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Computational modeling of the adsorption and photodegradation of 4-chlorophenol on anatase TiO_2 particles

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ABSTRACT

In the present work, the adsorption and photodegradation of 4-chlorophenol (4-CP) on the (100) surface of TiO_2 anatase with semiempirical SCF MO method MSINDO has been investigated. The (100) surface is modeled with free clusters $(TiO_2)_n$, where $n = 20–80$. The surface lattice titanium atoms, which are Lewis acid sites, are considered as adsorption sites. Molecular dynamics (MD) simulations have been used for the investigation of 4-CP adsorption conformations and the surface reaction mechanism studies. The 4-CP molecule has revealed parallel adsorption upon optimization, whereas under excitation conditions the perpendicular configuration is dominant. The aromatic ring cleavage by atomic oxygen has been studied computationally and accordingly, the relevant mechanism was suggested. By comparison with experimental and other theoretical calculations, it is shown that MSINDO can reproduce literature data with acceptable accuracy.

1. Introduction

The adsorption of phenolic compounds on TiO_2 surfaces is generally governed by several parameters [1]. The inductive or mesomeric effect of the substituted groups on the aromatic ring plays a significant role in the degree of adsorption of these molecules [2]. Rodriguez et al. [3] have stated that the molecules possessing electron donor groups, and particularly those with high ionic contribution to bonding, adsorb to a great extent on oxides surfaces.

There is some evidence to indicate that the degradation of an organic moiety occurs on the surface of the photocatalyst [4,5]. It is therefore logical to expect that the adsorption of the organic molecule is an important factor in determining the photocatalytic degradation rates [6,7].

The adsorption of aromatic substrates on TiO_2 surfaces, usually, exhibits different geometries. Some researchers [8,9] have found a perpendicular conformation of the benzene ring on the surface for the chemisorptions of benzoic acid [8] and 4-chlorophenol [9]. Whereas, Robert et al. [1], in their diffuse reflectance fourier infrared spectroscopic (DRIFT) study of phenol and *p*-nitrophenol chemisorptions, have concluded the possibility of a parallel adsorption of the aromatic ring.

A number of studies have shown that the oxidizing species other than the ·OH radical can also contribute to the reactivity in the photocatalysis systems. Li et al. [10,11] suggested that the ring opening reactions are induced by single electron transfer from the aromatic compound to the TiO_2 surface, rather than hydroxyl type chemistry. In electrochemically assisted photocatalysis of 4-Chlorophenol (4-CP), Vindogopal et al. [12] have noticed that the photocatalytic disappearance of 4-CP is significantly retarded in the absence of an electron scavenger such as O_2, and pointed out that hydroxyl radical may not be exclusively responsible for the photooxidation of 4-CP, and the role of oxygen is more than that of merely an electron scavenger.

As long as the nature of chemisorbed oxygen on TiO_2 is important in understanding the chemistry that is taking place on TiO_2 surface, Teichner and Formenti [13] have reported that the presence of holes (h^+) could split adsorbed oxygen into atoms as follows:

$$O_2(g) \leftrightarrows O_2(ads) \quad (1)$$

$$O_2(ads) + h^+ \rightarrow O(ads) + O(ads) \quad (2)$$

Some theoretical studies [14,15] have supported the above approach by concluding that the barrier to dissociation of O_2 is on the order of 1 eV. As a result, the dissociative adsorption of O_2 is entropically favoured [16].

The photoactive neutral atomic oxygen species (O), which is also known in the literature as O (^3P), is classified as a highly selective and important oxidant [17]. Chia et al. [18] have stated that O (^3P) reacts with aromatic compounds through addition reactions.

A study of the scope of a complicated surface reaction mechanism [19] is not feasible with ab initio or density functional theory (DFT) methods. As a compromise between the accuracy and

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feasibility, the semiemperical MSINDO method has been selected for our calculations.

2. Computational method

The quantum chemical model calculations are performed with the semiempirical MO method MSINDO, which is extensively documented for the first, second row elements [20,21] and the third row transition elements [22]. The transition metal atoms are described by a pseudo minimal Slater basis set (3d,4s,4p) and the first row elements have a (2s,2p) basis set with different Slater exponents for intra- and inter-atomic integrals comparable to the Pople 6-31G basis set. Inner shells are taken into account by a pseudo potential after Zerner [23]. Molecular dynamics (MD) has been used for the studying of the dynamics of certain cluster–substrate models (increase the kinetic energy of the atoms at constant temperature). Constant temperature dynamics are performed using Nosé-Hoover-Chain (NHC) thermostat.

The adsorption energies (E_{ads}) for different adsorption modes have been computed from the quantum chemical total energies of the cluster–substrate system, $E^{cluster-substrate}$, the substrate, $E^{substrate}$ and the cluster, $E^{cluster}$according to the following expression [24];

$$E_{ads} = E^{cluster-substrate} - (E^{substrate} + E^{cluster}) \quad (3)$$

A negative value for E_{ads} therefore, designates a stabilization of the cluster–substrate system due to adsorption.

