



Cite this: *Environ. Sci.: Nano*, 2017, 4, 2388

Structure–activity relationship of surface hydroxyl groups during NO₂ adsorption and transformation on TiO₂ nanoparticles†

Chang Liu,^{‡ab} Qingxin Ma,^{‡ac} Hong He,^{‡*ac} Guangzhi He,^{‡a} Jinzhu Ma,^{ac} Yongchun Liu^{ac} and Ying Wu^a

The role of hydroxyl groups (OH) is significant in understanding the surface reactions on oxides. Here we combined spectroscopic experiments and theoretical calculations to reveal the role of OH in the heterogeneous reactions of NO₂ on TiO₂ nanoparticles with various crystal structures. The interaction between OH and NO₂ was determined to be a critical step, giving rise to the formation of surface HNO₃. HNO₃ was found to be either a stable product on amorphous TiO₂, or an important intermediate of nitrate on anatase TiO₂ due to its further reaction with nearby OH. The lack of surface OH on rutile limited its reactivity toward NO₂. This study presents clear evidence that the reactivity of TiO₂ toward NO₂ greatly depends on the surface OH as well as the crystalline form. Considering the ubiquitous presence of TiO₂ nanoparticles in catalysts and in natural environments, our results could provide insights helpful to future research in both environmental catalysis and atmospheric chemistry.

Received 30th September 2017,
Accepted 1st November 2017

DOI: 10.1039/c7en00920h

rsc.li/es-nano

Environmental significance

With the increasing interest in the removal of NO_x (NO and NO₂), TiO₂ nanoparticles and TiO₂-based catalysts have been reported to be efficient materials for NO_x abatement. Previous mechanistic studies revealed that hydroxyl groups (OH) are ubiquitous on the TiO₂ surface and could act as reactive sites. However, the role of OH remains controversial due to the multiplicity and complexity of these OH species. In this study, we observed an excellent example illustrating the structure–activity relationship of OH in the adsorption and reaction of NO₂ on TiO₂ nanoparticles. It is demonstrated that the crystal phase of TiO₂ determines the nature of the surface OH, which then determines the reaction pathway of NO₂ on TiO₂. Considering the wide usage of TiO₂ nanoparticles in environmental chemistry, this work could provide a new approach to design TiO₂-based catalysts with superior catalytic performance.

Introduction

Interfaces in natural and anthropogenic oxide particles are usually covered with hydroxyl groups (OH) formed by the dissociative chemisorption of water. These OH groups act as effective adsorptive or reactive sites for adsorbed substances, and can even dominate the activity of these substances. Therefore, the chemistry of OH groups has been a major concern in environmental catalysis and surface chemistry.

The different types of surface hydroxyls are not fully equivalent structurally or chemically. It has been proposed that the types of OH groups on oxides include terminal, bridging, and triple bridging configurations according to their coordination states.¹ Typically, surface OH groups are considered to be basic and nucleophilic, and these properties are greatly dependent on the coordination structure.² Gas probes, such as CO, CO₂, SO₂, pyridine, and so on, have been used to characterize the properties of surface OH groups, and have shown that the terminal OH group may be more basic than the others.² However, the multiplicity and the complexity of hydroxyl groups still present great challenges for research on OH-related reactions. Here, we used the heterogeneous reaction of NO₂ on TiO₂ as a probe reaction to explore the role of different types of OH groups in surface chemistry.

NO₂ plays a key role in atmospheric chemistry. It initiates the photochemical production of O₃ in daytime,³ depletes O₃ and produces NO₃ radicals at night,⁴ leads to the formation of nitric acid and nitrate aerosols,⁵ contributes to the sources of OH radicals *via* forming HONO,⁶ and causes respiratory

^a State Key Joint Laboratory of Environment Simulation and Pollution Control, Research Center for Eco-Environment Sciences, Chinese Academy of Sciences, Beijing 100085, China. E-mail: honghe@rcees.ac.cn; Fax: +86 10 62923563; Tel: +86 10 62849123

^b State Key Laboratory of Severe Weather & Key Laboratory of Atmospheric Chemistry of China Meteorological Administration, Chinese Academy of Meteorological Sciences, Beijing 100081, China

^c Center for Excellence in Urban Atmospheric Environment, Institute of Urban Environment, Chinese Academy of Sciences, Xiamen 361021, China

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c7en00920h

‡ These authors contributed equally to this work.

diseases in polluted regions.⁷ Therefore, the transformation and elimination of NO₂ is of significant environmental and health importance.

With the increasing interest in the removal of NO_x (NO and NO₂), TiO₂, which is a multifunctional material widely used as a heterogeneous catalyst⁸ and photo-catalyst⁹ as well as in solar cells¹⁰ and gas sensors,¹¹ has been reported to be an effective material for NO_x removal. TiO₂-based catalysts have been widely used in the catalytic reduction of NO_x.^{12,13} TiO₂ is also considered an environmentally friendly material and is added to building walls and roads for the efficient photocatalytic removal of NO_x under ambient conditions.¹⁴ Moreover, TiO₂ can alter the cycling of NO_x by providing a medium for heterogeneous and photochemical reactions in the biosphere, since it is an important component of crustal soil and mineral dust.^{15,16} Thus, the adsorption and reaction of NO₂ on TiO₂ surfaces has attracted much attention in both NO_x removal technology and NO_x atmospheric chemistry.

