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Density functional study of the primary events on TiO_2 photocatalyst

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Density functional calculations at the B3LYP/6-311G**//B3LYP/6-311G level of theory were used to study the initial process of ethylene degradation on the TiO_2 photocatalyst by adopting the dimeric titanium structure $Ti_2O_6H_4$ as a model of the catalyst surface. Adsorption energies of water and ethylene were calculated to be 31.9 and 20.4 $kcal\,mol^{-1}$. The photogenerated OH radical does not desorb from the catalyst surface and the further reaction with ethylene proceeds since the adsorption energy was estimated to be 39.3 $kcal\,mol^{-1}$. Our calculation also indicated that under steady illumination, ethylene directly attacks the OH radical bound to the TiO_2 surface even though the surface has vacant sites available for ethylene adsorption.

Keywords: density functional theory, titanium oxide, photodegradation, ethylene

1. Introduction

Much attention has been focused on photocatalytic oxidations of organic compounds over illuminated TiO_2 in order to establish systems remediating contaminated groundwaters [1]. On the TiO_2 surface in the gas phase, photogenerated holes oxidize OH^- ions and/or water molecules to yield OH radicals which can react with most volatile organic compounds (VOCs). The generation of OH radicals on the TiO_2 surface has been also reported upon irradiation of aqueous solutions by use of the spin-trap method of electron paramagnetic resonance [2].

Most studies regarded the TiO_2 as the source producing OH radicals and the adsorption sites for heterogeneous processes [3]. It is commonly accepted that the OH radicals on the surface react with adsorbed contaminants. In spite of various efforts, however, the detailed mechanism of the degradation of VOCs on the TiO_2 surface remains unclear. This is because there is little information concerning the interaction between VOCs and the TiO_2 surface.

In previous papers, we reported photodegradation experiments of gaseous trichloroethylene (TCE) on porous TiO_2 pellets and discussed the reaction mechanism by using *ab initio* molecular orbital (MO) calculations [4]. We treated the reaction as homogeneous without considering the interaction between intermediates and the TiO_2 catalyst surface. We have recently found that the photocatalytic activity for the degradation of ethylene was quite different from that of TCE [5]. This finding forced us to extend our theoretical investigation involving the effect of the catalyst surface.

There are some published papers which describe theoretical studies of the surface of TiO_2. Horsley examined the titania–platinum interaction with TiO_6^{8-} and TiO_5^{6-} models by Xα-SW-SCF calculations [6]. Hagfeldt et al. used *ab initio* MO theory at the STO-4G* level to investigate electronic structures of $(TiO_2)_n$ clusters ($n = 2$, 3) [7]. Kobayashi and Yamaguchi studied the CO adsorption on surface models of Ti_3O_6, Ti_4O_8 and Ti_5O_9 with split-valence basis sets [8]. Minot and his coworkers adopted a model surface which has one-dimensional planar structure containing titanium atoms with tetracoordination of equatorial oxygens and investigated the adsorption of NH_3 or CO on TiO_2 [9]. Recently, density functional theory (DFT) adopting the pseudopotentials was applied to exploring the nature of oxide surfaces and the interaction between the surface and adsorbates [10]. These studies represented the oxide surface as a slab of infinite thickness with periodic boundary conditions. The adsorption energy of CO calculated on the TiO_2 surface was in good agreement with that evaluated using temperature-programmed desorption (TPD) experiments [11].

In the photodegradation of organic compounds on the TiO_2 photocatalyst, it has been often postulated that the photogenerated holes react with adsorbed water molecules to form OH radicals which oxidize organic compounds. Thus, two adsorption sites, one for the OH radical and the other for an adsorbate, are required to simulate the photocatalytic reaction on the surface. In the present work, we treated the initial process of ethylene degradation by using the method based on DFT. Although the slab model has more resemblance to the actual TiO_2 surface, we estimated the interactions between reactants and the surface by using a dimeric titanium compound, as shown in figure 1.

