Theoretical Analysis of Photocatalytic Interaction Between TiO$_2$ Cluster and H$_2$O

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Ab initio MO calculations were performed for the (rutile TiO$_2$ cluster)/H$_2$O bimolecular system at the ground state and with the single excitation configuration interaction (CIS) method to clarify the electronic state of photocatalytic interaction between H$_2$O and Ti-site of rutile TiO$_2$ (110) surface. We obtained stabilization energies for (H$_2$O$\cdots$Ti-site), and (HO$^-$$\cdots$Ti-site) of rutile TiO$_2$ cluster interaction models as 28.5 and 88.2 kJ/mol, respectively at the ground state in the restricted Hartree-Fock (RHF) approximation. The theoretical absorption energies for these interaction systems with CIS method may predict the experimental ones.

INTRODUCTION

Considerable plenty of researchers are interested in photocatalytic reaction for TiO$_2$, after discovery of photoelectrolysis for water on TiO$_2$ electrodes [1] and photocatalytic mineralization of water pollutants in the presence of TiO$_2$ colloids [2]. Until now, many works have been performed to improve the materials as the titanium oxide photocatalyst for widespread industrial applications in demanding fields of solar energy conversion and environmental cleanup. As well as we know, the mechanism of TiO$_2$ photocatalysis is not still clear in spite of numerical experimental studies. We think the most fundamental question is whether water adsorbs in molecular or in dissociated form on the TiO$_2$ surface. Then, we will investigate the electronic state of the interaction system between H$_2$O and TiO$_2$ surface for the most studied rutile (110) surface.

Experimental studies on single crystal TiO$_2$ (110) surface showed that water is adsorbed in molecular form at low coverages [3-7], although they could not observe the dissociated water on the rutile (110) surface. However, *ab initio* studies [8-11] on periodic models for the interaction system between H$_2$O and TiO$_2$ (110) surface indicated that the dissociative chemisorption (Ti-site$\cdots$OH$^-$) is more stable than molecular adsorption (Ti-site$\cdots$OH$_2$). In this paper, we will clarify the electronic state of the photocatalytic interaction between H$_2$O and Ti-site of rutile TiO$_2$ (110) surface by *ab initio* MO calculations using rutile type of Ti$_7$O$_{14}$ cluster model at the ground state and with single excitation configuration interaction (CIS) method [12] in the restricted Hartree-Fock (RHF) approximation.

COMPUTATIONAL DETAILS

We use the RHF calculation at the ground state and the single excitation configuration interaction (CIS) method to analyze the electronic state of the interaction between H$_2$O and TiO$_2$ surface. In the CIS method, the total wave function can be written as a linear combination of all possible singly excited determinants. Then, we can express the difference of total atomic charge between ground state and excited state, and the difference of the charge is related to the overlap matrix S and delta density matrix ΔP in Eq. (1).

$$\Delta q = q_{\mathrm{G}} - q_{\mathrm{E}} = \sum_{\mu=\mathrm{A}} \left(S^{1/2} \Delta P S^{1/2} \right)_{\mu\mu} , \quad (1)$$

where μ means atomic orbital number. The delta density matrix is written with expansion coefficients, ($C^k_{i,a}$, $C_{\mu, a}$, and so on) of CI and MO, respectively in Eq. (2).

$$\Delta P = \sum_{i,a} \left| C^k_{i,a} \right|^2 \left(C^*_{\mu a} C_{a\sigma} - C^*_{\mu i} C_{i\sigma} \right) \qquad (2)$$

The difference of bond order (ΔB) is also defined in the following Eq. (3) [13].

$$\Delta B = \sum_{\lambda \, A\sigma \, B} \Delta P^2_{\lambda\sigma} . \qquad (3)$$

We used Gaussian 03 program [14] for all *ab initio* MO calculations. The geometrical structures of Ti_7O_{14} cluster and the cluster/H_2O bimolecular system were optimized by ab initio Hartree-Fock MO calculations with 6-31G** bases [15]. The geometry of the frame for the rutile TiO_2 (110) model in Fig. 1 was referred to the X-ray diffraction study [16]. We adopted the LANL2DZ-ECP bases [17] to titanium and oxygen a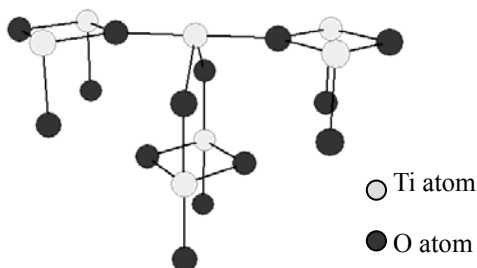toms of the model. Two types of the interaction models were considered as (a) molecular adsorption and (b) dissociative chemisorption shown in Fig. 2. For the interaction systems, we estimated the total energies with varying intermolecular distances (r and R), and angle (θ) shown in Fig. 2 using the RHF SCF calculations at the ground state. In minimum points of total energies, we obtained stabilization energy (ΔE) for each interaction system,

$$\Delta E = E_{Ti_7O_{14}/H_2O} - \left(E_{Ti_7O_{14}} + E_{(H_2O, OH+H)} \right) \qquad (4)$$

Furthermore, in order to discuss the electronic state of the photocatalytic interaction system, we performed the CIS calculations for the Ti_7O_{14} cluster, and two types of interaction models as (a) molecular adsorption and (b) dissociative chemisorption.

