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Size dependent catalytic effect of TiO_2 clusters in water dissociation

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ABSTRACT

We performed systematic first principles calculations based on density functional theory to probe the energetics of dissociation of water molecules on small $(TiO_2)_n$ ($n = 3, 4, 6, 8$, and 10) clusters. We found that the $(TiO_2)_n$ clusters have a strong ability to adsorb water molecules and the dissociative adsorption of water molecules on the surface of $(TiO_2)_n$ clusters with a three step process is irreversible, size-dependent and energetically more favorable than the same on the surfaces of titanium oxide. Charged $(TiO_2)_n$ cluster also have strong ability in H_2O molecule splitting similar as neutral ones. The efficiency of water molecules dissociating on $(TiO_2)_n$ cluster surface varies inversely with the cluster size due to the steric effect. Our results indicate a higher efficiency of small clusters of titanium oxide in dissociating water molecules than its low index surfaces of bulk terminated.

1. Introduction

Since the discovery of photocatalytic dissociation of water on a TiO_2 electrode under ultraviolet light by Fujishima and Honda in 1972 [1], the interactions between H_2O and TiO_2 have been extensively studied [2–14]. At room temperature, bulk TiO_2 exists in three natural phases: rutile, anatase and brookite [15]. Both bulk rutile and anatase phases are efficient in dissociating water molecules. In particular, rutile TiO_2 (1 1 0) has become a model surface for the fundamental studies of metal oxide reactivity [2,8,13,16–19].

Nanoparticles often offer novel properties differing from both solids and typical molecules [20]. The large available surface area in small particles facilitates the occurrence of reaction or interaction on the surface or at the interface. It is generally believed that the size of a material is an important indicator of its reactivity. As such, reactivity is often associated to the materials of small size. Powders and dispersed catalysts are indeed more reactive than terraces of crystalline materials for their porosity [2]. Atomic clusters have long been considered as models for fundamental mechanistic insight into complex surfaces and catalysts. Owing to its technological importance, numerous experimental and theoretical investigations have been carried out on isolated titanium oxide clusters to correlate their structures and properties with their bulk counterparts [21–29]. Yu and Freas have experimentally studied the formation and fragmentation of positive ions of titanium/oxygen cluster in the gas-phase [25]. Their results showed that titanium/oxygen cluster ions sputtered from the foil have the form of $[Ti_nO_{2n-\delta}]^+$, where $n = 1–8$ and $\delta = 0–4$. Sputtering titanium dioxide powder yields abundant $[Ti_nO_{2n-\delta}]^+$ clusters, where $n = 1–7$ and $\delta = 1–3$. Li and Dixon have done theoretical research on molecular structures and energetics of the $(TiO_2)_n$ ($n = 1–4$) clusters and their anions [21]. Hamad et al. [22] performed a theoretical calculation on Ti_nO_{2n} clusters ($n = 1–15$) with a combination of simulated annealing, Monte Carlo basin hopping simulation and genetic algorithms methods. Zhai and Wang studied electronic structures and band gap evolution of titanium oxide clusters $(TiO_2)_n^-$ ($n = 1–10$) using photoelectron spectroscopy [30]. Shevlin and Woodley performed theoretical calculations on electronic and optical properties of undoped $(TiO_2)_n$ nanoparticles and doped $(TiO_2)_n$ nanoparticles with C, N and S [28].

Despite several experimental and theoretical studies on isolated titanium oxide clusters, a clear and an in-depth understanding of the interaction between water molecules and nano-sized titanium oxide particles has not yet emerged. To meet this, first principles calculations based on density functional theory (DFT) have been performed in this work to probe into the detailed energetics and pathways for the dissociation of water molecules on $(TiO_2)_n$ ($n \leq 10$) clusters.