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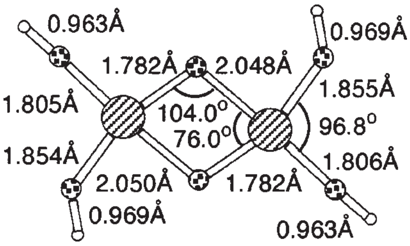

Figure 1. Optimized structure of surface model, $Ti_2O_6H_4$.

As will be discussed later, the simple model gives a good, qualitative description of the adsorption feature.

2. Computational procedures

The GAUSSIAN94 program was used for all the calculations [12]. We employed the DFT method using Becke's three-parameter functional combined with the Lee–Yang–Parr correlation functional (B3LYP) [13]. The usage of the method makes it possible to consider electron correlation effects which were not included in our previous calculations and there are many successful applications to various radical systems [14]. The calculations were performed by using the 6-311G basis set, where Wachters–Hay basis set was used for Ti [15]. Figure 1 displays the fully optimized geometry of $Ti_2O_6H_4$ as a model which has a planar geometry with two bridging oxygen atoms and four OH^- ions. All the other compounds were optimized on the model surface, i.e., the $Ti_2O_6H_4$ fragment which was kept fixed. For a better energy description, we calculated B3LYP/6-311G**//B3LYP/6-311G energies and used them for discussion.

3. Results and discussion

Ethylene, water, OH and C_2H_4OH radicals were optimized on the model surface. Table 1 lists the total energies and bond lengths in the optimized structures.

The two Ti–C distances in ethylene on the surface were calculated to be 2.717 and 2.698 Å. Figure 2 displays the isodensity surface of the 52nd MO of the surface with C_2H_4.[1] We can observe the interaction between the π orbital of ethylene and the d_{z^2} orbital of Ti. These geometrical and electronic features indicate the existence of π-donation from ethylene to Ti.

Equation (1) defines the adsorption energies (E_{ads}) for each adsorbate X,

$$E_{\mathrm{ads}} = E_{\mathrm{X}} + E_{\mathrm{TiO_2}} - E_{(\mathrm{X\text{–}TiO_2})} \qquad (1)$$

where E_{X}, $E_{\mathrm{TiO_2}}$, and $E_{(\mathrm{X\text{–}TiO_2})}$ denote total energies of the isolated X, the surface model and the complex which has adsorbate(s) on the surface, respectively. Table 2 lists the total energies in vacuum and adsorption energies on the surface of H_2O, C_2H_4, OH and C_2H_4OH radical.

Table 1

Total energies in hartrees, and bond lengths in Å for the optimized structures on the model surface.

Adsorbate	Total energy (hartree)		Bond length (Å)	
	B3LYP/6-311G	B3LYP/6-311G** //B3LYP/6-311G	Ti–O	Ti–C
H_2O	−2229.47526	−2229.58542	2.121	–
C_2H_4	−2231.62141	−2231.73456	–	2.698, 2.717
OH	−2228.79829	−2228.90492	2.008	–
C_2H_4, OH	−2307.41971	−2307.55086	2.022	2.686, 2.718
C_2H_4OH	−2307.43936	−2307.57466	2.126	2.555

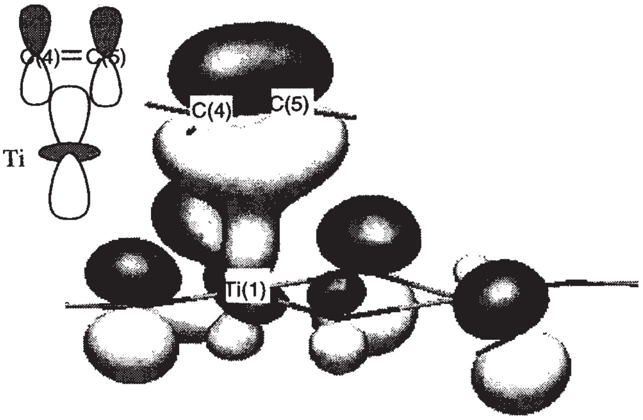

Figure 2. Isodensity surface of the 52nd MO indicating electron donation from the π orbital of ethylene to the d_{z^2} orbital of Ti.