RESULTS AND DISCUSSION

In order to clarify the electronic state of photocatalytic reaction between H_2O and Ti-site of rutile TiO_2 (110) surface, we performed *ab initio* MO

Fig.1 Geometrical structure of Ti_7O_{14} surface model.

Fig. 3 Potential energy surface of molecular Adsorption.

(a)

(b)
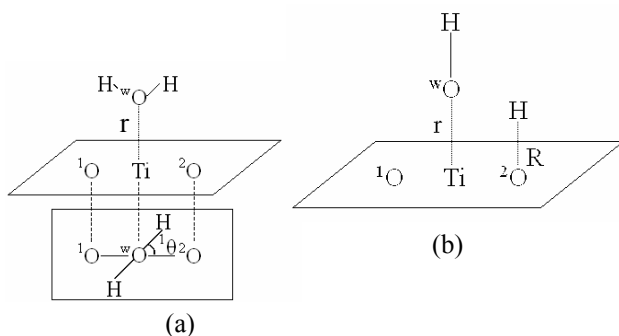
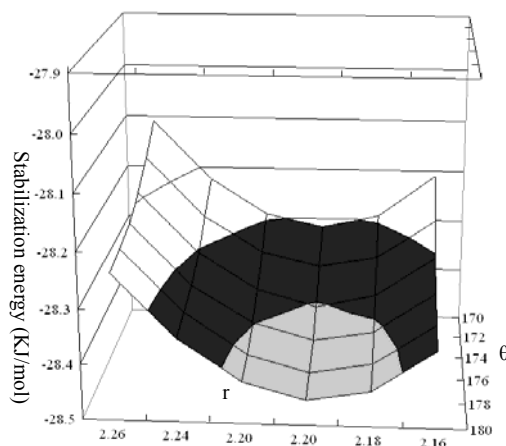Fig. 2 Geometrical structure of interaction systems
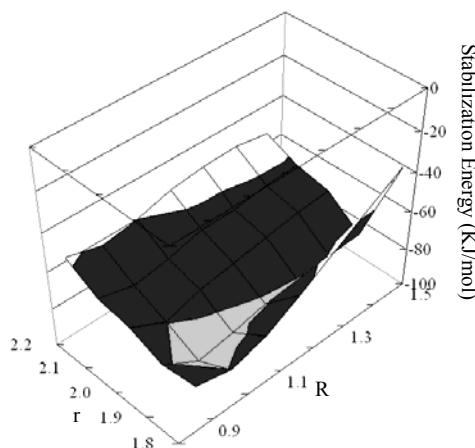a) molecular adsorption, b) dissociative chemisorption.

Fig. 4 Potential surface of dissociative Chemisorption.

calculations of molecular adsorption (Ti-site···OH$_2$), and dissociative chemisorption (Ti-site···OH$^-$) types for the (rutile TiO$_2$ cluster)/H$_2$O bimolecular system at the ground state and with the CIS method. Then we are able to discuss the electronic state of the reaction between rutile TiO$_2$ and H$_2$O, since we obtain various single excitation energies in the CIS method.

1) *Rutile TiO$_2$ cluster/H$_2$O bimolecular system at the ground state*

Figures 3 and 4 show the potential energy surface of molecular adsorption (Ti-site···OH$_2$), and dissociative chemisorption (Ti-site···OH$^-$) types for the (rutile TiO$_2$ cluster)/H$_2$O bimolecular system at the ground state. From this result, the stabilization energy (88.2 kJ/mol) of dissociative adsorption model is more stable than that (28.5 kJ/mol) of molecular adsorption model, as indicated in other *ab initio* studies [8-11]. In the two interaction models, the energy minimum points are at (r = 2.2 Å, θ = 0°), and (r = 1.9 Å, R = 0.9 Å) for molecular adsorption (Ti-site···OH$_2$), and dissociative chemisorption (Ti-site···OH$^-$) types, respectively. These values correspond to ones in other *ab initio* studies [8-11].