Previous mechanistic studies revealed that both Ti sites^{17–19} and surface hydroxyl groups^{20–23} could be active sites for the NO₂ reaction on TiO₂. A well-accepted mechanism of NO₂ adsorption on TiO₂ *via* Ti sites is as follows. The adsorption of NO₂ on Ti sites leads to the formation of nitrite. Nitrite can then react with another surface nitrite (Langmuir–Hinshelwood type) or gas-phase NO₂ (Eley–Rideal type), resulting in the formation of surface nitrate and gas-phase NO under dark conditions.¹⁸ On the other hand, the surface hydroxyl groups on TiO₂ were also established to be quite active and have a nearly complete reactivity toward NO₂.²² Hydroxyl groups were found to increase the efficacy of the NO₂ reaction by reacting with three NO₂ molecules *via* disproportionation, leaving two nitrate ions and one molecule of NO.^{20–22} Previous infrared spectroscopic studies demonstrated that more than one type of hydroxyl group is consumed during the NO₂ reaction on TiO₂.^{22,23} However, the exact role of each type of OH on the adsorption and reaction of NO₂ on TiO₂ is still not clear.

The present study aims to recognize the multiplicity of surface hydroxyls on TiO₂ and determine the significance of each hydroxyl species in NO₂ adsorption and reaction. The results could give insight into the structure–activity relationship of surface OH groups in OH-related surface reactions at a molecular level.

Experimental section

Preparation and characterization of TiO₂ samples

All samples were prepared from amorphous TiO₂ nanoparticles (206-11272, Wako Pure Chemical Industries, Ltd., with purity of 99.9% and average size of 50 nm) to eliminate the influence of commercial sources. Amorphous nano TiO₂ was used as purchased. Anatase and rutile TiO₂ samples were obtained by calcining amorphous TiO₂ at 873 and 1273 K for 3 h, respectively. The crystalline structure of the obtained samples was characterized using a powder X-ray diffractometer (XRD; X'Pert PRO, PANalytical, Netherlands) with Cu K α

($\lambda = 0.154056$ nm) radiation at 40 kV and 40 mA with scans from 10° to 90° in increments of 0.026°. The surface areas of the samples were measured with a physisorption analyzer (Autosorb-1C-TCD, Quantachrome, USA) by N₂ adsorption–desorption at 77 K. The surface area (S_{BET}) was determined by applying the Brunauer–Emmett–Teller (BET) method to the adsorption isotherm in the range of 0.05–0.35. The BET surface areas of the samples are summarized in Table S1 in the ESI.†

In situ diffuse reflectance infrared Fourier transform spectroscopy (*in situ* DRIFTS) measurements

The heterogeneous reactions of NO₂ on TiO₂ samples were measured by *in situ* DRIFTS (Nicolet 6700, Thermo Fisher Scientific, USA), with an *in situ* diffuse reflection chamber and a high-sensitivity mercury cadmium telluride (MCT) detector cooled with liquid N₂. Before the experiment, TiO₂ samples were finely ground and placed into a ceramic crucible in the *in situ* chamber. The samples were first purged overnight in a stream of synthetic air (80% N₂ and 20% O₂) with a total flow of 100 mL min⁻¹. Then the samples were exposed to 200 ppmv NO₂ balanced with 100 mL min⁻¹ synthetic air for at least 3 h. All treatments and experiments were carried out at room temperature (303 K). The infrared spectra were collected using a computer with OMNIC 6.0 software (Nicolet Corporation, USA). All spectra were recorded at a resolution of 4 cm⁻¹ for 100 scans in the spectral range of 600 to 4000 cm⁻¹. The low frequency cutoff of the spectra was due to the strong lattice oxide absorption of the samples.

Density functional theory (DFT) calculations

All calculations were performed using the Perdew–Burke–Ernzerhof (PBE) functional²⁴ as implemented in the Vienna *ab initio* simulation package (VASP).²⁵ The projector augmented wave method (PAW)^{25,26} was used to describe the interaction between the ions and the electrons.^{26,27} The energy cutoff of the plane wave was taken to be 400 eV. A (2 × 3) supercell of the anatase (101) surface with four stoichiometric TiO₂ layers was used (Fig. 1) and the vacuum gap was set at 20 Å. During geometrical optimization, the NO₂ molecule and the two top TiO₂ layers of the slab were allowed to relax, while the two bottom layers were fixed at their bulk position. Atoms were relaxed until forces were smaller than 0.05

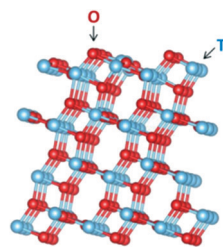


Fig. 1 Anatase (101) surface model used in the DFT calculation. Blue and red balls represent Ti and O atoms, respectively.

eV \AA^{-1} . The Brillouin zone was sampled using a Monkhorst-Pack $2 \times 2 \times 1$ mesh. The Gaussian smearing method with a smearing width of 0.2 eV was employed to accelerate the convergence of integration in the Brillouin zone.

