



Removal of nitric oxide by the highly reactive anatase TiO₂ (001) surface: A density functional theory study



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ABSTRACT

In this paper, density functional theory (DFT) calculation was employed to study the adsorption of nitric oxide (NO) on the highly reactive anatase TiO₂ (001) surface. For comparison, the adsorption of NO on the (101) surface was also considered. Different from the physical adsorption on the (101) surface, NO molecules are found to chemisorb on the TiO₂ (001) surface. The twofold coordinate oxygen atoms (O_{2c}) on the anatase (001) surface are the active sites. Where NO is oxidized into a nitrite species (NO₂) trapping efficiently on the surface, with one of the surface Ti_{5c}–O_{2c} bonds adjacent to the adsorption site broken. Our results, therefore, supply a theoretical guidance to remove NO pollutants using highly reactive anatase TiO₂ (001) facets.

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1. Introduction

Nitrogen oxides (NO_x) are considered as one of the major air pollutants that can cause acid rain, photochemical smog, and health problems [1,2]. Removing NO_x, especially NO (the primary product), before emission has always been a worldwide concern [3,4]. Among various methods, photocatalytic conversion of NO on TiO₂ photocatalyst is an attractive technology [5–7]. However, the conversion efficiency has been relatively low and the mechanism involved is still unclear [8,9]. Thus the study of NO adsorption mechanism on the surface of TiO₂ is needed to enhance the efficiency of their removal and conversion.

The key step of the removal or conversion of NO molecules is their efficient trap by catalyst surfaces in the treatment processes [10,11], which can not only reduce NO concentration in the environmental atmosphere, but also provide chances for further conversion of NO molecules. Consequently, the catalysts, which can activate or trap NO efficiently, are imminently expected. According to the available data [12–18], thermally stable surfaces without modifications, such as deposition, defects and hydrogenation, cannot efficiently trap NO molecules. It has been demonstrated that

NO molecules can only weakly physisorb on the stoichiometric rutile (110) surface, which is one of the thermally stable surfaces of TiO₂ [12–16]. And the adsorption of NO on the other thermally stable surface, anatase (101), is also weak (0.35 eV for ON–Ti_{5c} bonding mode [17]). Such weak adsorption is due to the relatively low reactivity of these thermally stable surfaces. To this end, another reactive surface of anatase TiO₂, (001), which has been successfully synthesized recently [18–21], should be a promising candidate.

The (001) surface has been found to be highly reactive in photocatalytic decomposition of various harmful organic compounds, such as trimethyl acetate [22], acetone [23,24], and methyl orange [24]. Whether the highly reactive surface can bring different phenomenon in NO_x conversion is worthy to be detected. In fact, some experimental studies have revealed that NO_x can be oxidized by anatase TiO₂ to form products, such as nitrite and nitrate species [25–27]. Hashimoto et al. have ever found that NO adsorption on the anatase TiO₂ caused the interaction between nitrosyl species and the surface oxygen atoms, which led to the formation of bidentate nitrate [25]. A similar bidentate nitrate was also observed after NO₂ adsorption on anatase TiO₂ surfaces [26]. In infrared (IR) spectroscopy study, Hadjiivanov et al. [27] found the formation of both N₂O and nitro compounds in the adsorption of NO on P-25 (75% anatase and 25% rutile). Considering rutile TiO₂ can usually introduce reduced product of N₂O according to the previous studies

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[12–15], the oxidation product of nitro compounds should probably be formed on the anatase TiO₂. In fact, several researchers have disclosed the prominent ability of anatase (001) surface in the oxidation of NO recently [28–30]. While on the theoretical side, the work on the NO adsorption on the anatase surfaces is rare, and the oxidation product of NO (nitrite or nitrate species) has not been verified to date. Mguig et al. [31] have found that NO is physically adsorbed on both of the Ti_{5c} and O_{2c} sites on the anatase (001) surface through density functional theory (DFT) calculations. And they proposed that nitrite or nitrate species can be formed if there are more reactive oxygen atoms, such as onefold coordinated oxygen (O_{1c}), on the surface. Wanbayer et al. [17] also gave a relatively low adsorption energy (0.48 eV) for ON–Ti_{5c} bonding mode on (001) surface. Therefore, there is an experiment–theory discrepancy. To explain such discrepancy, further study is still necessary. In this paper, DFT calculations were performed to investigate the adsorption of NO on the highly reactive anatase (001) surface.

2. Computational method

In this paper, all geometrical structures are optimized using DMol3 [32,33] package in Material Studio. Exchange–correlation function is constructed by Perdew–Bruke–Ernzerhof (PBE) of generalized gradient approximation (GGA) [34]. The double-numeric-quality basic set with polarization functions (DNP) [35] is adopted to describe the valence orbital of the atoms. The core electrons are substituted by DFT semi-core pseudopotentials (DSPPs) [36]. The geometries are considered to be converged until the energy dropped below 2.0×10^{-5} Ha/atom, the force dropped below 0.004 Ha/Å and the max displacement dropped below 0.005 Å.