The adsorption energy for water was calculated to be 31.9 kcal mol^{-1}. Hungenschmidt et al. studied the interaction of water with rutile $TiO_2(110)$ surfaces with TPD and reported that the heat of adsorption of molecularly adsorbed water at the Ti^{4+} site was estimated to be 17.0–2.1θ (kcal mol^{-1}), where θ is the surface coverage ranging from 0 to 1. This value is smaller by 14.9–17.0 kcal mol^{-1} than the calculated value.[2] A similar result was reported by Markovits et al. for a tetracoordinated Ti system. They calculated the adsorption energy to be 36.6 kcal mol^{-1} by using the PS-31G basis sets on a one-dimensional polymer structure. They also described the double polymer model, whose surface has pentacoordinated titanium atoms, lowers the adsorption energy. Although the tetracoordinated titanium atoms tend to overestimate the energy, the trends remain the same whether the fifth ligand of Ti exists or not.

The adsorption energy for ethylene was calculated to be 20.4 kcal mol^{-1}, which is smaller than that for water by 11.5 kcal mol^{-1}. Thus, water adsorbs more strongly on TiO_2 than ethylene. This is consistent with the experimental findings with TPD by Larson and Falconer [16]. They employed TiO_2 powder for TCE degradation and observed that water was strongly bound to TiO_2 while TCE weakly adsorbed. Ethylene would be more weakly bound to the

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[1] Win MOPAC Ver.2 (Fujitsu) was used to draw the isodensity surface.

[2] Larson et al. estimated the binding energy of TCE on TiO_2 surface to be ca. 23.9 kcal mol^{-1} by TPD experiments. They stated that TiO_2 powders bind water stronger than TCE, i.e., the adsorption energy of water should be larger than that of TCE. See [16].

Table 2
Total energies of free species in hartrees and their adsorption energies on the model surface in kcal mol^{-1}.

	Total energy[a] (hartree)		Adsorption energy[a] (kcal mol^{-1})	
	6-311G	6-311G**	6-311G	6-311G**
H_2O	−76.41593	−76.44740	37.6	31.9
C_2H_4	−78.59178	−78.61489	19.0	20.4
OH	−75.73610	−75.75518	39.4	39.3
C_2H_4OH	−154.36419	−154.41591	47.6	45.0
$Ti_2O_6H_4$	−2152.99935	−2153.08711		

[a] 6-311G and 6-311G** denote the energies calculated by the B3LYP/6-311G and B3LYP/6-311G**//B3LYP/6-311G levels of theory, respectively.