The minimum energy paths (MEP) and transition states of the reactions were calculated using the climbing image nudged elastic band (CI-NEB) method, with a spring constant of 5.0 eV \AA^{-2} to restrain the images on the elastic band.²⁸ The initial structures of the intermediate images (six to nine images in the present calculations) were interpolated linearly from the optimized reactant (initial state) and product (final state) configurations. The vibrational frequencies were calculated using the finite difference approach with a step size of 0.015 \AA .

Results and discussion

Reactions of NO_2 on TiO_2 samples

Reactions of NO_2 on TiO_2 with various crystal structures including amorphous, anatase, and rutile phases were investigated using *in situ* DRIFTS. Anatase and rutile TiO_2 were obtained by calcining amorphous TiO_2 at 873 and 1273 K for 3 h, respectively, as verified by the XRD patterns shown in Fig. 2.

The *in situ* DRIFTS spectra of the TiO_2 samples exposed to NO_2 for 3 h are shown in Fig. 3. The peaks observed in the range of $1200\text{--}1700 \text{ cm}^{-1}$ are due to the formation of surface species, while the negative peaks in the range of $3600\text{--}3800 \text{ cm}^{-1}$ were attributed to the consumption of surface OH groups. Detailed assignments of the surface species are summarized in Table S2.†

The main peaks in the range of $1200\text{--}1650 \text{ cm}^{-1}$, as the characteristic vibrations of nitrate species, implied that nitrates were the dominant surface products on TiO_2 regardless of the crystal structure. This is in accordance with the previous literature on the adsorption of NO_2 on TiO_2 .^{29–31} However, several distinctions exist among the reactions of NO_2 on amorphous, anatase, and rutile TiO_2 . Firstly, the intensities of the nitrate peaks as well as the negative peaks of surface OH on rutile were much weaker than those on amorphous and anatase TiO_2 , suggesting that rutile TiO_2 is less reactive

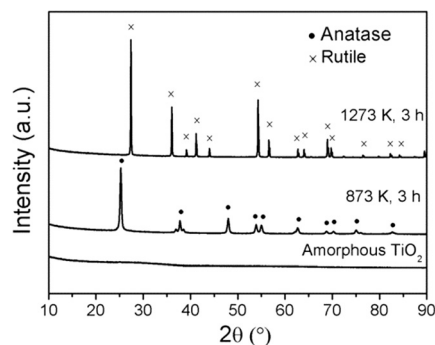


Fig. 2 XRD patterns of TiO_2 samples. Amorphous TiO_2 was used as purchased. Anatase and rutile TiO_2 samples were obtained by calcining amorphous TiO_2 at 873 and 1273 K for 3 h, respectively.

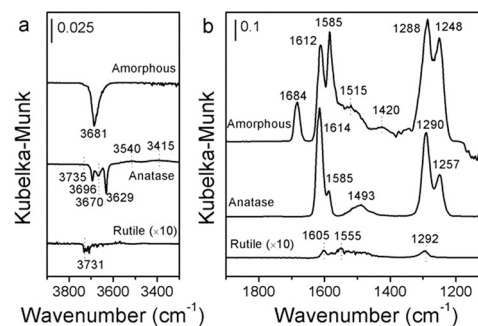


Fig. 3 *In situ* DRIFTS spectra of NO_2 reactions. (a) Consumption of OH groups after 3 h NO_2 reaction on amorphous, anatase, and rutile TiO_2 . (b) Formation of surface species after 3 h NO_2 reaction on amorphous, anatase, and rutile TiO_2 . Reaction conditions: 200 ppmv NO_2 , 303 K, 3 h reaction, total flow of 100 mL min^{-1} (80% N_2 and 20% O_2).

toward NO_2 . This might be due to its small specific surface area ($4.6 \text{ m}^2 \text{ g}^{-1}$), which provided a minimal amount of active sites. Secondly, nitrite, with a band at 1195 cm^{-1} , was observed at the beginning of the reaction and disappeared after the generation of nitrates on amorphous and anatase TiO_2 (Fig. S1†). This is in agreement with the previous finding that nitrite is a critical intermediate for the NO_2 reaction on Ti atoms.¹⁸

In addition, a band near 1684 cm^{-1} was observed only on amorphous TiO_2 . This band could be assigned to surface HNO_3 species rather than nitrate. For instance, two peaks at 1680 and 1310 cm^{-1} were observed in the adsorption of HNO_3 on mineral oxides (such as SiO_2 , $\alpha\text{-Al}_2\text{O}_3$, TiO_2 , $\gamma\text{-Fe}_2\text{O}_3$, CaO , and MgO).^{30,32–34} These two peaks were attributed to the asymmetric and symmetric stretching modes of surface-adsorbed HNO_3 , respectively. In this work, the band at 1310 cm^{-1} could be resolved by spectrum deconvolution fitting analysis (Fig. S2†). Moreover, a stable band at 1684 cm^{-1} was observed in the adsorption of HNO_3 on amorphous and anatase TiO_2 (Fig. S3†), supporting the assignment of this peak to chemically adsorbed HNO_3 on the TiO_2 surface.

Role of H_2O and OH in HNO_3 formation

To our knowledge, this is the first time that the formation of surface-adsorbed HNO_3 has been detected during the NO_2 reaction on TiO_2 under dry and dark conditions. The generation of surface HNO_3 has been found in the reaction of NO_2 on UV-illuminated TiO_2 due to its combination with OH radicals.^{21,35} Since the OH radicals were produced from the photolysis of surface water by UV-illumination, this reaction does not occur under dark conditions and could not contribute to the HNO_3 formation in this work.

