vibration frequency for scissoring mode of  $\text{NH}_2$  species on (001) relaxed cluster fits with the other experimental value of  $1540 \text{ cm}^{-1}$ .

#### 4. Conclusions

The molecular adsorption and dissociation of  $\text{H}_2\text{O}$  and  $\text{NH}_3$  on (101) and (001)  $\text{TiO}_2$  anatase surfaces both represented by totally fixed and partially relaxed  $\text{Ti}_2\text{O}_9\text{H}_{10}$  cluster models are simulated by use of Density Functional Theory (DFT) calculations. The results indicate that the favorable adsorption mode of these molecules depend on the surface relaxations. Molecular water adsorption is more favorable on relaxed (101)  $\text{Ti}_2\text{O}_9\text{H}_{10}$  cluster than dissociative water adsorption; however, on the fixed cluster it is seen that the opposite situation is valid. Non-activated dissociation of water takes place on relaxed (001)  $\text{Ti}_2\text{O}_9\text{H}_{10}$  cluster while on fixed (001) cluster molecular adsorption is found to be more favored. The adsorption

of water with previously  $\text{H}_2\text{O}$  dissociated surfaces is also considered. The adsorption energy and vibration frequency of water molecule adsorbed by H-bonding on relaxed (001) and (101) cluster, and on (101) fixed cluster compare very well with the experimental estimates.

For ammonia adsorption, molecular adsorption is found to be more favorable than dissociative adsorption on both relaxed and fixed (101)  $\text{Ti}_2\text{O}_9\text{H}_{10}$  cluster models. On (001) fixed  $\text{Ti}_2\text{O}_9\text{H}_{10}$  cluster, ammonia dissociation turns out to be an energetically unfavorable process while on (001) relaxed cluster surface dissociation occurs with a slight activation barrier having an exothermic relative energy difference. As in the case of water adsorption, the adsorption of ammonia with H-bonding with previously  $\text{NH}_3$  dissociated systems is also considered. The adsorption energy of ammonia molecule adsorbed by H-bonding on (101) relaxed and fixed clusters agree with the experimental data. Moreover, it is found that these geometries whose adsorption energy compares with TPD results show agreement with the experimental data for vibration frequencies as well.

#### References

- [1] U. Diebold, Appl. Phys. A. 76 (2002) 186.
- [2] R. Hengerer, B. Bolliger, M. Erbudak, M. Grätzel, Surf. Sci. 460 (2000) 162.
- [3] C.H. Lin, H. Bai, Appl. Catal. B 42 (2003) 279.
- [4] T. Bredziona, G. Puchkovska, V. Shymanovska, J. Baran, H. Ratajczak, J. Mol. Struct. 700 (2004) 175.
- [5] M. Primet, P. Pichat, M-V. Mathieu, J. Phys. Chem. 75 (1971) 1216.
- [6] C. Morterra, J. Chem. Soc. Faraday Trans. 1 84 (1988) 1617.
- [7] T.Z. Srnak, J.A. Dumesic, B.S. Clausen, E. Tornqvist, N.Y. Topsoe, J. Catal. 135 (1992) 246.
- [8] G. Munuera, F. Moreno, F. Gonzales, A model for anatase  $\text{TiO}_2$  surfaces: interpretation of some interface processes. reactivity of solids, in: Proceedings of the 7th International Symposium Reaction Solids, Chapman & Hall, London, 1972, p. 681.

- [9] D. Sprinceana, M. Caldararu, N.I. Ionescu, A. Auroux, J. Therm. Anal. Calorim. 56 (1999) 109.
- [10] N-Y. Topsøe, H. Topsøe, J.A. Dumesic, J. Catal. 151 (1995) 226.
- [11] N-Y. Topsøe, H. Topsøe, J.A. Dumesic, J. Catal. 151 (1995) 241.
- [12] G. Ramis, L. Yi, G. Busca, M. Turco, E. Kotur, R.J. Willey, J. Catal. 157 (1995) 523.
- [13] G. Ramis, L. Yi, G. Busca, Catal. Today 28 (1996) 373.
- [14] G. Busca, L. Lietti, G. Ramis, F. Berti, Appl. Catal. B 18 (1998) 1.
- [15] A. Vittadini, A. Selloni, F.P. Rotzinger, M. Gratzel, Phys. Rev. Lett. 81 (1998) 2954.
- [16] T. Bredow, K. Jug, Surf. Sci. 327 (1995) 398.
- [17] N.A. Kachurovskaya, E.P. Mikheeva, G.M. Zhidomirov, J. Mol. Catal. 178 (2000) 191.
- [18] A. Fahmi, C. Minot, Surf. Sci. 304 (1994) 343.
- [19] A. Selloni, A. Vittadini, M. Grätzel, Surf. Sci. 402–404 (1998) 219.
- [20] P.C. Redfern, P. Zapol, L.A. Curtiss, T. Rajh, M.C. Thurnauer, J. Phys. Chem. B 107 (2003) 11419.
- [21] W. Kohn, L.J. Sham, Phys. Rev. 140 (1965) A1133.
- [22] A. Beltran, J.R. Sambrano, M. Calatayud, F.R. Sensato, J. Andres, Surf. Sci. 490 (2001) 116.
- [23] G.N. Kryukova, D.O. Klenov, G.A. Zenkovets, React. Kinet. Catal. Lett. 60 (1997) 179.
- [24] M.T.M. Koper, R.A. van Santen, J. Electroanal. Chem. 472 (1999) 126.
- [25] R.A. van Santen, M. Neurock, Catal. Rev.-Sci. Eng. 37 (1995) 557.
- [26] A.D. Becke, Phys. Rev. B 38 (1988) 3098.
- [27] A.D. Becke, M.R. Roussel, Phys. Rev. A 39 (1989) 3761.
- [28] C. Lee, W. Yang, R.G. Parr, Phys. Rev. B 37 (1988) 785.
- [29] R.W.G. Wyckoff, second ed. Crystal Structures, vol. 2, John Wiley & Sons, New York, 1963.
- [30] W. W Ming, Chem. Phys. Lett. 256 (1996) 391.
- [31] J.M.G. Amores, V.S. Escibano, G. Ramis, G. Busca, Appl. Catal. B 13 (1997) 45.
- [32] K. Teramura, T. Tanaka, T. Funabiki, Langmuir 19 (2003) 1209.
- [33] H. Schneider, S. Tschudin, M. Schneider, A. Wokaun, A. Baiker, J. Catal. 147 (1994) 5.
- [34] L. Lietti, G. Ramis, F. Berti, G. Toledo, D. Robba, G. Busca, P. Forzatti, Catal. Today 42 (1998) 101.