3. Results and discussion

3.1. Cluster models of the anatase bulk and surfaces

The conventional unit cell of the anatase phase contains 12 atoms, i.e., four TiO_2 units [25] (Fig. 1). The titanium atom (Ti^{4+}) is surrounded by six oxygen atoms (O^{2-}) at the corners of a slightly distorted octahedron and each O^{2-} is surrounded by three Ti^{4+} lying-in a plane at the corners of an equilateral triangle [26].There are two different Ti–O distances in these octahedra.

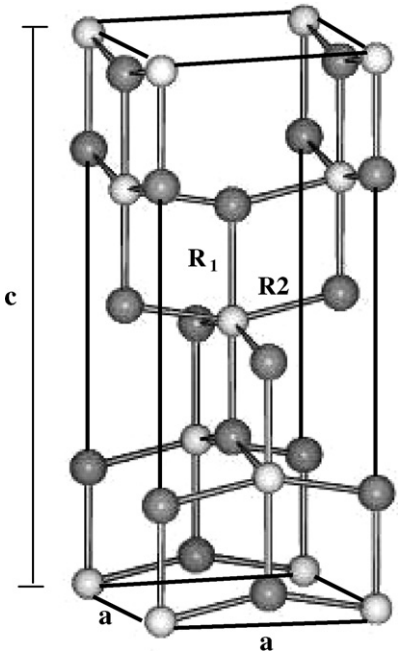

Fig. 1. TiO_2 conventional unit cell in the anatase structure. Light spheres represent titanium atoms and the dark spheres represent oxygen atoms.

(a) A long one involving the two oxygen atoms directed along the c crystallographic axis (apical oxygen), which is labeled R_1.
(b) A short one, R_2, with the four equatorial oxygens left.

Before adoption of the generated cluster models for the adsorption and photocatalysis processes, the accuracy of the approach has been investigated by comparing calculated anatase bulk properties and heats of atomization with accurate literature data.

For the characterization of model clusters used for bulk simulations, Jug and Geudtner [27] introduced a relative average coordination number (K), which was subsequently used in the studies of ionic compounds [28].

$$K = \sum_I \frac{N_I^C}{N_I^B} \quad (4)$$

The summation is performed overall cluster atoms I; N_I^C and N_I^B are the coordination numbers of the atoms in the cluster and the bulk, respectively.

Fig. 2 illustrates the modeled structures of $Ti_{20}O_{40}$, $Ti_{21}O_{42}$, $Ti_{36}O_{72}$, $Ti_{42}O_{84}$, $Ti_{54}O_{108}$ and $Ti_{80}O_{160}$, free clusters, respectively. One of these clusters ($Ti_{36}O_{72}$) will be, after saturation with dissociative water molecules, the basis for the adsorption and photodegradation mechanistic studies described later on in the present work.

Table 1 presents explicitly that the extrapolated bulk value ($K = 1$) of 2000 kJ/mol obtained with the present MSINDO, is 105 kJ/mol higher than the value of 1895 kJ/mol for the heat of atomization ΔH_a obtained from experimental data [29].The absolute value of this MSINDO deviation is similar to that of the DFT B3LYP method for this system, −115 kJ/mol, as obtained from periodic boundary calculations [30]. Furthermore, another MSINDO calculation with the cyclic cluster model gave an extrapolated binding energy per TiO_2 unit (E_{Bu}) value of 2014 kJ/mol [31], which is slightly more than that obtained in this work. From this, it can be concluded that the deviation from experiment is not an effect of the cluster model but a consequence of the approximations in the MSINDO method. In the same manner, it could also be seen from Table 1 that the accuracy of MSINDO calculation, in which the experimental ΔH_a was approximated as E_{Bu}, from the literature value for TiO_2, is in the range of 5.5%. Moreover, a systematic increase in binding energy by increasing the cluster size has also been noticed. This phenomenon is mainly attributed to higher number of Ti–O bonds and the enhanced electronegativity due to the increased number of oxygen atoms [32].

The optimized apical and equatorial Ti–O distances are exhibited in Table 2. The experimental bulk values [24] are also presented for comparison purpose, and the differences between the calculated bond lengths for the optimized minimum energy structures and the corresponding bulk values become smaller with increasing cluster size. The extrapolated cluster values (for $K = 1$) agree well with the corresponding literature values with average deviation of 1.69%. Moreover, for the present cluster models the experimentally observed relation $R_1 > R_2$ is reproduced by MSINDO calculations. The error of MSINDO R_1(−0.032Å) and R_2 (−0.034Å) are comparable to those of recent periodic boundary calculations at GGA-DFT (Generalized Gradient Approximation) level [33] for R_1 (+0.014Å) and R_2 (+0.026Å).

For the present bulk anatase free clusters, the average deviation of MSINDO calculations from the literature values is 5.5% for ΔH_a and 1.69% for the geometry, which are reasonable for a semiempirical technique. Moreover, these are similar to the errors in energy and geometry previously reported for bulk NaCl and MgO in MSINDO calculations [20,21]. Thus, the present approach reproduces results of experiments and high level calculations with satisfactory accuracy, which is an important pre-requisite for any adsorption studies.