Previous studies also showed that the disproportionation reaction between NO_2 and surface-adsorbed H_2O leads to the formation of surface HNO_3 on the hydrated SiO_2 surface.^{36–38} To determine the role of surface water in the formation of HNO_3 on amorphous TiO_2 , the reactions of NO_2 on dehydrated and hydrated amorphous TiO_2 surfaces were compared (Fig. 4). For the hydrated amorphous TiO_2 , the

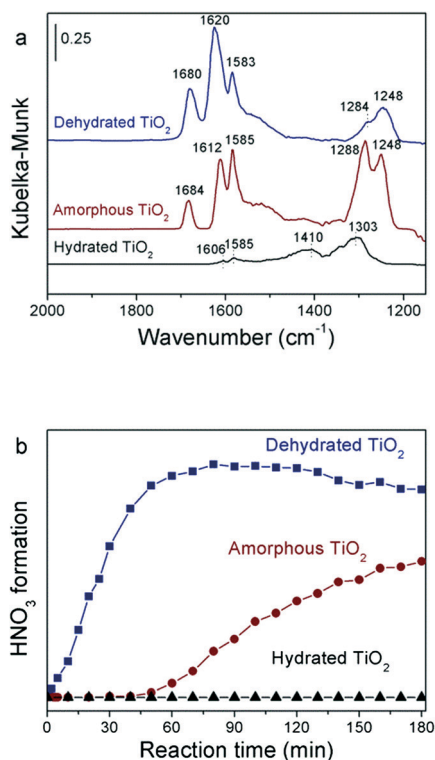


Fig. 4 Effect of surface water on HNO₃ formation on amorphous TiO₂. (a) DRIFTS spectra obtained after 3 h NO₂ reaction on dehydrated amorphous TiO₂, hydrated amorphous TiO₂ and untreated amorphous TiO₂. (b) Comparison of HNO₃ formation during NO₂ reaction on dehydrated amorphous TiO₂, hydrated amorphous TiO₂ and untreated amorphous TiO₂. Dehydrated amorphous TiO₂ was obtained by heating at 423 K for 1 h, and then a dry NO₂ flow was introduced into the system. Hydrated TiO₂ was obtained by water absorption at 30% RH and 303 K for 1 h, and then a humid (30% RH) NO₂ flow was injected into the system. NO₂ reactions were carried out at 303 K for 3 h with a total flow of 100 mL min⁻¹ (80% N₂ and 20% O₂). The formation of HNO₃ was determined from the integrated areas of the HNO₃ bands at 1684 cm⁻¹ (for untreated amorphous TiO₂) and 1680 cm⁻¹ (for dehydrated amorphous TiO₂).

surface was first exposed to a humid air flow with a relative humidity (RH) of 30% for 1 h, and then 30% RH was maintained during the subsequent NO₂ reaction. Dehydrated amorphous TiO₂ was prepared by heating the samples at 423 K for 1 h before NO₂ reaction.

As shown in Fig. 4a, NO₂ reaction on hydrated amorphous TiO₂ leads to the formation of nitrates, in which water-solvated nitrate with bands at 1410 and 1303 cm⁻¹ is the dominant species.^{18,36} The HNO₃ band at around 1680 cm⁻¹ was not detected on this hydrated surface. In contrast, it is clearly seen that HNO₃ (1680 cm⁻¹) formed on the dehydrated amorphous TiO₂ surface. Fig. 4b illustrates that HNO₃ formation on dehydrated TiO₂ was much faster than that on the untreated amorphous sample; meanwhile the amount of HNO₃ was greatly enhanced due to the desorption of surface water. These results verified the inhibiting effect of water adsorption on HNO₃ formation, implying that the disproportionation mechanism between NO₂ and H₂O should not con-

tribute to HNO₃ formation on amorphous TiO₂. In addition, adsorbed water could also lead to the dissociation of HNO₃ on the surface,¹⁶ causing less molecularly adsorbed HNO₃ on hydrated TiO₂.

It should be noted that the formation of surface species was accompanied by the consumption of OH species, as shown in Fig. 3. These OH species should be important active sites for the NO₂ reaction. On amorphous TiO₂, only one OH group with a band at 3681 cm⁻¹ was consumed during the reaction. It is thus considered to be the active site for the formation of both HNO₃ and nitrate. Consumption of peaks at 3735, 3696, 3670, and 3629 cm⁻¹ was detected on anatase TiO₂, indicating that the reaction of NO₂ and OH species was more complicated on the anatase surface. On rutile TiO₂, the slight decrease in the intensity of the OH peak at 3731 cm⁻¹ together with the minimal generation of nitrates implied that the scarcity of active sites (*i.e.* OH groups) might contribute to the weak activity of the rutile surface. To further establish the role of OH species in the NO₂ reaction on TiO₂ samples, theoretical calculations were conducted to identify the structures of surface OH groups and explore the formation mechanism of surface products, especially surface-adsorbed HNO₃.