2. Computational methods

The DFT calculations for structural relaxation and the energy barriers for bare TiO_2 clusters and TiO_2 clusters with water

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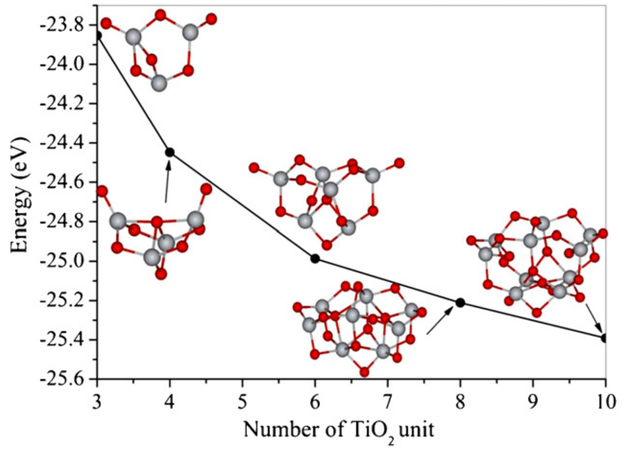

Fig. 1. The optimized structures of $(TiO_2)_n$ ($n = 3$, 4, 6, 7, and 10) and their total energies per TiO_2 unit. The red and gray spheres represent oxygen and titanium, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

molecule molecularly or dissociatively adsorbed on it were performed using the plane-wave self-consistent field (PWSCF) method of the QUANTUM-ESPRESSO package [31]. The initial structures of $(TiO_2)_n$ ($n = 3$, 4, 6, 7 and 10) used in our model studies were obtained from the earlier reported ones [21–23,26–28]. Generalized gradient approximation (GGA) parameterized with the PBE exchange-correlation functional and Vanderbilt ultrasoft pseudopotentials was used. Reciprocal space integrations were carried out using the Gamma point. The energy cut-offs of the plane-wave basis and electron density were 30 Ry and 350 Ry, respectively. The convergence threshold for self-consistency was set to 10^{-8} Ha, and that of the total energy tolerance to 10^{-5} Ha. The geometry optimization was performed with the force criterion on each atom being below10^{-3} Ha/Å. The clusters were placed into a super-cell with the length of a side equal to 40 Bohr to avoid spurious interactions. The convergences of the optimized geometry and the total energy of the adsorbate complexes have been carefully checked with respect to the above parameters. Energy barriers for a water molecule adsorbed molecularly or dissociatively on $(TiO_2)_n$ clusters were calculated using the climbing-image nudged elastic band (cNEB) method for locating the transition state [32]. The initial inter-image distance we used in our calculation is about 1.0 Bohr. The cNEB is a very useful method in finding the minimum-energy path between a given initial and final states of a reaction step. It can give a continuous path even when multiple minimum-energy paths exist.

3. Results and discussion

3.1. Structures and reaction profiles

The optimized structures of $(TiO_2)_n$ ($n = 3$, 4, 6, 8, and 10) and their total energies per TiO_2 unit are shown in Fig. 1. In general, the small cluster tends to form a sphere-like compact structure with a large number of unsaturated titanium atoms on the surface. For $n = 3$, 4 and 6, pendant and terminal oxygen atoms are bonded to the titanium atoms of the surface of clusters. For $n = 8$ and 10, all the oxygen atoms at the outermost layer of the clusters bridge two titanium atoms. From the previous reports as well as our results, we can conclude that when the size of the clusters is relatively big ($n \geq 8$), no terminal oxygen atom is found to exist at the surface, while for cluster sizes with $n < 8$, mono-coordinated terminal oxygen atoms are more likely to exist at the surface. The total energies per TiO_2 unit of $(TiO_2)_n$ clusters decrease rapidly with the increasing of the size, exhibiting a strong size effect.