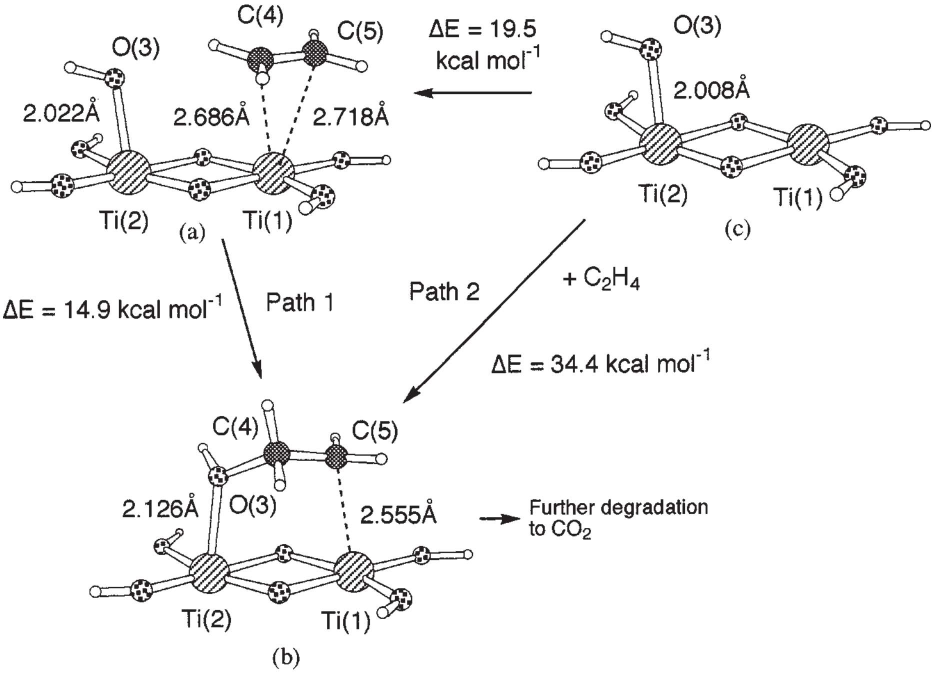

Figure 3. Energy changes and optimized geometries of the related complexes for the ethylene degradation.

surface than TCE. Because of such strong adsorption feature of water, high humidity in the reactant gas streams causes a significant reduction in the rate of photooxidation of ethylene on the TiO_2 photocatalyst, as observed in [5,17]. This result also explains why the photocatalytic activity of TiO_2 decreases dramatically in aqueous solution in comparison with that in the gas phase [18].

It has been often argued whether the oxidation reactions of VOCs occur on the catalyst surface or in the bulk. The adsorption energy evaluated for OH radicals was 39.3 kcal mol^{-1}, that is, the radical adsorbs stronger than water by 7.4 kcal mol^{-1}. It is unlikely that the produced OH radicals diffuse into the bulk.

As dynamic equilibrium is achieved between the gas phase and the solid surface in the initial conditions of our experiments [5], both ethylene and water occupy Ti sites on the surface before irradiation. Photoillumination to TiO_2 first produces an OH radical, whose optimized geometry on the surface is displayed in figure 3(a). The OH radical reacts with adjacent ethylene to generate a C_2H_4OH radical (Path 1), which is degraded further to carbon dioxide. The radical formation was calculated to be exothermic by 14.9 kcal mol^{-1}.

The O(3) in the C_2H_4OH radical binds to Ti(2) with a bondlength of 2.126 Å, as shown in figure 3(b). The other Ti(1) interacts with the terminal carbon C(5) because the Ti(1)–C(5) length is 2.555 Å. The spin density turned out to be localized on C(5), as expected. The adsorption energy of the C_2H_4OH radical was calculated to be 45.0 kcal mol^{-1} which is larger by 24.6 and 13.1 kcal mol^{-1} than those for ethylene and water, respectively. The reactants in the gas phase cannot replace the radical, so that further oxidation proceeds on the surface.

There is an alternative route to forming the C_2H_4OH radical (Path 2). Ethylene in the gas phase directly attacks the OH radical on the TiO_2 surface (figure 3(c)). The C–O bond formation is exothermic by as much as 34.4 kcal mol^{-1}, which is larger by 14.9 kcal mol^{-1} than the adsorption energy of ethylene on the vacant Ti site (19.5 kcal mol^{-1}). Therefore, the direct attack of ethylene to the OH radical is preferred to its adsorption to the Ti site. While Path 1 proceeds immediately after the photo-excitation, as discussed above, the calculated results indicate that Path 2 preferably occurs under illumination.

The direct attack competes with the reaction of the OH radicals and water molecules in the gas phase. Therefore, at high water vapor content, water molecules in the gas phase prevent ethylene from attacking the OH radicals. We observed, the degradation of ethylene was significantly dependent on the water vapor content in the reactant gas stream [5].

It is necessary to gather knowledge of the behavior of reactants on the catalyst surface in order to understand the mechanism in detail. We are currently investigating another Ti model, $Ti_2O_8H_6$, with addition of OH^- ions in the *trans* position to make two five-coordinated Ti.

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