Types of surface OH groups on TiO₂

Surface OH groups on metal oxides can be generally classified into isolated (or free) OH and hydrogen-bonded OH.^{1,39,40} The difference between them is whether OH interacts with adjacent OH groups *via* hydrogen bonding. According to previous infrared studies, the absorption frequencies of isolated OH groups on TiO₂ surfaces are always higher than those of H-bonded OH groups.^{1,40} For example, Primet *et al.* assigned high (3715 cm⁻¹) and low (3665 cm⁻¹) frequency bands detected on anatase to isolated and H-bonded OH groups, respectively.⁴⁰ Isolated OH groups could be further categorized into terminal and bridging OH groups on the TiO₂ surface.^{1,39-41} The assignment of the infrared peaks of these isolated OH groups still remains controversial. Some infrared research based on the work of Primet *et al.*⁴⁰ and Tsyganenko *et al.*¹ proposed that the OH stretching frequency decreased from terminal OH (at around 3725 cm⁻¹) to bridging OH (at ~3670 cm⁻¹);^{42,43} whereas Jackson and Parfitt³⁹ supposed that the thermally stable infrared peak at 3725 cm⁻¹ should be bridging OH, because it has a higher stability due to its bidentate attachment. Other authors also attributed the lower frequency at 3666 cm⁻¹ to terminal OH.⁴⁴

DFT calculation, which is widely used for the study of surface chemistry on TiO₂,^{45,46} was conducted in this work to establish the infrared frequency of various OH groups and explore their activity toward NO₂. Based on the previous studies, we supposed that terminal, bridging and H-bonded OH groups exist on TiO₂. The geometric structures of these OH groups are shown in Fig. 5. Anatase TiO₂, which possesses the most diverse hydroxyls, was chosen as the representative for the DFT study. A (2 × 3) supercell of the anatase

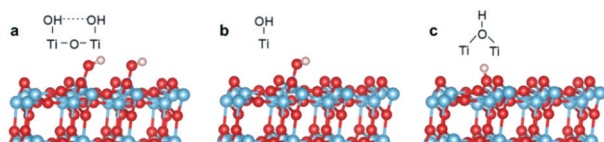


Fig. 5 Geometric structures of OH groups on anatase (101) surfaces. (a) H-bonded terminal OH groups. (b) Isolated terminal OH group. (c) Isolated bridging OH group. Blue, red, and pink balls represent Ti, O, and H atoms, respectively.

(101) surface plane with four stoichiometric layers (Fig. 1) was used in the calculations.

DFT-calculated vibrational frequencies are typically overestimated due to the harmonic approximation, and the anharmonic correction has been estimated to be about 72 cm^{-1} for OH stretching frequencies, as estimated by Arrouvel *et al.*⁴⁷ Therefore, the calculated frequencies presented in Table 1 were obtained by subtracting the anharmonic correction. As listed in Table 1, the calculated frequencies of OH stretching modes increased from 3624 cm^{-1} (H-bonded OH, with another band at 3659 cm^{-1}) to 3627 (terminal OH) and 3727 cm^{-1} (bridging OH). According to this trend of frequency, the OH bands observed on anatase TiO_2 during the DRIFTS experiments were attributed to H-bonded (3629, 3696 cm^{-1}), terminal (3670 cm^{-1}), and bridging (3735 cm^{-1}) OH groups. The band at 3681 cm^{-1} on amorphous TiO_2 was assigned to the terminal OH group, while the band at 3731 cm^{-1} on rutile TiO_2 corresponded to the bridging OH group.

Reactivity of OH groups toward NO_2

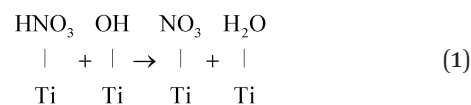
To investigate the reactivity of OH groups toward NO_2 , the MEP of NO_2 reaction with H-bonded, terminal, and bridging OH groups on the anatase (101) surface was predicted by DFT calculations, as shown in Fig. 6.

When the NO_2 molecule approached one OH of the H-bonded hydroxyl (Fig. 6a), the NO_2 rotated around its N atom towards the O atom of the hydroxyl. Then the Ti–OH bond was weakened and formed a bond with the NO_2 , forming an adsorbed HNO_3 species. The H atom of HNO_3 further transferred to the adjacent OH group, generating an

adsorbed H_2O molecule and a monodentate nitrate. This process is barrier-less and exothermic, indicating that the reaction of NO_2 with the H-bonded OH group is quite facile.

The reaction pathway of H-bonded OH and NO_2 on anatase could be verified by the DRIFTS experiment shown in Fig. S1b.† Quantitative analysis of H-bonded OH and monodentate nitrate on the anatase surface was conducted by integrating the areas of the relevant bands (Fig. 7). The results indicated that the consumption of H-bonded OH (3696 and 3629 cm^{-1}) accompanied the formation of monodentate nitrate (1493 cm^{-1}). The intensities of the two broad bands with centers at 3540 and 3415 cm^{-1} increased as the reaction proceeded. These bands are attributed to the O–H stretching vibration of surface H_2O .^{30,48} The H–O–H bending vibration of H_2O at 1638 cm^{-1} was also detected at the beginning of the reaction, which then overlapped with the strong vibration band of bridging nitrate at 1614 cm^{-1} .^{30,48} These bands indicated the generation of surface-bound water during the reaction.