Our theoretical results show that a H_2O molecule can dissociate on the surface of the titanium/oxygen clusters in three steps. For $(TiO_2)_n$ ($n = 3$, 4 and 6): First, the H_2O molecule was adsorbed on an unsaturated Ti on the surface of the clusters. Secondly, the H_2O molecule was dissociated to form a terminal hydroxyl ($-OH_t$) and a hydrogen atom. The hydrogen atom interacts with the next bridging oxygen atom and forms a bridging hydroxyl ($-OH_b$). Thirdly, the hydrogen atom of the $-OH_b$ interacts with the mono-coordinated oxygen atom nearest to the $-OH_b$ and forms another $-OH_t$. This pathway shows that the $-OH_b$ exists at a metastable state. For $(TiO_2)_n$ ($n = 8$ and10), the structures do not contain mono-coordinated oxygen atom, so there is some difference in the dissociation pathway of the H_2O molecule. The first step and the second step of this path are similar to the former. But for the third step, the Ti—O bond between the oxygen atom of $-OH_b$ and the Ti atom of $-OH_t-Ti$ breaks down and forms two terminal $-OH$ ($-OH_t$). The initial state, the metastable state and the final state structures in the dissociation of a water molecule on the $(TiO_2)_n$ cluster are displayed in Fig. 2. The structures in the second column of Fig. 2 are the metastable states. We define the binding energy as

$$\Delta E = E_{(TiO_2)_n \cdot mH_2O} - E_{(TiO_2)_n} - mE_{H_2O} \quad (1)$$

$E_{(TiO_2)_n \cdot mH_2O}$ is the energy of $(TiO_2)_n$ with m water molecules adsorbed molecularly or dissociatively on it. As for the structures in Fig. 2 with $m = 1$, one H_2O molecule interacts with every $(TiO_2)_n$ cluster. The binding energies of Fig. 2(a1), (a2) and (a3) are −1.77 eV, −2.46 eV and −3.58 eV, respectively, which implies that adsorption and subsequent dissociation of water molecule upon adsorption on the $(TiO_2)_n$ is energetically favored. The negative binding energies imply an exothermic process for water adsorption and dissociation on the cluster and water molecule is favored to be adsorbed and split on the $(TiO_2)_n$ clusters. Fig. 2 also shows that the binding energy increases with the increasing of the cluster size. The results are due to the bond relaxation as the effective coordination number reduces. Associated with the unsaturated atoms, nonbonding electrons are strongly and locally polarized by the deeply and densely entrapped bonding electrons. Coupling of the entrapment and the polarization originates properties that bulk materials do not exhibit [33].

In order to assess the likelihood for dissociation of water molecule(s) on the surface of $(TiO_2)_n$ clusters, cNEB calculations were performed to locate the transition state and calculate energy barriers. Figs. 3–5 display the reaction energy profile and the selected intermediate states of the H_2O molecule dissociation on $(TiO_2)_3$, $(TiO_2)_6$ and $(TiO_2)_{10}$ clusters calculated by the cNEB method. For the $(TiO_2)_3$, the barrier between the initial state and metastable state is 0.56 eV and the barrier between the metastable state and final state is 0.91 eV in the pathway of water molecule dissociating on it. For $(TiO_2)_6$, the first barrier and the second barrier are 0.39 and 0.61 eV, respectively. For $(TiO_2)_{10}$, the barrier between the initial state and metastable state is 0.13 eV, while the barrier between the metastable state and final state is 0.03 eV. For larger sizes of $(TiO_2)_n$ clusters, the barrier gets smaller, as shown in Figs. 3–5. In this work, all the reactions are two step reactions involving two transition states and one intermediate. According to transition state theory [33], the rate determining step is determined by the step with higher barrier. Therefore, although we compare all the two steps in each reaction in above discussion, we understand that the rate determining step is the one with the higher barrier. We can see that the potential energy surfaces presented in Figs. 3 and 4 are rather steep, especially between *d* and *e* points. However, our calculations with a finer inter-image distance at 0.6 Bohr show no difference in the potential energy profile.