2) *Photocatalytic interaction between H$_2$O and Ti-site of rutile TiO$_2$ (110) surface*

a) Molecular adsorption

We showed the total atomic charge and bond order of H$_2$O and the interaction site TiO$_2$ for this molecular adsorption model using the MO calculations at the ground state and with CIS method in Table 1. It can be seen from the table that there are slight deviations in comparison of the total charge and bond order at the ground state with ones at the excited state in the adsorption type. We can, then, conclude that the electronic state in this adsorption type depends mainly upon that at the ground state, although it involves a slight amount of the electronic state at the excited state. As a result with CIS calculation, we obtain a new peak of absorption at 380.9 nm (3.25 eV) in Fig. 5. The transition is from pσ-(O 2p-H 1s) bonding orbital to pπ*-like (Ti 3p-O 2p; Ti 3d-O 2p) anti-bonding orbital.

b) Dissociative chemisorption

Table 1 also indicates the total atomic charge of OH, H, and the interaction site TiO$_2$, and the bond order of Ti-OH$_b$, and O-H$_t$ for the dissociative chemisorption model using the MO calculations at the ground state and with CIS method. Fig. 6 shows absorption peaks at 389.3 and 401.7 nm due to the CIS calculations. These transitions are also from pσ-(O2p-H1s) bonding orbital to pπ*-like (Ti3d-O2p) anti-bonding orbital.

In the first excitation energy at 389.3 nm, absolute values of the total charge for OH, H, and TiO$_2$ at the excitation state are much smaller than those at the ground state. In the chemisorption model, we can see that the differences between the total charges contribute to the excited state: the values for OH, H, and TiO$_2$ are -0.244, 0.114, and 0.131, respectively. This indicates that electron transfer occurs from the OH to this surface in the excited state. On the other hand, from the differences of the bond order for Ti-OH$_b$, and O-H$_t$, we can find that at the excited state the bond of Ti-OH$_b$ is weaker, while that
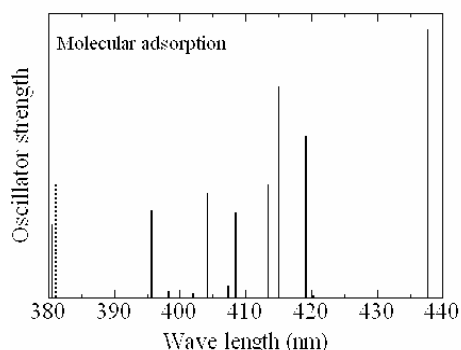
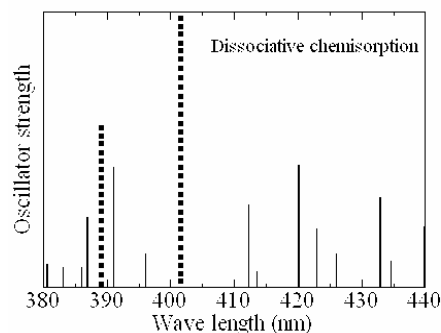Fig.5 Absorption spectrum for molecular adsorption.

Fig. 6 Absorption spectrum of dissociativel chemisorption

Table 1. Total atomic charge and bond order at the ground state and with CIS method

model	molecule	sum of total atomic charge			chemical bond	bond order		
		ground state in RHF	excited state with CIS	deviation		ground state	excited state	deviation
(a)			(380 nm)					
	H_2O	0.082	0.086	-0.004	HO-H	0.813	0.812	-0.001
	TiO_2	-0.082	-0.086	0.004	$Ti\text{-}OH_2$	0.032	0.030	-0.002
(b)			(389 nm)					
	OH	-0.581	OH -0.336	-0.244	$Ti\text{-}OH_b$	0.776	0.766	-0.010
	H	0.338	H 0.225	0.114	$O\text{-}H_t$	0.807	0.813	0.006
	TiO_2	0.243	TiO_2 0.112	0.131				
			(402 nm)					
			OH -0.586	0.005	$Ti\text{-}OH_b$	0.776	0.773	0.003
			H 0.330	0.008	$O\text{-}H_t$	0.807	0.805	0.002
			TiO_2 0.256	-0.013				

* Chemical bonds OH_b and OH_t mean the bridge OH and terminal OH respectively.

of $O\text{-}H_t$ stronger $O\text{-}H_t$ at the ground state with ones at the excited state. We may, thus, describe that the electronic In the second excitation energy at 401.7nm, it can be seen from Table 1 that   there are also slight deviations in comparison of the total charge of (OH, H, and TiO_2), and bond order of $Ti\text{-}OH_b$, and state in this chemisorption type depends mainly upon that at the ground state, although it involves a slight amount of the electronic state at the excited state.

CONCLUSIONS

Our *ab initio* RHF MO calculations at the ground state indicated that the stabilization energy (88.2 kJ/mol) of dissociative adsorption model is more stable than that (28.5 kJ/mol) of molecular adsorption model, as described in previous *ab initio* studies by others.

We can conclude from the MO calculations at the ground state and with CIS method that the electronic state in the molecular adsorption (Ti-site···OH_2) type depends mainly upon that at the ground state, although it involves a slight amount of the electronic state at the excited state. For the dissociative chemisorption (Ti-site···OH^-) model,in the first excitation energy at 389.3 nm, electron transfer occurs from the OH to this surface in the excited state, and from the differences of the bond order for $Ti\text{-}OH_b$, and $O\text{-}H_t$, we found that at the excited state the bond of $Ti\text{-}OH_b$ is weaker, while that of $O\text{-}H_t$ stronger.

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