As shown by the MEP in Fig. 6b, the reaction of NO_2 with terminal OH resulted in the formation of adsorbed HNO_3 . This reaction took place without any energy barrier, indicating that the terminal OH group is quite active in the NO_2 reaction. This reaction could explain the formation of surface-adsorbed HNO_3 during the NO_2 reaction on amorphous TiO_2 . Although only the terminal OH group was consumed during the NO_2 reaction on amorphous TiO_2 , various surface products, including both HNO_3 and nitrates, were generated (Fig. 3). The results suggest that HNO_3 is the final surface species in the reaction of terminal OH and NO_2 only if the OH group is isolated from other OH groups. Otherwise, HNO_3 will act as an intermediate and react with the adjacent OH groups, leading to the formation of nitrate species:



Due to its disordered structure, amorphous TiO_2 possesses plentiful defects such as oxygen vacancies and step

Table 1 Types of OH species on TiO_2 and their vibration frequencies

OH species	Representation ^a	DFT calculation ^b (cm^{-1})	DRIFTS measurement (cm^{-1})
H-Bonded OH	$\begin{array}{c} \text{OH} \cdots \cdots \text{OH} \\ \quad \quad \\ \text{Ti} - \text{O} - \text{Ti} \end{array}$	3624, 3659	3629, 3696 (anatase)
Terminal OH	$\begin{array}{c} \text{OH} \\ \\ \text{Ti} \end{array}$	3627	3670 (anatase) 3681 (amorphous)
Bridging OH	$\begin{array}{c} \text{H} \\ \\ \text{O} \\ / \quad \backslash \\ \text{Ti} \quad \text{Ti} \end{array}$	3727	3735 (anatase) 3731 (rutile)

^a Drawn according to the work of Tsyganenko *et al.*¹ ^b Anatase TiO_2 (101) surface with four stoichiometric TiO_2 layers was used in the DFT calculations.

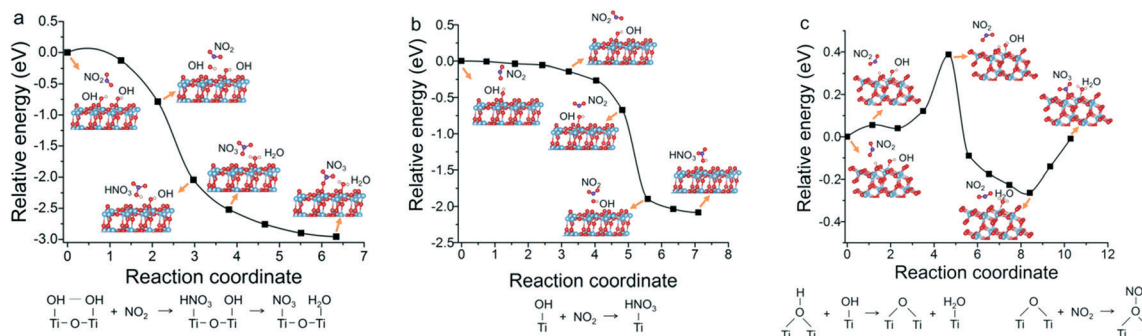


Fig. 6 Minimum energy paths for NO_2 reactions on anatase TiO_2 . (a) NO_2 reacting with the H-bonded OH group. (b) NO_2 reacting with the terminal OH group. (c) NO_2 reacting with bridging OH. The images show the initial and final configurations, as well as the representative intermediate images. Blue, red, pink, and purple balls represent Ti, O, H, and N atoms, respectively.

edges.^{19,49,50} Thus, isolated OH groups instead of H-bonded OH groups might be dominant on amorphous TiO_2 , and formation of HNO_3 was observable on this disordered surface.

As illustrated in Fig. 6c, bridging OH tended to react with the adjacent terminal OH groups. An adsorbed H_2O molecule was the product of this process, and had the lowest energy in this MEP. This process was exothermic by 0.26 eV, with an energy barrier of 0.39 eV. In the lowest-energy configuration, the NO_2 molecule interacted with the deprotonated bridging oxygen and was stabilized by the electrostatic attraction between the positively charged N atom and the negatively charged surface O atom. When the NO_2 molecule moved closer to the deprotonated bridging oxygen, an adsorbed NO_3^- species was formed. The increase in steric repulsion between the approaching NO_2 and the adjacent surface H_2O gave rise to an increase in the energy of the adsorbed nitrate at the bridging site. Therefore, this process was endothermic by 0.25 eV. It is implied that the activity of bridging OH with NO_2 is quite weak, and nitrate formation *via* this reaction is unlikely. As illustrated by the DRIFTS experiment (Fig. 3), bridging OH was the dominant OH group consumed on the rutile surface. Therefore, besides the lack of active sites, the

weak reactivity of rutile TiO_2 with NO_2 could be also attributed to the inactivity of bridging OH.

Conclusions

In this study, we observed an excellent example illustrating the structure–activity relationship of surface OH groups during NO_2 reaction on TiO_2 and the generation of special nitrogen-containing species. The results showed that the activities of H-bonded and terminal OH groups are much higher than that of bridging OH groups. Isolated terminal OH on amorphous TiO_2 dominates the reaction with NO_2 , which resulted in the formation of chemisorbed HNO_3 . Meanwhile, H-bonded OH on anatase exhibited a different reactivity toward NO_2 , which gave rise to the formation of the intermediates HNO_3 and monodentate nitrate. In contrast, bridging OH, as the primary type of OH on the rutile surface, led to its weak reactivity toward NO_2 . These results demonstrated that the reaction mechanism of NO_2 with TiO_2 is greatly dependent on the structure of OH groups.