The anatase TiO₂ (001) and (101) surfaces were simulated by the periodic (2 × 2) slab models with four O–Ti–O layers as shown in Fig. 1a and b. During the geometric optimization processes, the Monkhorst–Pack k-point meshes of 3 × 3 × 1 and 2 × 3 × 1 were adopted for the (001) and (101) surfaces, respectively. When the geometries were optimized, the two bottom layers were fixed equivalent to bulk structure, while the rest atoms were allowed to relax freely. There are two adsorption sites on the (001) surface (see Fig. 1a), including fivefold coordinated Ti (denoted as Ti_{5c}) and twofold coordinated O (O_{2c}). On the (101) surface (see Fig. 1b), Ti_{6c}, Ti_{5c}, O_{3c} and O_{2c} are exposed. Generally, undercoordinated atoms are active sites. Thus, only adsorption of NO on the Ti_{5c} and O_{2c} sites has been considered here. The adsorption energy E_{ads} was calculated as following [37–39],

$$E_{\text{ads}} = E_{\text{NO}} + E_{\text{surface}} - E_{\text{NO/surface}}$$

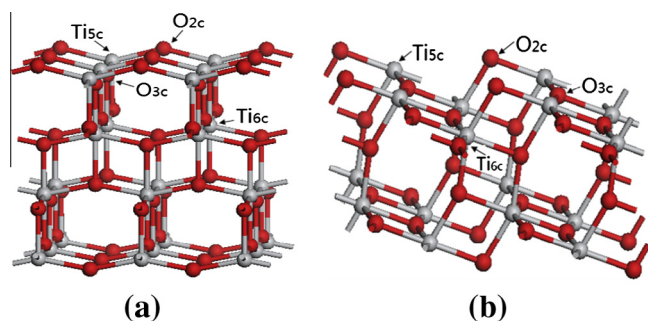


Fig. 1. Slab models of clean anatase TiO₂ surfaces: view along the [010] direction. (a) The (001) surface, (b) the (101) surface. Gray and red spheres represent Ti and O atoms, respectively. The slabs are used throughout this paper. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

where E_{NO} is the energy of an isolated NO molecule, E_{surface} is the energy of clean (001) or (101) surface slab, and $E_{\text{NO/surface}}$ is the total energy of the surface with NO adsorption. According to this equation, a positive value of E_{ads} indicates a favorable process.

3. Results and discussion

In order to verify the accuracy of the calculation methods, full optimizations of pure anatase TiO₂ structure and an isolated NO molecule were carried out firstly. A $5 \times 5 \times 2$ k-point mesh was used for bulk TiO₂. And a $10 \times 10 \times 10 \text{ \AA}^3$ unit cell was used for NO molecule. The calculated parameters of the anatase TiO₂ structure and the bond length of NO molecule are listed in Table 1. The calculated results are in good agreement with previous theoretical [28,40] and experimental [41,42] values, indicating that our calculation method is appropriate to produce reasonable results.

3.1. Adsorption of NO on anatase TiO₂ (001) surface

Previous studies showed that the adsorbed NO molecules are usually perpendicular to the TiO₂ surfaces [13–17]. To this end, three configurations were considered with NO molecules perpendicular to the (001) surface in this study. The optimized adsorption configurations are given in Fig. 2. In one configuration, the N atom of the NO molecule interacts with the surface O_{2c} atom (denoted as ON–O_{2c}, the same in hereafter). In other two configurations, the N or O atom of the NO molecule adsorbs on the Ti_{5c} site (ON–Ti_{5c} and NO–Ti_{5c}).

3.1.1. NO adsorption on the O_{2c} site (ON–O_{2c})

In the ON–O_{2c} configuration (Fig. 2a), both of the surface and the NO molecule are relaxed significantly after the adsorption. The surface O_{2c} is dragged out obviously from the surface plane to bind with the N atom of NO molecule, which causes one adjacent Ti_{5c}–O_{2c} bond broken, with the bond length elongated from 1.929 Å to 3.242 Å. This manifests chemisorption occurring. The adsorption energy of this configuration is 0.80 eV (see in Table 2), which is much higher than that reported on perfect and hydrogenated rutile (110) surface (0.45 eV [14], 0.40 and 0.64 eV [16], respectively). The phenomena of dragging low-coordinated O_{2c} out of the surface and breaking the adjacent Ti_{5c}–O_{2c} bond are also observed during the adsorption of other molecules on the anatase (001) surface, such as methanol [43], dimethyl methylphosphonate (DMMP) [44], HCHO [45], H₂O [46], and 2-propanol [47]. It confirms the high reactivity of the anatase (001) surface.

After adsorption, the N–O bond in the NO molecule is elongated from 1.154 Å to 1.259 Å. At the same time, the newly formed N–O_{2c} bond length is 1.268 Å. The similar lengths of these two N–O bonds indicate the formation of a new unity of NO₂ species. Meanwhile, the bond lengths (1.259 and 1.268 Å) of the NO₂ species are close to the N–O bond length in the isolated HNO₂ molecule (1.236 Å), and far from the corresponding N–O bond length of the NO₂ molecule (1.201 Å). The angle of O–N–O_{2c} is 119.9°, which is close to the O–N–O angle of 115.4° of HNO₂ molecules, and smaller than

Table 1

Comparison of the calculated structure parameters of TiO₂ anatase and bond length of NO with previous studies.

System	Parameters	This work	Ref. [28]	Ref. [37]	Exp. [38,39]
Anatase TiO ₂	a (Å)	3.776	3.763	3.801	3.782
	c (Å)	9.486	9.593	9.711	9.502
	c/a	2.512	2.549	2.555	2.513
	u	0.208	0.2065	0.207	0.208
	d_{NO} (Å)	1.154	1.174		1.150 [39]

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