Previous studies have shown that anatase is active in both catalysis and photocatalysis, and is the most used polymorph of TiO_2 .^{15,46,51,52} Although several factors such as facets and surface areas have been considered to contribute to the high activity of anatase,⁵³ the type and activity of surface OH groups might also play a critical role. The present work demonstrated that the crystal phase of TiO_2 determines the nature of the surface OH groups, which then determines the reaction of NO_2 on TiO_2 . These results may also provide a potential formation pathway of nitrate *via* the HNO_3 intermediate on atmospheric nanoparticles having plenty of OH groups.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This research was financially supported by the National Key R&D Program of China (2016YFC0202700) and the National Natural Science Foundation of China (41305116). The authors

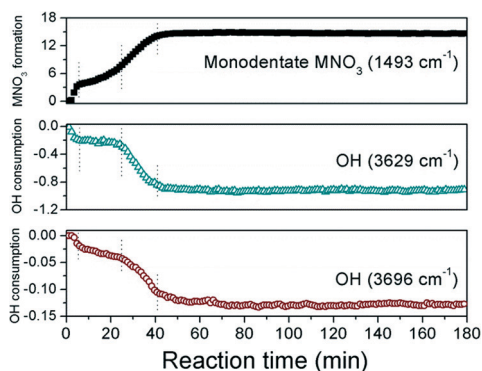


Fig. 7 Comparison of nitrate formation and OH consumption on anatase TiO_2 . Nitrate formation and OH consumption were represented by the integrated areas of the bands corresponding to monodentate nitrate (1493 cm^{-1}) and OH species (3629 and 3696 cm^{-1}). Reaction conditions: 200 ppmv NO_2 , 303 K, total flow of 100 mL min^{-1} (80% N_2 and 20% O_2).

also appreciate the Youth Innovation Promotion Association, CAS (2017064).

Notes and references

- 1 A. A. Tsyganenko and V. N. Filimonov, *Spectrosc. Lett.*, 1972, **5**, 477–487.
- 2 J. C. Lavalley, *Catal. Today*, 1996, **27**, 377–401.
- 3 R. Atkinson, *Atmos. Environ.*, 2000, **34**, 2063–2101.
- 4 S. S. Brown, T. B. Ryerson, A. G. Wollny, C. A. Brock, R. Peltier, A. P. Sullivan, R. J. Weber, W. P. Dubé, M. Trainer, J. F. Meagher, F. C. Fehsenfeld and A. R. Ravishankara, *Science*, 2006, **311**, 67–70.
- 5 J. G. Calvert, A. Lazrus, G. L. Kok, B. G. Heikes, J. G. Walega, J. Lind and C. A. Cantrell, *Nature*, 1985, **317**, 27–35.
- 6 A. Indarto, *Res. Chem. Intermed.*, 2012, **38**, 1029–1041.
- 7 R. Rahila and M. Siddiqui, *Int. Res. J. Environ. Sci.*, 2014, **3**, 70–73.
- 8 J. C. Matsubu, V. N. Yang and P. Christopher, *J. Am. Chem. Soc.*, 2015, **137**, 3076–3084.
- 9 X. Chen, L. Liu, Y. Y. Peter and S. S. Mao, *Science*, 2011, **331**, 746–750.
- 10 F. Giordano, A. Abate, J. P. C. Baena, M. Saliba, T. Matsui, S. H. Im, S. M. Zakeeruddin, M. K. Nazeeruddin, A. Hagfeldt and M. Graetzel, *Nat. Commun.*, 2016, **7**, 10379.
- 11 J. Bai and B. Zhou, *Chem. Rev.*, 2014, **114**, 10131–10176.
- 12 P. Granger and V. I. Parvulescu, *Chem. Rev.*, 2011, **111**, 3155–3207.
- 13 X. Chen, P. Wang, P. Fang, H. Wang, C. Cen, W. Zeng and Z. Wu, *Environ. Sci.: Nano*, 2017, **4**, 437–447.
- 14 Q. Wu and R. van de Krol, *J. Am. Chem. Soc.*, 2012, **134**, 9369–9375.
- 15 H. Chen, C. E. Nanayakkara and V. H. Grassian, *Chem. Rev.*, 2012, **112**, 5919–5948.
- 16 M. Tang, D. J. Czaczo and V. H. Grassian, *Chem. Rev.*, 2016, **116**, 4205–4259.
- 17 J. A. Rodriguez, T. Jirsak, G. Liu, J. Hrbek, J. Dvorak and A. Maiti, *J. Am. Chem. Soc.*, 2001, **123**, 9597–9605.
- 18 G. M. Underwood, T. M. Miller and V. H. Grassian, *J. Phys. Chem. A*, 1999, **103**, 6184–6190.
- 19 U. Diebold, *Surf. Sci. Rep.*, 2003, **48**, 53–229.
- 20 K. Hadjiivanov, V. Bushev, M. Kantcheva and D. Klissurski, *Langmuir*, 1994, **10**, 464–471.
- 21 J. S. Dalton, P. A. Janes, N. G. Jones, J. A. Nicholson, K. R. Hallam and G. C. Allen, *Environ. Pollut.*, 2002, **120**, 415–422.
- 22 C. E. Nanayakkara, W. A. Larish and V. H. Grassian, *J. Phys. Chem. C*, 2014, **118**, 23011–23021.
- 23 M. M. Kantcheva, V. P. Bushev and K. I. Hadjiivanov, *J. Chem. Soc., Faraday Trans.*, 1992, **88**, 3087–3089.
- 24 J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865–3868.
- 25 G. Kresse and J. Furthmüller, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1996, **54**, 11169–11186.
- 26 P. E. Blöchl, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1994, **50**, 17953–17979.
- 27 G. Kresse and D. Joubert, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1999, **59**, 1758–1775.
- 28 G. Henkelman, B. P. Uberuaga and H. Jónsson, *J. Chem. Phys.*, 2000, **113**, 9901–9904.
- 29 C. Liu, Q. Ma, Y. Liu, J. Ma and H. He, *Phys. Chem. Chem. Phys.*, 2012, **14**, 1668–1676.
- 30 A. L. Goodman, E. T. Bernard and V. H. Grassian, *J. Phys. Chem. A*, 2001, **105**, 6443–6457.
- 31 Q. Ma, Y. Liu and H. He, *J. Phys. Chem. A*, 2008, **112**, 6630–6635.
- 32 A. M. Rivera-Figueroa, A. L. Sumner and B. J. Finlayson-Pitts, *Environ. Sci. Technol.*, 2003, **37**, 548–554.
- 33 J. Baltrusaitis, J. Schuttlefield, J. H. Jensen and V. H. Grassian, *Phys. Chem. Chem. Phys.*, 2007, **9**, 4970–4980.
- 34 Y. Fang, M. Tang and V. H. Grassian, *J. Phys. Chem. A*, 2016, **120**, 4016–4024.
- 35 Y. Bedjanian and A. El Zein, *J. Phys. Chem. A*, 2012, **116**, 1758–1764.
- 36 A. L. Goodman, G. M. Underwood and V. H. Grassian, *J. Phys. Chem. A*, 1999, **103**, 7217–7223.
- 37 B. J. Finlayson-Pitts, L. M. Wingen, A. L. Sumner, D. Syomin and K. A. Ramazan, *Phys. Chem. Chem. Phys.*, 2003, **5**, 223–242.
- 38 G. Lammel and J. N. Cape, *Chem. Soc. Rev.*, 1996, **25**, 361–369.
- 39 P. Jackson and G. D. Parfitt, *Trans. Faraday Soc.*, 1971, **67**, 2469–2483.
- 40 M. Primet, P. Pichat and M. V. Mathieu, *J. Phys. Chem.*, 1971, **75**, 1216–1220.
- 41 M. A. Henderson, *Langmuir*, 1996, **12**, 5093–5098.
- 42 H. Lin, J. Long, Q. Gu, W. Zhang, R. Ruan, Z. Li and X. Wang, *Phys. Chem. Chem. Phys.*, 2012, **14**, 9468–9474.
- 43 L. Ferretto and A. Glisenti, *Chem. Mater.*, 2003, **15**, 1181–1188.
- 44 Y. Lei, B. Liu, J. Lu, J. A. Libera, J. P. Greeley and J. W. Elam, *J. Phys. Chem. C*, 2014, **118**, 22611–22619.
- 45 M. Setvin, J. Hulva, H. Wang, T. Simschitz, M. Schmid, G. S. Parkinson, C. Di Valentin, A. Selloni and U. Diebold, *J. Phys. Chem. C*, 2017, **121**, 8914–8922.
- 46 A. Vittadini, M. Casarin and A. Selloni, *Theor. Chem. Acc.*, 2007, **117**, 663–671.
- 47 C. Arrouvel, M. Digne, M. Breyse, H. Toulhoat and P. Raybaud, *J. Catal.*, 2004, **222**, 152–166.
- 48 H. A. Al-Hosney and V. H. Grassian, *Phys. Chem. Chem. Phys.*, 2005, **7**, 1266–1276.
- 49 X. Zhou, V. Häublein, N. Liu, N. T. Nguyen, E. M. Zolnhofer, H. Tsuchiya, M. S. Killian, K. Meyer, L. Frey and P. Schmuki, *Angew. Chem., Int. Ed.*, 2016, **55**, 3763–3767.
- 50 M. A. Vargas and J. E. Rodríguez-Páez, *J. Non-Cryst. Solids*, 2017, **459**, 192–205.
- 51 K. I. Hadjiivanov and D. G. Klissurski, *Chem. Soc. Rev.*, 1996, **25**, 61–69.
- 52 N. Liu, C. Schneider, D. Freitag, U. Venkatesan, V. Marthala, M. Hartmann, B. Winter, E. Spiecker, A. Osvet and E. M. Zolnhofer, *Angew. Chem.*, 2014, **126**, 14425–14429.
- 53 W. Q. Fang, X. Q. Gong and H. G. Yang, *J. Phys. Chem. Lett.*, 2011, **2**, 725–734.